

INKJET PRINTING AND STRUCTURE-PROPERTY RELATIONS OF FERROELECTRIC THIN-FILM STRUCTURES

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Doctoral Dissertation
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BRIZGALNO TISKANJE IN STRUKTURNO POGOJENE
LASTNOSTI FERROELEKTRIČNIH TANKOPLASTNIH
STRUKTUR

Doktorska disertacija

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Abstract

The additive manufacturing of functional structures by inkjet printing offers a unique and powerful alternative to conventional top-down patterning methods. Yet, multi-layer inkjet deposition is challenging due to problems with the wetting and drying. The wetting depends on the properties of the ink and the surface of the substrate. The latter can be regulated by the deposition of a few-nanometres-thick polymeric layer. The chemical nature of the polymer determines the surface properties of the newly formed surface. A precise control over the wetting is achieved by modifying the polymer layer, in our case poly(methyl methacrylate), by (i) a partial thermal decomposition, (ii) an O_2 -plasma treatment and (iii) a UV/ O_3 treatment. A smooth transition in wetting occurs when exposing the polymeric layer to a modification method, which enables the printing of complex structures with high resolution. While the thermal decomposition is effective for wetting adjustments only on unpatterned surfaces, the other two methods can be applied to pre-patterned surfaces.

The solvent composition of the ink determines its wetting behaviour on a selected surface, the drying process and the morphology of the dried deposit. Mixtures of solvents with a large difference in the surface tension and the volatility are commonly used to suppress the coffee-stain effect, which is mainly attributed to the modification of the internal liquid flows. However, a reconstruction of the drop height profiles during the drying reveals a distinct difference in the contact-line dynamics for the ink formulations that produce ring-like or dome-like deposits. A pinned contact line promotes the formation of a ring-like deposit, whereas a dynamic contact line promotes the formation of a dome-like deposit. Flat structures are printed only when the contact line exhibits dynamic behaviour; the latter can be regulated by the solvent composition and the initial contact angle.

These findings were used to establish a reliable inkjet printing process that is highly efficient and enables the conformal stacking of functional oxide layers according to the user-defined geometry, sequence arrangement and layer thickness. Ferroelectric thin-film capacitors (proof-of-concept devices) consisted of lanthanum nickelate electrodes and a lanthanum-doped lead zirconate titanate (PZT) ferroelectric layer. The capacitors could be printed on various substrates, including silicon wafers, alumina plates and nickel foils. A detailed structural and electrical characterization reveals the excellent functional properties of the printed single-layer devices. These easily achieve the properties of devices prepared by spin coating. The printed multi-layer devices, however, greatly exceed the performance of single-layer devices, which is indicated by an increase in the capacitance density and the electromechanical response in comparison to the single-layer devices.

In the last part, a soft-chemistry technique was devised for the deposition of nanostructured PZT films with greatly enhanced piezoelectric properties. The method utilizes the self-assembly of organic precursors in a polymer matrix to fabricate nanostructured oxide thin films by spin coating. The implemented macro-porosity leads to local elastic relaxations and greatly enhances the electromechanical response. The large piezoelectric coefficient—reaching the level of bulk ceramics—is associated with the increased elastic compliance of the nanostructured films and the highly mobile ferroelastic domain walls.

Povzetek

Brizgalno tiskanje je edinstvena alternativa konvencionalnim metodam oblikovanja funkcionalnih struktur. Vendar zaradi obstoječih težav, povezanih z omakanjem in sušenjem, nanašanje večjega števila prekrivajočih se plasti predstavlja velik izziv. Omakanje je odvisno od površinskih lastnosti tekočine za tiskanje (črnila) in podlage. Lastnosti podlage lahko spreminjamo z nanosom nekaj nanometrov debele plasti polimera, katerega kemijska narava določa lastnosti novo formirane površine. Omakanje podlage s črnilom lahko poljubno spreminjamo z nadaljnjo obdelavo tanke plasti polimera, v našem primeru polimetilmetakrilata, z (i) delnim termičnim razpadom, (ii) obdelavo s kisikovo plazmo ali z (iii) obdelavo z UV/O₃. S časom obdelave lahko poljubno določimo kot omakanja, kar nam omogoča tiskanje kompleksnih struktur z visoko ločljivostjo. Pri obdelavi polimerne plasti s termičnim razpadom lahko kot omakanja spreminjamo le na površinah brez obstoječih struktur, s preostalima dvema metodama pa tudi na predhodno strukturiranih površin.

Topila v črnilu vplivajo na omakanje izbrane podlage, na sušenje in na morfologijo tiskane strukture po sušenju. Pristop k zmanjšanju pojava tako imenovanega kavnega roba temelji na uporabi kombinacije topil z različnimi površinskimi napetostmi in hlapnostjo, ki naj bi vplivala na razvoj tekočinskega toka. Vendar rekonstrukcija profilov kapljic med sušenjem razkriva bistveno razliko v dinamiki kontaktnih linij, ko gre za črnila, s katerimi tiskamo strukture z obliko kavnega roba (konkavne) ali z obliko kupole (konveksne). Konkavne strukture nastanejo, kadar je med sušenjem kontaktna linija pripeta, konveksne pa, kadar se kontaktna linija premika - v tem primeru lahko tiskamo tudi ravne strukture. Na dinamiko kontaktne linije lahko vplivamo z izborom topil v črnilu in z začetnim kotom omakanja.

Na osnovi opisanih ugotovitev smo razvili proces tiskanja, ki je zanesljiv in učinkovit, ter omogoča konformen nanos plasti kovinskih oksidov z izbranimi dimenzijami, obliko, debelino plasti in njihovim zaporedjem. Za potrditev koncepta smo izdelali feroelektrični tankoplastni kondenzator, sestavljen iz plasti prevodnega lantanovega nikelata (elektroda) in feroelektrične plasti svinčevega cirkonata titanata (PZT). Kondenzatorje smo natisnili na različne podlage, med drugim na silicijeve rezine, ploščice iz aluminijevega oksida in nikljevo folijo. Tiskane komponente z eno plastjo feroelektrika smo podrobno strukturno in električno analizirali. Komponente izkazujejo odlične funkcijske lastnosti - njihov odziv je primerljiv tankoplastnim kondenzatorjem, pripravljenim z uveljavljeno metodo vrtenja. Tiskani večplastni kondenzatorji znatno presegajo odziv enoplastnih, kar se kaže v večji kapacitivnosti in velikem elektromehanskem odzivu.

V zadnjem delu doktorske disertacije je predstavljena metoda priprave nanostrukturiranih tankih plasti PZT z močno izboljšanimi piezoelektričnimi lastnostmi. Metoda temelji na samourejanju organskega prekursorja PZT v polimerni matrici med nanašanjem na podlago z metodo vrtenja. Makro-poroznost, ki se razvije v plasti po žganju, omogoča lokalne elastične relaksacije in s tem močno poveča elektromehanski odziv. Velik piezoelektrični koeficient, ki doseže vrednost, značilno za volumensko keramiko, je posledica tako povečane elastičnosti nanostrukturnih filmov kot velike mobilnosti feroelastičnih domenskih sten.

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Abbreviations

1,2PD	... 1,2-propanediol
2EE	... 2-ethoxyethanol
AC	... alternating current
AFM	... atomic force microscope
BSE	... backscattered electrons
CAH	... contact-angle hysteresis
CCA	... constant contact angle
CDR	... constant drop radius
CL	... contact line
CSD	... chemical solution deposition
CW	... complete wetting
DC	... direct current
DEG	... diethylene glycol
DF	... dark field
DOD	... drop-on-demand
DW	... domain wall
EA	... ethanolamine
EELS	... electron energy loss spectroscopy
EG	... ethylene glycol
FEM	... finite-element method
FTIR	... Fourier-transform infrared spectroscopy
GLY	... glycerol
ITO	... indium-tin-oxide
LNO	... lanthanum nickelate
MLC	... multilayer capacitors
MIM	... metal-insulator-metal
MOE	... 2-methoxyethanol
MPB	... morphotropic phase boundary
OCT	... 1-octanol
OWRK	... Owens-Wendt-Rabel-Kaelble
PD	... 1,3-propanediol
PMMA	... poly(methyl methacrylate)
PS	... poly(styrene)

PTFE	... poly(tetrafluoroethylene)
PVA	... poly(vinyl alcohol)
PVP	... poly(vinyl pyrrolidone)
PZT	... lead zirconate titanate
RTA	... rapid thermal anneal
SFE	... surface free energy
SEI	... secondary-electron imaging
SEM	... scanning electron microscopy
SIMS	... secondary ion mass spectrometry
SLC	... single-layer capacitors
TEC	... thermal expansion coefficient
TEM	... transmission electron microscopy
TFC	... thin-film capacitor
TFT	... thin-film transistor
UV	... ultraviolet

Symbols

α	... angle of incidence of the light wave
α_{ε}	... irreversible dielectric Rayleigh parameter
α_{d33}	... irreversible piezoelectric Rayleigh parameter
γ_L, γ_{lv}	... surface tension, liquid–vapour interfacial energy
γ_L^D	... dispersive contribution to the surface tension of a liquid
γ_L^P	... polar contribution to the surface tension of a liquid
γ_S, γ_{sv}	... surface free energy, solid–vapour interfacial energy
γ_S^D	... dispersive contribution to the surface free energy of a substrate
γ_S^P	... polar contribution to the surface free energy of a substrate
γ_{sl}	... solid–liquid interfacial energy
δ_{LF}	... quality of the fit
ε	... dielectric permittivity
$\varepsilon_{\text{init}}$	... reversible dielectric Rayleigh parameter
η	... viscosity
θ_A	... advancing contact angle
θ_{eq}	... equilibrium contact angle
θ_i	... initial contact angle
θ_R	... receding contact angle
λ	... wavelength of the light
λ_S	... thermal conductivity of a substrate
ρ	... density
ρ_{ox}	... density of an oxide layer
ϕ	... volume fraction
a	... drop diameter
A	... area
A_m	... measured area
Bo	... Bond number
c	... (vapour) concentration
c_{∞}	... ambient vapour concentration
c_s	... concentration of a saturated vapour just above the liquid–air interface
C_i	... capacitance of each capacitor
d	... layer thickness
d_{33}	... piezoelectric coefficient

$d_{33,\text{init}}$	... reversible piezoelectric Rayleigh parameter
D_i^{vap}	... diffusion coefficient in the vapour phase
D_s^{liq}	... diffusion coefficient of a solute in the liquid phase
E_{BIAS}	... DC bias electric field
E_C	... coercive field
h	... local height of the drop
J	... evaporation rate
m	... integer corresponding to the interference order
M_{ox}	... mass concentration of oxide material in the ink
n	... surface coverage
n_{ink}	... refractive index of the ink
N	... number of connected capacitors
Oh	... Ohnesorge number
p	... drop spacing, pitch
p_{tot}	... total vapour pressure above the solvent mixture
p_i°	... partial vapour pressure of a solvent
p_i^{sat}	... saturated vapour pressure
P	... polarization
P_{max}	... maximum polarization
P_R	... remanent polarization
r	... distance from the drop center
R	... radius of a drop
RH	... relative humidity of air
Re	... Reynolds number
S	... strain
t	... time
$\tan\delta$	... dielectric losses
T	... temperature
T_S	... temperature of a substrate
T_{amb}	... air temperature
v	... drop velocity
v_t	... transverse print-head velocity
V, V_d	... (drop) volume
We	... Weber number
x_i	... mole fraction of a solvent in the liquid phase
x_s	... solute mole fraction of a solute
y_i	... fraction of the solvent in the vapour phase

Chapter 1

Introduction

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1.1 Inkjet Printing Process

Inkjet printing has been in use for more than half a century to print documents in small offices and homes. More recently, it has been recognized as a highly flexible manufacturing tool in 2D and 3D applications. Easy pattern modifications, micrometer resolution, and the absence of additional patterning steps make inkjet printing attractive for the manufacture of electronic devices. This has governed the development of printed electronics—a huge market based on the production of low-cost, large-area electronics.

The printing process relies on the accurate generation of small droplets of a liquid, which are ejected from a reservoir through a nozzle and deposited at digitally determined locations on a substrate. There are two modes of drop formation: continuous and drop-on-demand (DOD) [1]. Due to better accuracy, smaller drop size and larger flexibility, DOD printing is better suited for home/small office and research applications. In order to form the droplets only when needed, the fluid is modulated by an acoustic wave that is generated by thermal or piezoelectric excitation. Thermal DOD is typically used for conventional printing applications, while for patterning of functional materials in research piezoelectric DOD inkjet printing prevails.

In piezoelectric inkjet printing an electric signal, often referred to as a waveform, is applied to a transducer (Figure 1.1). The design of the waveform determines the jetting

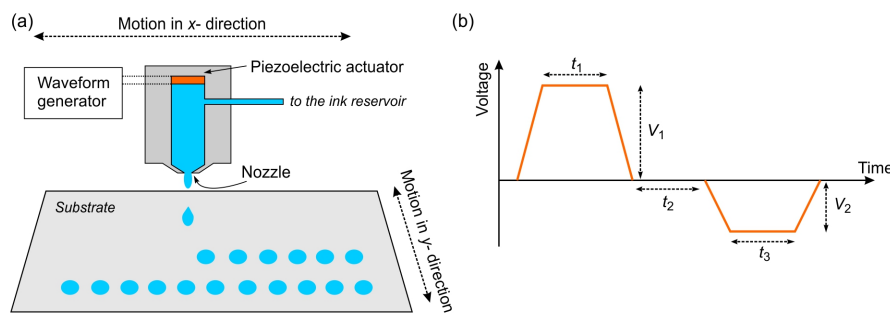


Figure 1.1: (a) Schematic representation of piezoelectric drop-on-demand inkjet printing. (b) A typical waveform that is applied to a piezoelectric actuator for the ejection of a drop. After [2].

stability, the drop size and its velocity. The simplest waveform consists of a trapezoid with a positive voltage (the left-hand part of the waveform shown in Figure 1.1b); however, additional segments are often added. A pulse of the opposite voltage can follow the initial pulse, with the objective being to cancel out the remaining oscillations present in the print-head (waveform shown in Figure 1.1b) [3]. After successful ejection from the nozzle, the drop lands at a predetermined location on the substrate. The substrate and the print-head move during the printing process to determine the location of the deposited material. In theory the process is simple; however, in practice it can become challenging. The specific requirements of the fluid represent a major restriction for inkjet printing. The ink should have a viscosity and a surface tension that are within certain ranges, roughly 10–12 mPa s and 28–33 mN m⁻¹ [4]. A Newtonian behavior of the viscosity is preferred, because viscoelastic effects could cause problems with the jet breaking up into drops. The wrong ink design can result in the formation of satellite drops, dripping through the print-head nozzles, orifice plate wetting, and nozzle clogging [5], [6].

A large number of parameters—spanning from specific fluid requirements to drying—

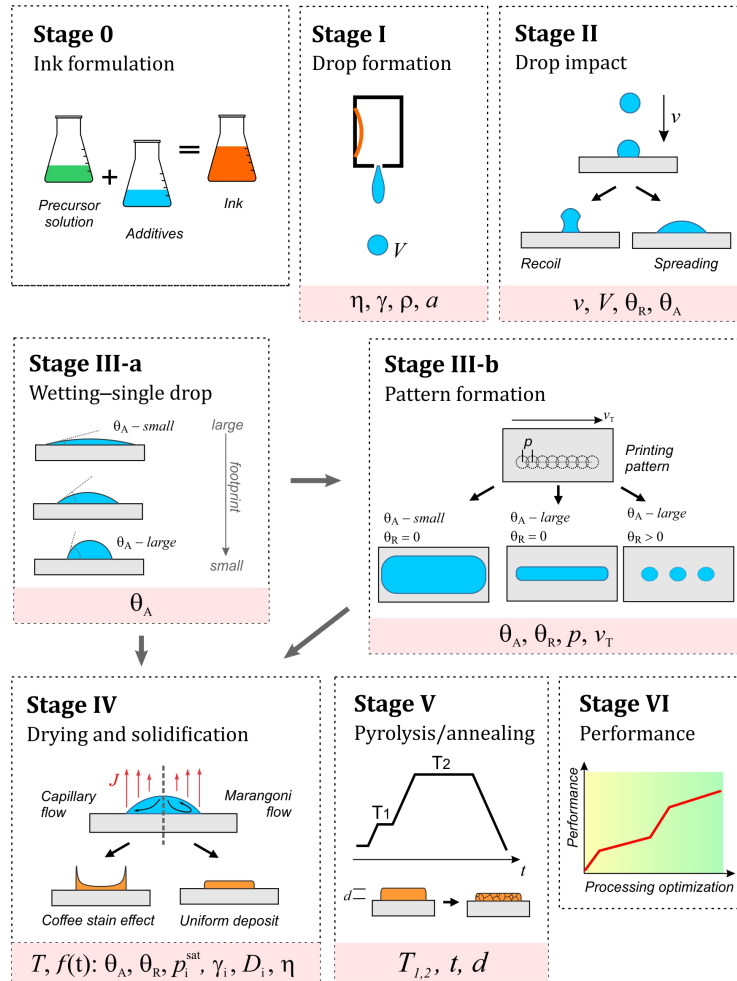


Figure 1.2: Schematic representation of the inkjet printing process. Symbols correspond to: η – viscosity, γ_i – surface tension, ρ – density, a – drop diameter, v – drop velocity, V – drop volume, $\theta_{A,R}$ – advancing and receding contact angles, p – drop spacing, v_t – transverse print-head velocity, T – temperature, p_i^{sat} – saturated vapour pressure, D_i – diffusion coefficient, J – evaporation rate, t – time, d – layer thickness. After [2].

contribute to the complexity of the inkjet printing process. General guidelines have been established in terms of stable drop formation [7], the stability of the printed lines [8], [9], and the uniformity of the dried deposits [10], [11]. Depending on the physical form of the solute in the ink we distinguish solution-based inks, where the solute is completely dissolved in a particular solvent, and particle-dispersion based inks, where the solid (nano)particles are dispersed in a liquid medium. This thesis focuses on solution-based inks, which are used to pattern layers with thicknesses from a few nanometers to roughly the micron range.

The inkjet printing process is schematically shown in Figure 1.2. The pre-printing phase (Stage 0) is the formulation of the ink, keeping in mind that the operating principles set certain limits on the ink's physical properties. The viscosity (η), surface tension (γ) and density (ρ) need to be balanced for a stable drop formation, and the vapour pressure should be low enough to prevent clogging of the nozzle(s). After successful ejection (Stage I), the drop eventually collides with the substrate (Stage II) and undergoes several shape changes until it reaches an equilibrium state. In the latter, the drop wets the substrate according to the balance of the surface energies of the ink and the substrate. The wetting (Stage III-a) is quantified by the contact angle. With a decreasing contact angle the diameter of the printed drop increases; the wetting thus strongly impacts on the resolution. Depending on the printing pattern, individual drops can overlap to form more complex geometrical objects, such as lines and rectangles (Stage III-b). In this case the wetting directly affects the shape of the pattern: a low contact angle results in large and poorly defined patterns, while a high contact angle promotes the occurrence of pattern instabilities. After the printing process the wet pattern is dried, which transforms it into a solid deposit (Stage IV). Drying often produces a pattern with pronounced edges, which is known as the "coffee-stain" effect [12]. Several factors influence the morphology of a dried deposit, including the solvent's formulation, the substrate's surface properties, the humidity of the air and the temperature. Finally, the dried deposit is heated to decompose the organic residues in the so-called pyrolysis step, and obtain the functional material. Depending on the material and the application, the heating conditions are selected to result in amorphous or crystalline material with a certain microstructure (Stage V). As all stages in the printing process influence the final performance of the functional oxide, it is important that individual processing parameters, such as ink chemistry, drying and heat treatment, are mutually optimized to maximize the functional properties of printed layers (Stage VI).

1.2 Ink Formulation

1.2.1 Drop formation

The ink's formulation should fulfil the fluid requirements set by a printer type. The flow of the ink through the nozzle is described by fluid mechanics, or more specifically by the dimensionless Reynolds (Re) and Weber (We) numbers, Equation 1.1 and 1.2. The Ohnesorge number (Oh), which is the ratio $\sqrt{We}/Re$ (Equation 1.3), includes all the fluid's physical properties relevant to the drop's formation, i.e., the viscosity, η , the surface tension, γ , and the density, ρ [13]:

$$Re = \frac{v\rho a}{\eta}, \quad (1.1)$$

$$We = \frac{v^2\rho a}{\gamma}, \quad (1.2)$$

$$Oh = \frac{\eta}{\sqrt{\rho\gamma a}}. \quad (1.3)$$

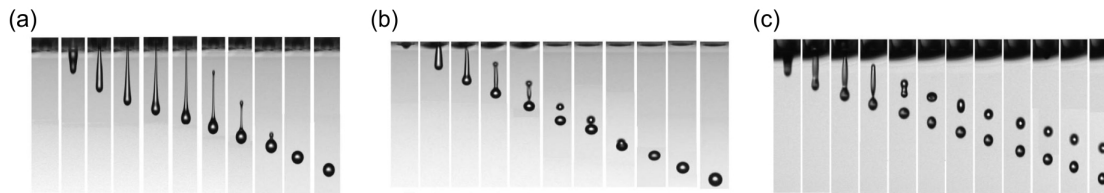


Figure 1.3: Sequence of stroboscopic images showing the drop formation during the inkjet printing of ethylene-glycol-water mixtures with different Z values: a) $Z = 2.2$, b) $Z = 6.6$, c) $Z = 17.3$. The drops were jetted at a constant driving voltage of 25 V and a frequency of 1 kHz. The photographs were taken using a stroboscopic camera with 20 μ s decay. Reproduced from [17].

v is the fluid velocity and a is a characteristic dimension, in our case the diameter of the nozzle.

The inverse of the Ohnesorge number—also known as the Z number—has often been used in relation to the drop formation. Reis and Derby [7] used numerical modelling to investigate the drop formation in inkjet printing and proposed the range $1 < Z < 10$ for stable drop formation. The experiments show that the Z range for a stable drop formation depends on the ink formulation and the waveform used [14]–[16]. For example, Jang et al. [17] showed for ethylene-glycol-water mixtures that Z values between 4 and 14 produce stable drops.

The stable drop formation is limited by two extremes, i.e., the low and high Z numbers. At low Z values, the high viscosity inhibits the drop's ejection, i.e., the pressure required for the drop's ejection is too large. By increasing the Z value to the lower limit of the printable range, the ejected drops have long tails (Figure 1.3a, $Z = 2.2$). For $Z = 6.6$, the tail of an ejected drop first separates from the main drop and forms a satellite drop, which later merges with the main drop (Figure 1.3b). At even higher Z values, the ejected drop separates into two or more satellite drops (Figure 1.3c, $Z = 17.3$), which remain separated from the main drop. The occurrence of satellite drops should be avoided as they reduce the resolution of the printing.

1.2.2 Chemical solution deposition (CSD)

A common approach to formulating a solution-based ink is to first synthesize a functional oxide precursor solution for the chemical solution deposition of thin films, and then adjust its physical properties to reach the values suitable for inkjet printing, see Refs. [18]–[20].

The chemical solution deposition (CSD) of functional oxide thin films has been the subject of many reviews and books, for example Refs. [21]–[23], and only a brief overview of CSD is given here. Depending on the solution chemistry, we distinguish the sol-gel, chelate or hybrid routes. More recently, the aqueous CSD has been intensively researched as an environmentally friendly alternative to the traditional solvent based CSD [24]. The synthesis of a precursor solution (also called a sol) involves the dissolution of one or more metal reagents in a suitable solvent or a mixture of solvents, usually followed by a reaction.

Metal reagents include metal alkoxides, $M(OR)_n$ [25], and/or short- or long-chain carboxylates, $M(R-COO)_n$ [26], or both, either mixed or undergoing a reaction [27]. Metal nitrates, $M(NO_3)_n$, have also been used due to their good solubility in organic solvents [28], [29]. The reactivity of transition-metal alkoxides is often reduced by the addition of small amounts of alkanolamines, e.g., $NH_2-(CH_2)_n-OH$, or $HO-(CH_2)_n-NH-(CH_2)_{n'}-OH$, β -diketones, $R_1-CO-CH_2-CO-R_2$, or carboxylic acids, $R-COOH$. The choice of solvent is

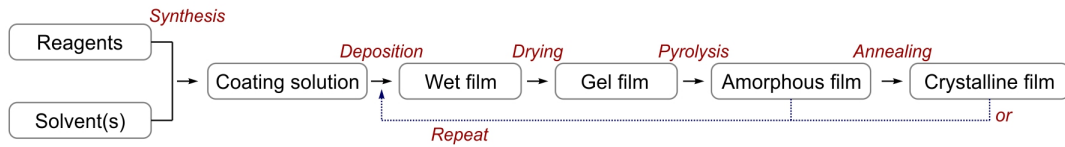


Figure 1.4: Schematic representation of the CSD process. Figure adapted after [2].

dictated by the choice of the reagents, which need to be fully dissolved, and the solution should be stable for weeks or even months. The concentrations of the solutions are quite low, usually in the range of a few 0.01 M to a few 0.1 M. Frequently used solvents include alkyl alcohols and ether alcohols, some of which are collected in Table 1. The common features of these solvents include low viscosity and low surface energy, implying good wettability and spreading on a substrate, and low boiling points to enable easy solvent removal upon drying. We note that diols, such as the 1,3-propanediol used in the diol-based route, are not included in this list [30].

In CSD the sol is deposited on a suitable substrate, very often by spin-coating [31]. In the drying and pyrolysis steps the evaporation of residual solvent(s), continued reactions, dehydroxylation, thermal oxidation of functional groups and usually partial densification occur. The crystallization step is needed to establish the long-range order, for example, in ferroelectrics [32], but this is optional in materials for transparent electronics, i.e., dielectrics and conductive oxides [33]. A schematic overview of the CSD process is included in Figure 1.4.

From the perspective of inkjet printing a typical CSD solution will have a much too low viscosity (usually in the range of only a few mPa s) and an almost adequate surface tension, between 20–30 mN m⁻¹, which means its Z value will be around 15–20, i.e., too high. Admixing viscous solvents, such as polyols (1,3-propanediol, ethylene glycol, glycerol, refer to Table 1.1), will increase the viscosity of the solvent mixture and thus of the solution. As an example, the changes in the viscosity, surface tension and Z -number of 2-methoxyethanol (2MOE), an often used solvent in CSD, upon the addition of two viscous solvents, 1,3-propanediol (PD) and glycerol (GLY), are shown in Figure 1.5. After the addition of the viscous solvent the viscosity steeply increases, which is especially evident in the case of the highly viscous glycerol. In parallel, the surface tension of the solvent

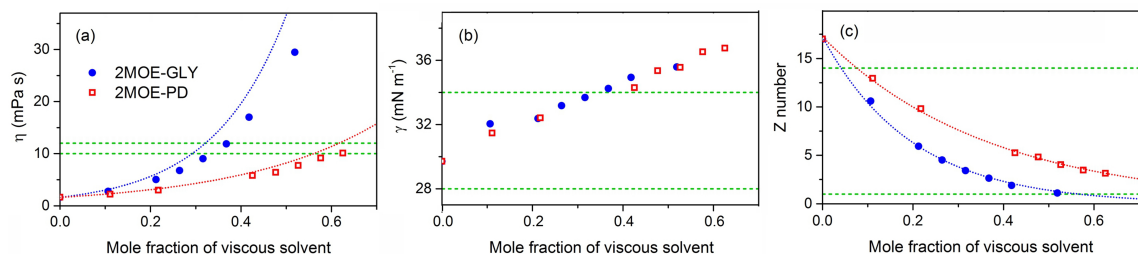
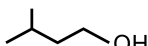
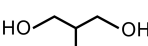


Figure 1.5: (a) Viscosity, (b) surface tension and (c) Z number of the 2-methoxyethanol (2MOE)–glycerol (GLY) and 2-methoxyethanol–1,3-propanediol (PD) solvent mixtures. The optimum ranges of viscosity and surface tension, as recommended by the printer producer [4], and the theoretical Z -number range for stable drop formation are given within the horizontal dashed lines. Reproduced from [19].

Table 1.1: Common solvents in CSD, and selected viscous solvents used in ink formulations. The physical parameters were obtained from Ref. [34] if not otherwise specified.

Component	Skeletal formula	η mPa s	γ mN m ⁻¹	T_b °C
CSD SOLVENTS				
Methanol		0.54	22.1	65
Ethanol		1.1	22.0	78
2-propanol		2.0	20.9	82
1-butanol		2.5	24.9	118
1-pentanol		3.6	25.4	138
3-methyl-1-butanol		3.7	23.7	131
2-methoxyethanol		1.7	30.8	124
2-ethoxyethanol		2.1	28.4	135
VISCOUS SOLVENTS				
Ethanolamine		21.1	47.3	171
Ethylene glycol		16.1	46.7	197
1,3-propanediol [19]		41.8	47.2	215
Glycerol [19]		828.5	63.1	287

mixture increases only gradually. As the Z number is proportional to $\sqrt{\gamma}/\eta$, it will decrease with the addition of the viscous solvents (Figure 1.5c). CSD solutions are usually diluted, so the behaviour of the solvent mixture will be similar to that of the solution [19].

1.3 Ink–Substrate Interaction

1.3.1 Drop impact

The principle of inkjet printing is the deposition of liquid drops onto a solid substrate. After the ejection, the drop flies towards the substrate with a velocity between 5 and 20 m s⁻¹ [35]. The impact of the drop on the substrate involves five sequential stages: kinematic, spreading, relaxation, wetting and equilibrium. The first three stages correspond to the impact-driven regime, while the latter two stages correspond to the capillarity-driven regime [36].

In the initial kinematic stage (Figure 1.6 I.), the drop obtains the shape of a truncated

sphere upon collision with the substrate. At this point, the physical properties of the liquid and the substrate are not important [37]. In the spreading stage (Figure 1.6 II.) the drop radially expands. Its spreading is, on the one hand, promoted by the impact velocity and, on the other, hindered by the high surface tension and viscosity. The onset of the relaxation stage (Figure 1.6 III.) is marked by the minimum height of the drop and the change of its shape from a flat disk into a spherical cap. In these impact-driven stages (I., II., III.), the drop can undergo several undesired scenarios, such as prompt and corona splash, receding breakup, or partial or complete rebound. These should be avoided in inkjet printing; fortunately, the small size of jetted drops and the ink’s fluid characteristics usually prevent their occurrence.

In the wetting stage (Figure 1.6 IV.), the capillary forces drive the spreading of a drop until the equilibrium state is reached (Figure 1.6 V.). The time scale in capillary-driven stages is much longer than in the impact-driven stages—note that the time in Figure 1.6 is plotted on a logarithmic scale. It is important to note that at low contact angles ($< 90^\circ$), the final diameter of the printed drop remains unaffected by the initial impact-driven regime and depends solely on the capillary spreading and wetting. This is exemplified by substrates exhibiting different wetting behaviours: corona-treated (a) or as-received (b) indium-tin-oxide (ITO) coated glass or poly(tetrafluorethylene), PTFE, coated glass (c) shown in Figure 1.6. The time required to reach equilibrium is longer for systems with low contact angles (example (a) in Figure 1.6) as the drop spreads in proportion to $t^{1/10}$. As mentioned, the final footprint of a drop is typically independent of the impact-driven regime [38]; thus, the wetting phenomena will be discussed in the subsequent sections.

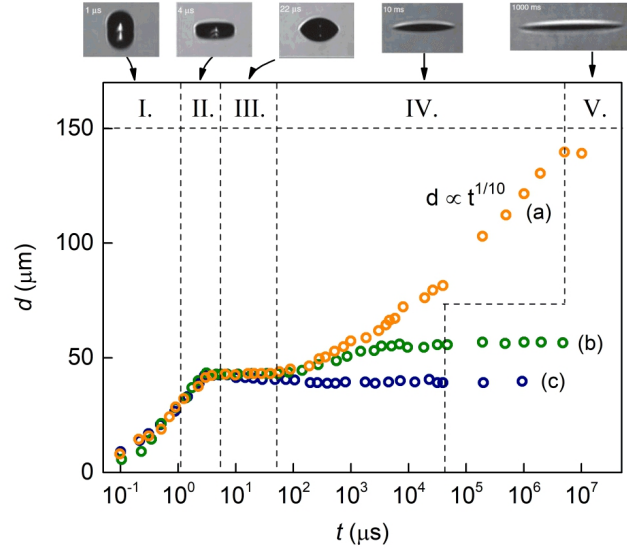


Figure 1.6: Time evolution of the drop diameter d on (a) corona-treated ITO-glass, (b) as-received ITO glass, (c) PTFE-coated glass substrates. Figure adapted after [38].

1.3.2 Basics of wetting

In the equilibrium stage (Figure 1.6 V.) the drop adopts the shape of a spherical cap due to the surface tension. The shape distortions due to gravity are usually negligible [14] and the shape of the cap is described by the Young–Laplace equation

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos(\theta_{eq}), \quad (1.4)$$

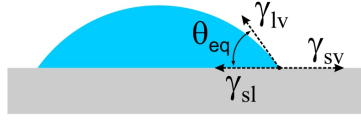


Figure 1.7: A schematic of a sessile drop on a substrate, showing the quantities in the Young–Laplace equation.

where γ_{sv} , γ_{sl} , γ_{lv} are the solid–vapour, solid–liquid, and liquid–vapour interfacial energies (Figure 1.7). Note that γ_{sv} , γ_{lv} are commonly referred to as the (solid) surface free energy and (liquid) surface tension, respectively. In the thesis γ_s is used to denote the solid surface free energy and γ_L is used to denote the liquid surface tension.¹ The equilibrium contact angle between the liquid–vapour interface and the solid surface, θ_{eq} , is a measure of the wetting. For $\gamma_{sv} = \gamma_{sl} + \gamma_{lv}$, the contact angle is 0° , indicating complete wetting. For $\gamma_{sv} < \gamma_{sl} + \gamma_{lv}$, the contact angle is non-zero, resulting in partial wetting. Only γ_{lv} can be directly measured, while the evaluation of γ_{sv} and γ_{sl} mainly depends on modelling and is obscured by the contact-angle hysteresis (refer to Section 1.3.3).

Several models have been developed to evaluate γ_{sv} , including Zisman [41], Fowkes [42], Wu [43], Owens–Wendt–Rabel–Kaelble (OWRK) [44]–[46], van Oss–Good [47], Neumann [48], and more recently also the Marmul–Valal [49] models. The models differ in terms of the type of accounted interactions and the method used to relate them. The OWRK model is quite widely used due to its simplicity and a reasonable agreement with experiments. A detailed description of the model is found in Appendix A. In brief, the wetting of a given solid surface by a liquid depends on the degree of interactions between the dispersive and polar contributions of the surface energies of the solid and the liquid. The division

Table 1.2: Overall surface tension (γ_L) of selected solvents/additives and respective dispersive (γ_L^D) and polar (γ_L^P) contributions. The equilibrium contact angle (θ_{eq}) on PMMA and glass is calculated using the OWRK model and surface-energy data from Ref. [40] and is in good agreement with experimental measurements. The polarity corresponds to γ_L^P/γ_L .

Solvent	γ_L mN m ^{−1}	γ_L^D mN m ^{−1}	γ_L^P mN m ^{−1}	Polarity %	θ_{PMMA} °	θ_{glass} °
Ethanol	22.1	17.5	4.6	21	0	0
2-ethoxyethanol	28.6	23.6	5.0	17	0	0
Ethanolamine	47.3	34.6	12.7	27	47	16
Ethylene glycol	46.7	31.9	14.8	32	47	0
Formamide	57.0	22.4	34.6	61	65	0
Glycerol	63.4	37.0	26.4	42	64	24
Water	72.8	26.4	46.4	64	76	6

¹ Surface tension has the dimension of force per unit length, or of energy per unit area. Both dimensions are equivalent, but when referring to energy per unit of area, it is common to use the term surface free energy, which is a general term which usually refers to solids [39].

of surface interactions into dispersive part (γ_L^D) and polar part (γ_L^P) is in place especially when treating liquids and solids of different polarities. The wetting can then be predicted by the wetting diagrams, which consist of wetting envelopes constructed for a given solid surface.

An example of a wetting diagram for a surface with $\gamma_L^D = 20 \text{ mJ m}^{-2}$ and $\gamma_L^P = 20 \text{ mJ m}^{-2}$ is shown in Figure 1.8. The 0° -wetting envelope marks the onset of complete wetting. Inks with the surface-tension contributions lying inside the 0° -wetting envelope wet the surface completely (example point C). On the other hand, inks that lie outside the 0° wetting envelope will only partially wet the surface (example points B and A). It is important to note that the wetting is not directly related to the absolute value of the surface energy, but rather depends on the interaction between the solid and the liquid. Non-polar liquids typically completely wet non-polar substrates and partially wet polar substrates. On the other hand, polar or moderately polar liquids better wet polar surfaces than non-polar ones. This is demonstrated by the contact angles of different liquids on two surfaces with different surface energy and polarity (γ_L^P/γ): glass and poly(methyl methacrylate). Glass has a high surface energy and polarity, while poly(methyl methacrylate), PMMA, is relatively non-polar with low surface energy. According to the OWRK model, the polar contribution to the surface energy of glass is 91 %, and 23 % for PMMA (see Chapter 4 for details). The contact angles of some solvents on glass and PMMA surfaces are collected in Table 1.2. Ethanol, 2-ethoxyethanol (ether alcohol, similar to, but less toxic than 2-methoxyethanol), ethylene glycol and formamide wet the glass completely ($\theta_R \approx 0^\circ$), while etanolamine, glycerol and water do not. On the other hand, solvents with a higher surface tension (ethanolamine, ethylene glycol, formamide, glycerol and water) exhibit much higher contact angles on the PMMA surface. Ethanol and 2-ethoxyethanol, which are frequently used in the CSD of thin films, completely wet the glass and even the PMMA surfaces. This is favourable in conventional thin-film deposition methods, such as spin coating, but not in inkjet printing. For the latter, the solvents with a higher surface tension and higher contact angles on PMMA are more appropriate. Such solvents can be, in principle, admixed with other solvents that have a lower surface tension to tailor the wetting behaviour of the ink.

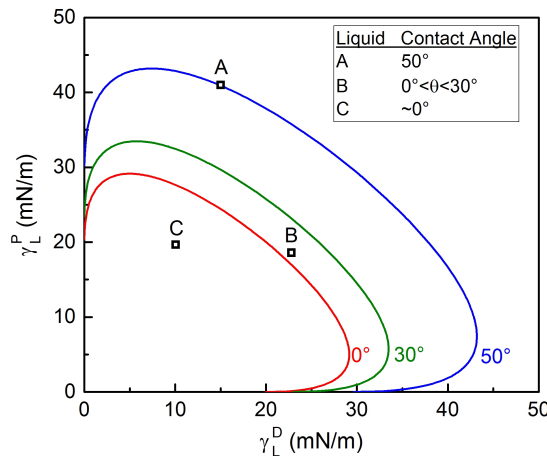


Figure 1.8: Wetting envelopes of a solid ($\gamma_S = 40 \text{ mJ m}^{-2}$, $\gamma_L^D = 20 \text{ mJ m}^{-2}$, $\gamma_L^P = 20 \text{ mJ m}^{-2}$) constructed for θ_{eq} of 0° , 30° and 50° . The positions of $\gamma_L^D - \gamma_L^P$ points predict $\theta_{eq} = 50^\circ$ for the liquid A, $0^\circ < \theta_{eq} < 30^\circ$ for the liquid B, and $\theta_{eq} \approx 0^\circ$ for the liquid C. Reproduced from [40].

1.3.3 Contact angle hysteresis

The Young–Laplace equation (Equation 1.4) is only valid for ideal surfaces, which are perfectly smooth, homogeneous and chemically inert. In reality, surfaces exhibit more than just one contact angle. The range of possible contact angles is limited by advancing and receding contact angles. The advancing contact angle, θ_A , is the maximum possible contact angle—the contact line advances when the momentary contact angle exceeds θ_A . The smallest contact angle is the receding contact angle, θ_R , which is the angle at which the contact line starts to recede. The difference between both angles is the contact-angle hysteresis (CAH), which arises due to the surface imperfections. CAH prevents the drop from sliding on inclined surfaces, such as rain drops resting on windows (Figure 1.9a) and has a crucial role in the stability of printed patterns and drying.

The advancing and receding contact angles can be measured using several techniques, including the Wilhelmy plate method [50], the tilted-plate method [51] and captive-drop goniometry [52]. The latter uses a needle immersed into a sessile drop, while the liquid is slowly pumped in/out of the droplet (Figure 1.9b). θ_A is measured by pumping in the liquid and recording the contact angle as a function of the advancing drop diameter. θ_R is determined similarly, but instead, the liquid is pumped out of the drop. The θ_{eq} lies between θ_A and θ_R ; it cannot be directly accessed but instead it is estimated from theoretical models (see Refs. [53]–[56], for more details).

In inkjet printing, the ink–substrate interaction would ideally result in a large θ_A and $\theta_R \approx 0^\circ$. The former is required for high resolution, while the latter is important for the stability of the pattern. However, at high θ_{eq} (and θ_A) the receding contact angle is often nonzero, which negatively affects the pattern’s stability. Therefore, both the ink’s solvent composition and the substrate should be carefully selected to fulfil these conditions. The contact-angle hysteresis greatly depends on the surface properties of the substrate. The CAH increases with the surface roughness and the chemical inhomogeneity of the surface. Topological defects act as pinning sites, which oppose the contact line’s movement and enlarge the hysteresis [58]. Additionally, the solute in the ink can promote the pinning of the contact line. This effect is especially pronounced in particle-dispersion inks and less so in solution-based inks. Therefore, it is easier to print well-defined and stable patterns with particle-dispersion inks on rough or chemically inhomogeneous substrates. For printing

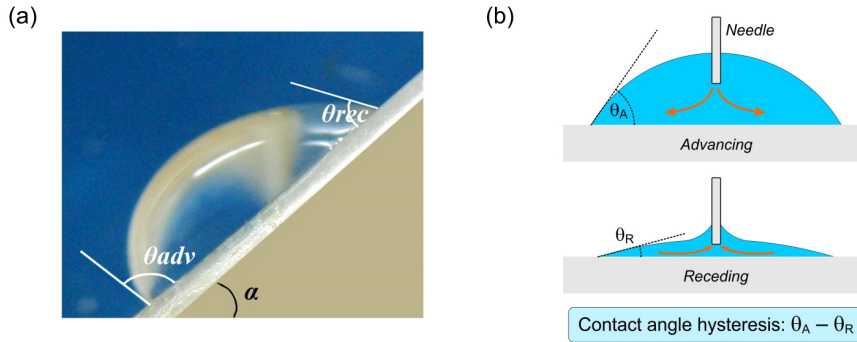


Figure 1.9: (a) A side view of a water drop resting on an inclined surface. Gravitational forces distort the shape of the drop in a way that the contact angle at the bottom is higher than at the top. Reproduced from [57]. (b) Captive-drop goniometry: the advancing and receding contact angles (θ_A , θ_R) can be measured by slowly pumping the liquid in or out of a sessile drop using a needle. Reproduced from [2].

solution-based inks on smooth substrates (which is often the case), control over the wetting is essential [40]. Special care is needed if the ink consists of more solvents with different wetting properties and volatility. Such inks can, in some cases, exhibit the evaporation-induced wetting transitions [59], resulting in a change of the pattern morphology.

1.3.4 Manipulation of wetting and spreading of the ink

Wetting and spreading of the ink on a given substrate can be manipulated either by modulating the surface properties of the substrate, or by locally restricting the spreading of the ink. The first approach relies on producing a partial wetting of the substrate. Here, the ink–substrate interaction needs to be well balanced to retain the stability and definition of the printed features. The surface properties of the substrates can be modified by coating them with polymeric layers [40], plasma and corona treatments [60], UV/ozone treatments, or by a combination of all these [61], [62].

In the second approach, the spreading of the ink is locally limited by surface-energy patterning [63]. Such patterns consist of low-surface-energy materials, such as self-assembled monolayers, polymers and siloxane. The approach exploits the ink-repelling nature of the surface-energy pattern, which forces the ink into the uncovered areas. The contact angle of the uncovered areas should be small to promote the spreading and stability of the pattern. Such patterns can be deposited by lithography-based processes, micro-contact printing [63], shadow-mask-assisted plasma treatment [64] and also inkjet printing.

Thin-film transistors with the channel layer width beyond the resolution of conventional inkjet printing provide an interesting case of local wetting manipulation. Wang et al. [65] used lithography to pattern the lines of perfluorodecyltrichlorosilane—a non-polar, low-surface-energy material [66]. The inkjet printing of aqueous polymer solutions on such lines resulted in de-wetting of the droplets in the areas of self-assembled monolayers. Such an approach enabled the fabrication of self-aligned source and drain electrodes in a thin-film transistor with a resolution as low as 250 nm. The same authors later reported the selective functionalization of a printed layer so that it repelled the next printed layer, resulting in sub-100-nm gaps between both layers [67]. In a more general approach, Li et al. exploited the "coffee stain" effect for patterning [68]. The inkjet-printed polymer-based ink formed approximately 3.5 μm wide edge deposits, which acted as ink-repelling stripes upon deposition of the functional material.

1.3.5 Stability of printed features

Printed devices and circuits usually consist of structures of different shapes, such as dots, lines or rectangles. While the printing of individual drops is straightforward, the printing of lines and rectangles requires individual drops to partially overlap and coalesce. The drop spacing, which is the distance between the centres of adjacent drops, also indicates the degree of overlap together with the drop size. Individual drops are always stable, while complex structures can exhibit instabilities. In 1980, Davis [69] investigated the stability of static rivulets as a function of the contact angle. He postulated that the ultimate conditions for a stable liquid bead included a contact angle smaller than 90° and a fixed contact line ($\theta_R = 0$). Both conditions have been subsequently experimentally validated [70]. Upon printing the lines with inks having a zero receding contact angle, periodically repeating bulges can appear [9], [36]. Duineveld [9] studied the bulging using a dynamic model and found that bulges occur when the momentary contact angle exceeds the advancing contact angle and the transported flow rate becomes larger than the applied flow rate. Consequently, a small drop spacing, a low deposition rate and a high advancing contact angle promote the occurrence of bulging.

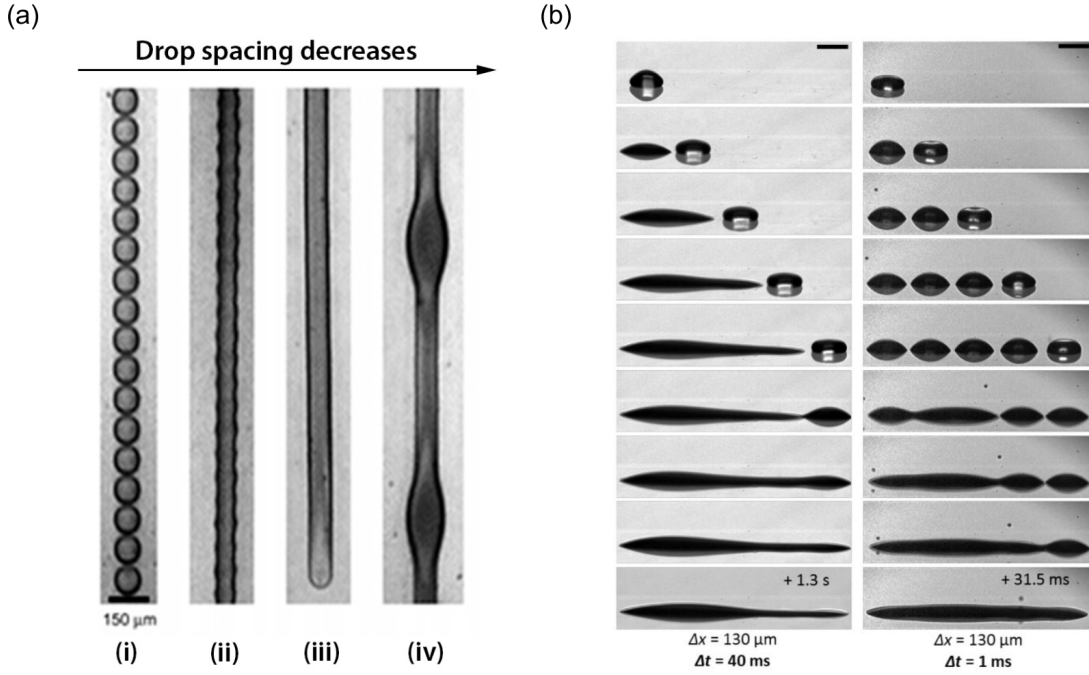


Figure 1.10: (a) Basic morphologies of printed lines depending on the drop spacing: (i) separated drops, (ii) scalloping, (iii) uniform, (iv) bulging. Figure adapted after [71]. (b) Dynamics of liquid track formation at two different deposition intervals. When the time between the depositions of consecutive drops is large, the drops coalesce before the deposition is complete (shown on the left-hand side). The pressure difference due to different curvatures causes the liquid flow from a newly deposited drop to the existing bead of liquid. At short deposition intervals, all the drops remain separated during the whole deposition process (right-hand side). After some time the drops merge due to the capillary spreading and form a liquid bead. Figure adapted after [72].

Several papers discuss the limits of line stability in terms of drop spacing and deposition rate for liquids with a zero receding contact angle. Soltman and Subramanian [71] investigated the printing of the lines across a range of drop spacings, deposition rates and substrate temperatures, see Figure 1.10a. For a drop spacing of twice the drop diameter or more the drops fail to coalesce and remain separated. Decreasing the drop spacing so that there is barely any overlap between drops produces lines with scalloped edges. An even smaller drop spacing results in narrow and stable lines with parallel edges, but if it is further reduced the bulging develops. Stringer and Derby [8] investigated the line stability at the onsets of scalloping and bulging. They reformulated the Duineveld model and mapped the regions of stability as a function of dimensionless print velocity, contact angle and drop spacing. It is clear that the attainable line width has an upper and a lower boundary. Bulging and scalloping respectively limit the largest and smallest widths of a printed line for a given contact angle [73].

The above analysis is valid for systems with pinned contact lines. Recently, Hsiao et al. [72] investigated the formation of liquid beads in a system with a non-zero receding contact angle, where the dynamics of line formation is also important. They used high-speed imaging to follow the coalescence of drops and liquid flow during the deposition on the substrate, see Figure 1.10b. Stable and relatively symmetrical lines formed at large drop

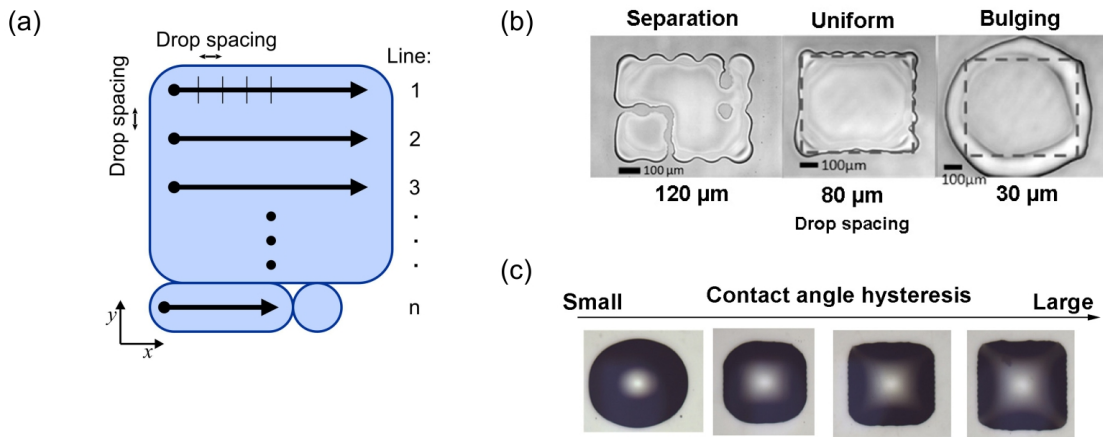


Figure 1.11: (a) Formation of a 2D pattern using a raster-scan technique. Figure adapted after [75]. (b) Possible instabilities for 2D patterns. The dotted line shows the desired shape of the $0.5 \times 0.5 \text{ mm}^2$ square. Figure adapted after [74]. (c) Influence of contact-angle hysteresis on the morphology of printed $1 \times 1 \text{ mm}^2$ squares. Figure adapted after [75].

spacings and short deposition times. In conventional inkjet printing 2D patterns are formed using a raster-scan technique. For example, a rectangular pattern is formed by printing individual lines in the x -direction and offsetting them in the y -direction (Figure 1.11a). Kang et al. [74] investigated the morphology of printed rectangular structures as a function of drop spacing. The printed 2D patterns exhibited essentially the same morphologies as printed lines. As shown in Figure 1.11, a large drop spacing prevented the coalescence of drops. Bulging occurred when the drop spacing was too low and the momentary contact angle exceeded the advancing contact angle.

The square-shaped patterns have much lower aspect ratios than the lines, and can remain continuous even at a nonzero receding contact angle. However, rounding of the corners occurs when the contact line is not pinned. Soltman et al. [75] demonstrated the evolution of a square morphology with increasing contact-angle hysteresis (Figure 1.11c). At a small hysteresis, the printed square-shaped pattern exhibited rounded edges and resembled a large drop. The rounding of the edges decreased with increasing hysteresis until squares with sharp edges formed; note that the diameter of an individual drop sets the edge curvature of a square pattern. A large contact-angle hysteresis—or more precisely, a zero or small receding contact angle—is essential for printing well-defined 2D patterns with sharp edges.

Thus far, we have only discussed single-solvent inks. In inks containing several solvents with different volatilities and surface tensions, the wetting and the stability of printed patterns can be functions of time. Evaporation of more volatile solvent(s) already in the course of the printing leads to changes in the ink formulation, which consequently results in a different wetting behaviour. While the printing of lines is relatively fast, the printing of 2D patterns is more time-consuming. The ink that contained two solvents with different boiling points and surface tensions, such as 2-methoxyethanol and 1,3-propanediol (refer to Table 1), produced well-defined 2D patterns, while according to the contact-angle measurements such an ink should exhibit complete wetting and thus spilling. This inconsistency was explained in terms of the preferential evaporation of the more volatile solvent during the raster-scan printing of a 2D pattern [40]. Another consequence of such a preferential evaporation is increased solute concentration in the ink, which can contribute

to contact-line pinning. Thus, optimization of the printing parameters often relies on experimental trials.

1.4 Drying and Consolidation

After the printing step, the as-deposited pattern is dried and usually heated to transform the organic precursor into a functional oxide. During drying, the solvents evaporate and the concentration of the solute in the deposit gradually increases. This results in an increase in viscosity until the sol-gel transition. In contrast to spin coating, where uniformly thick films are typically prepared [31], the drying of inkjet-printed structures often results in a non-uniform thickness. In fact, the deposition of uniformly thin structures is one of the challenges for the inkjet printing of functional materials. Further heating steps do not introduce major changes to the shape of the printed pattern.

The so-called coffee-stain effect refers to the evolution of a ring-like thickness profile of a deposit upon drying (Figure 1.12). Deegan et al. [12], [76] showed that it is a consequence of the preferential evaporation at the edge of the drying feature and pinning of the contact line. The combination of both phenomena results in an internal liquid flow from the interior to the edge to replenish the evaporated solvent. The associated transport of the solute due to the capillary flow eventually builds up the deposit at the edges.

Several strategies have been developed to eliminate or minimize the coffee-stain effect. The simplest way to suppress the edge-deposit formation is to eliminate the contact line pinning or preferential edge evaporation. The de-pinned contact line leads to the dome-shaped deposit with a much smaller diameter than the initial drop size. The inward motion of the contact line has been exploited in the self-assembly of colloidal spheres [77]. But due to the unpinned contact line (non-zero contact angle) the method is mainly limited to the printing of individual drops. The deposit uniformity can also be improved by retarding the evaporation from the edges of a drying feature [78], [79]. Berg et al. [80] exploited a temperature-induced gelation of a polymer to freeze the shape of a printed pattern before drying could produce a coffee stain. Similarly, Talbot et al. [81] studied the drying

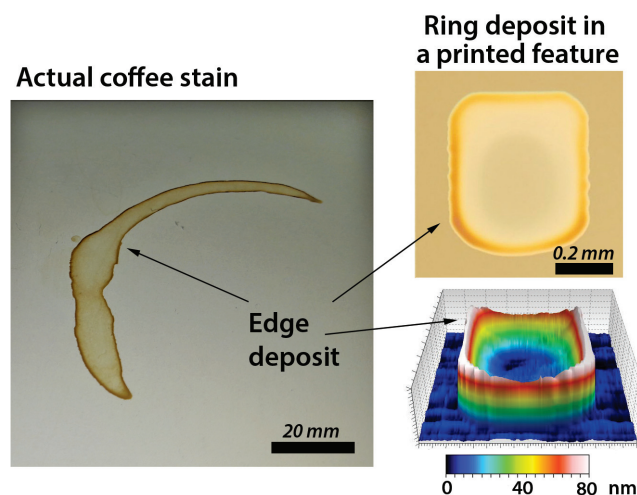


Figure 1.12: The left-hand figure shows a stain of coffee spilled and dried on a surface. A similar morphology often occurs when the inkjet-printed pattern dries, as shown in the optical micrograph and the corresponding thickness profile on the right. Reproduced from [2].

of laponite dispersions, which exhibit a strong increase in viscosity with the increasing concentration of the solute.

1.4.1 Multi-solvent inks

A common approach to reducing coffee-stain formation is by inducing a surface-tension gradient across the drying structure, which results in a recirculating Marangoni flow [82]. Such a gradient is produced by thermal fluctuations [82], added surfactants [83], [84], or a variation in composition [10]. The most convenient approach to induce the Marangoni flow in solution-based inks is a combination of solvents. Typically, such inks consist of two or more solvents with different viscosities, surface tensions and vapour pressures. The enhanced evaporation from the edge of the drying feature leads to local depletion of a more volatile solvent. The surface-tension gradient induces the Marangoni flow. As opposed to the directional capillary flow, the Marangoni flow is recirculating and is able to intensively mix the content of the drop in the course of drying (Figure 1.13a). The temporal evolution of the internal liquid flows upon drying thus depends on the ink's composition, the ambient conditions and the substrate's properties. Some of the parameters that influence the drying of solution-based inks are collected in Figure 1.13b.

The multi-solvent approach has been used to improve deposit uniformity in particle-dispersion inks [87], [88], polymer-solution inks [10], [89], [90], and metal-oxide precursor-solution inks [19], [61], [91]. In a study relevant to solution-based inks, Kajiya et al. [92] used fluorescence microscopy to follow the spatial concentration of fluorescent polystyrene dissolved in anisole upon drying. They observed a gradual increase in the solute concentration at the edge, eventually leading to a ring-like deposit. The morphology of a deposit depends on the choice of the solvents, their relative fractions in the ink [19], [89], solute concentration [93], drop spacing [61], [68], drying temperature [86], [94] and wetting [95], as well as the air humidity [96], the temperature of the substrate [71], [97], and the local environment [98]–[100]. Some examples of the influence of selected parameters on the morphology of a dried deposit are collected in Figure 1.14.

Recently, Diddens et al. [59], [101] developed a mathematical model to describe the drying of binary-solvent sessile drops based on a lubrication approximation. They demonstrated the preferential evaporation of a more volatile solvent and showed that the surface-

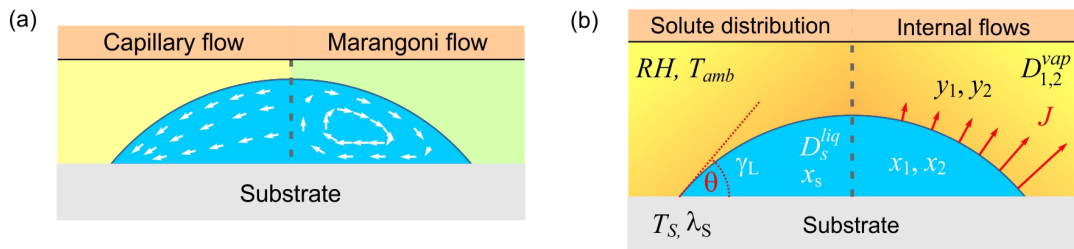


Figure 1.13: Schematic representation of a drop cross-section upon drying. (a) The comparison of capillary and Marangoni flows. (b) Selected variables that influence the morphology of a deposit. x_1, x_2, y_1, y_2 are the fractions of solvents 1 and 2 in the liquid and vapour phase, $D_{1,2}^{vap}$ is the diffusion coefficient of the solvents in the vapour phase, D_s^{liq} is the diffusion coefficient of the solute in the liquid phase, x_s is the solute concentration, γ_L is the surface tension of the ink, θ is the contact angle, T_s and the T_{amb} are the temperatures of the substrate and air, respectively, λ_s is the thermal conductivity of the substrate, RH is the relative humidity of air. Reproduced from [2].

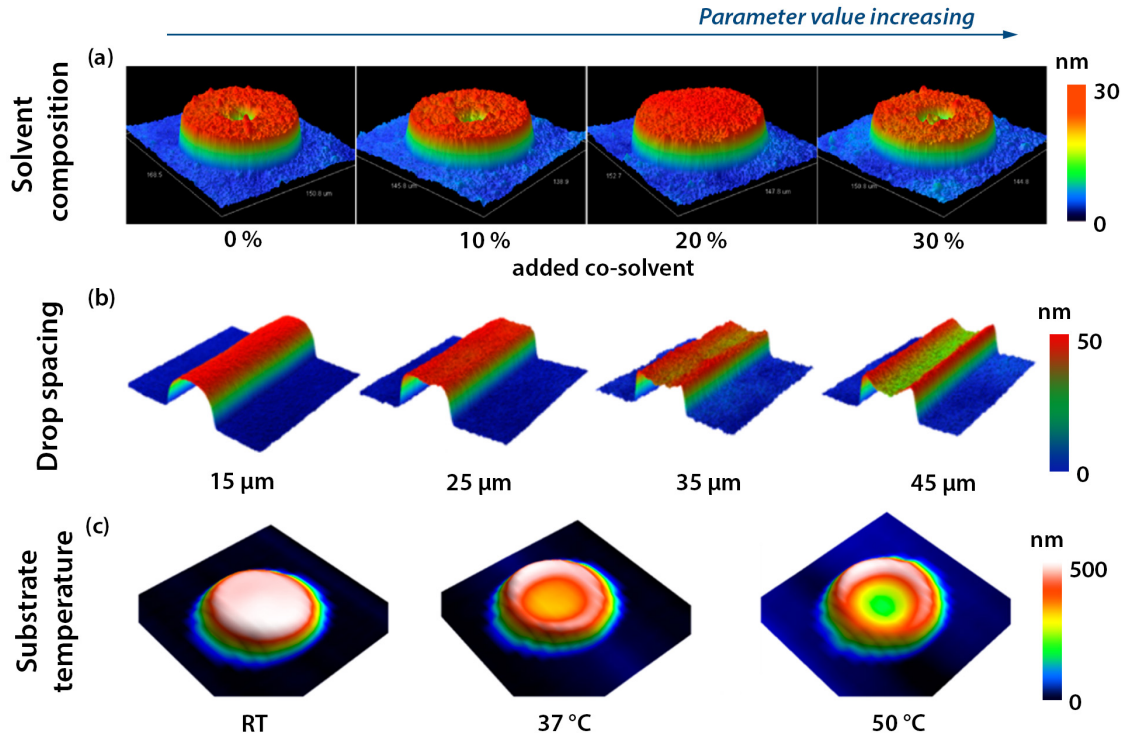


Figure 1.14: (a) 12-nm-diameter quantum-dot dispersion ink in cyclohexylbenzene with 0, 10, 20, 30 % 1,2-dichlorobenzene. Figure adapted after [85]. (b) Indium and gallium nitrate solution ink in 2-methoxyethanol with 50 vol.% ethylene glycol. Lines were printed at different drop spacings. Figure adapted after [68]. (c) Epoxy solution ink in cyclopentanone with 20 wt.% of added γ -butyrolactone dried at different temperatures. Figure adapted after [86].

tension-driven flow typically vanishes before the drying is complete. This is in agreement with experimental studies [19] and implies that the late stages of drop evaporation might be important for the final morphology of a deposit, especially in solution-based inks.

1.4.2 Drying of 2D geometrical shapes and patterns

In a recent study Sáenz et al. [102] showed that the drying of geometrically complex structures with non-spherical symmetry is somewhat different from the drying of axially symmetric features (Figure 1.15). Whereas symmetrical deposits have a constant contact angle along the whole liquid–solid interface this is not the case in patterns of lower symmetry. A triangular feature has higher and lower contact angles at the sides and at the corners, respectively. This results in the enhanced evaporation in the corners of the structure and hence a stronger capillary flow to these regions. Thus, the deposit height will be higher in the corners than at the sides of a triangular feature. Other geometries follow the same basic principle.

The printing pattern often consists of several features or arrays in proximity to each other. The evaporation fields of two neighbouring features can overlap if they are sufficiently close, which interferes with the drying process (Figure 1.16a). Consequently, the evaporation flux is reduced and the capillary flow to that area is weaker. In practice, the overlap of evaporation fields results in a smaller deposit height at adjacent sites

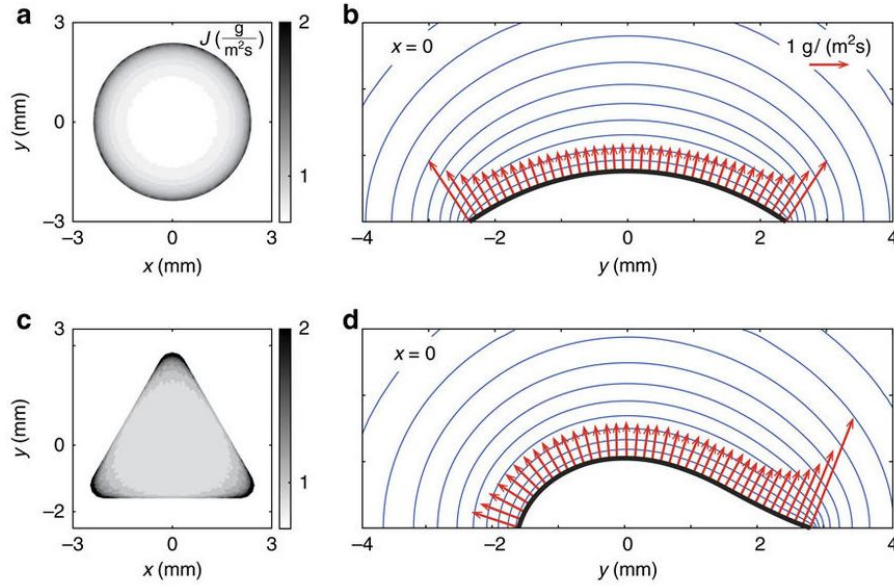


Figure 1.15: Simulations of the local evaporation flux for patterns with (a,b) circular and (c,d) triangular geometries. Figure adapted after [102].

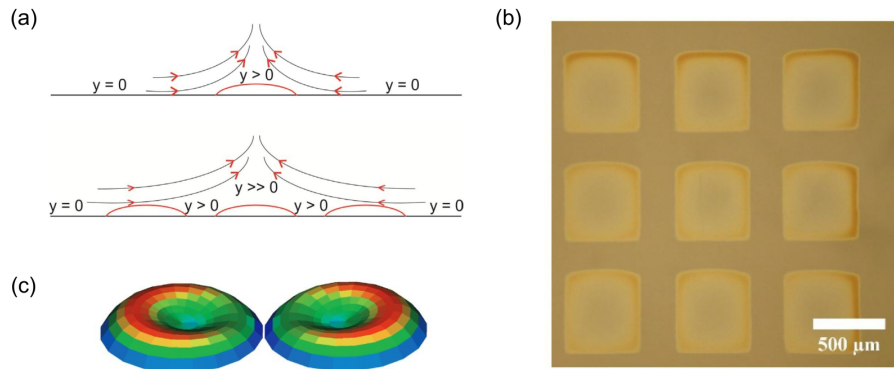


Figure 1.16: Schematic representation of vapour fields during the drying of an individual square and an array of squares. y corresponds to solvent fraction in the vapour. (b) Optical image of the edge part of an array of dried squares. The darker color at the edge of the outer squares corresponds to a thicker deposit. (c) The morphology of two drops dried adjacent to each other. Figure adapted after [100].

(Figure 1.16b,c). The phenomenon has been analytically and experimentally studied by Kobayashi et al. [100], Hu et al. [99] and Tao et al. [98].

1.5 Materials and Applications

The rich variety of electrical and optical properties of metal oxides makes them the materials of choice in printed electronics, ranging from conventional electronic components to sophisticated devices with new functionalities. Printed electronic devices typically consist of conductive and dielectric layers in metal–insulator–metal (MIM), or a planar configuration. A representative example of a MIM component is a thin-film capacitor (TFC), where

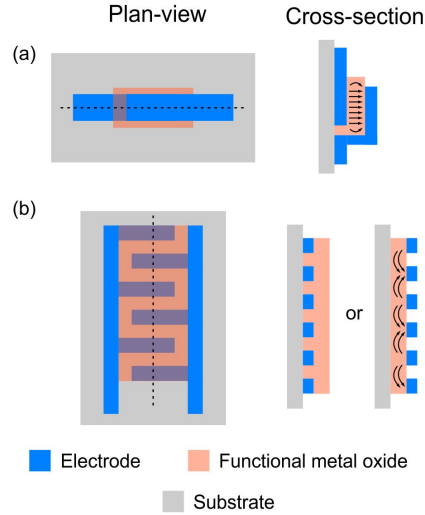


Figure 1.17: Plan-view and cross-sectional view of the electronic components with (a) metal-insulator-metal and (b) planar configuration. The dotted lines in plan-view show the cut for the cross-sectional view. Arrows in the cross-sectional view show the electric field propagation in these devices. The dimensions in the cross-sectional view are exaggerated for better presentation. Reproduced from [2].

a dielectric layer is sandwiched between the top and bottom electrodes (Figure 1.17a). In the planar configuration, the electrodes are interdigitated and fully embedded with the functional material or placed on top of it (Figure 1.17b). Such a configuration is particularly suitable for chemical sensors, where the high surface area of the functional layer is essential for the device's performance. Some electronic devices use both configurations for their operation, such as thin-film field-effect transistors (TFTs), in which the out-of-plane electric field modulates the in-plane conductivity of the channel layer. We note that only rare reports of fully printed components or devices exist, as such an approach requires the deposition of multiple overlapping layers.

In the field of transparent electronics, optically transparent electrical devices are obtained by depositing conductive and dielectric layers on transparent substrates, usually glass [33]. Due to the specific requirements an amorphous structure of metal oxides is desired. Jang et al. [61] reported fully printed TFTs on glass using $\text{SnO}_2\text{:Sb}$ as the electrodes, SnO_2 as the semiconductor and ZrO_2 as the dielectric. TFTs were transparent in the visible-light spectrum and exhibited good electrical properties. To regulate the wetting during the fabrication process they used a thin coat of PMMA and subsequent UV/ O_3 treatment. Similarly, Zeumault et al. [103] fabricated fully printed TFTs on flexible polyimide substrates at a maximum temperature of 300 °C. Again, the TFTs were transparent; however, they exhibited rather poor electrical properties, presumably due to the low processing temperature and the cracking. Li et al. [68] fabricated fully printed TFTs with excellent optical and electrical properties. Vescio et al. [104] fabricated flexible TFCs on polyimide substrates with hafnium-oxide-based dielectric and metal electrodes deposited from a silver-nanoparticle ink.

More often, inkjet printing has been used in combination with other deposition methods to fabricate the device. The common materials include zinc oxide [105], indium oxide [106]–[108] and tin oxide [61], or mixed oxides, such as indium-zinc oxide [16], [18], indium-tin oxide (ITO)[109]–[111], indium-gallium-zinc oxide [112], [113], indium-zinc-tin oxide [114], [115], zinc-tin oxide (ZTO) [94], [116], aluminum-zinc oxide [117] and others. In both, TFTs

and TFCs, the dielectric should exhibit a large breakdown field, low leakage current density, a large dielectric permittivity and good interface with other materials. Furthermore, the dielectric layer should be flat and uniform to ensure a uniform electric field distribution [118]. Reports on the printed metal oxide dielectrics include tantalum oxide [19], zirconium oxide [68], aluminum oxide [119] and silicon oxide [120].

Ferroelectrics are widely used in electronic and electro-mechanical applications, for example, in non-volatile ferroelectric random-access memories (FeRAMs), ceramic resonators, ultrasonic transducers and actuators, energy harvesters, ferroelectric capacitors, etc. Machida et al. [121] used a combination of surface-energy patterning of the substrate by self-assembled monolayers and inkjet printing to prepare patterned lead zirconate titanate (PZT) films on platinized silicon substrates. By repeating the printing process, the authors prepared $\approx 2 \mu\text{m}$ thick PZT films with (111) orientation and functional properties comparable to spin-coated films. The ink was obtained by adding a high-boiling-point solvent to a 2-methoxyethanol-based coating solution; however, further experimental details were not reported. Bathurst and Kim [91] printed uniform PZT structures on platinized silicon by adapting commercially available PZT precursor solutions. The 700 nm thick PZT layer formed after repeating the printing/annealing process 22 times. In combination with the etching process, they prepared a micro-machined ultrasonic transducer (pMUT) with good functional performance [122]. Kaydanova et al. [123] inkjet-printed barium strontium titanate on MgO substrates with a thickness between 280 and 420 nm. They fabricated tunable ferroelectric capacitors (varactors) with planar interdigitated electrodes by a combination of spray coating silver layer and lithography process. List et al. [124] successfully printed filaments of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ on Ni–W tapes. Later, Feys et al. [125] demonstrated the deposition of superconducting coatings of $\text{YBa}_2\text{Cu}_3\text{O}_7$ on strontium titanate single-crystal substrates and Ni–W tapes by inkjet printing metal-salt aqueous solutions. About 200 nm thick, flat and uniform tracks of superconductors with a strong *c*-axis orientation were obtained. Other reports on inkjet-printed functional oxide materials include Y_2O_3 -stabilized ZrO_2 [126], NiCo_2O_4 [127] and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$ [128], [129] for applications in solid-oxide fuel cells, NiO_x [130], [131] layers for applications in solar cells, and optically active phosphors $\text{YVO}_4:\text{Eu}^{3+}$ [132], $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ and $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ [133].

Functional properties and some potential applications of printed metal-oxide thin films are collected in Figure 1.18. Although the fabrication of printed devices is challenging due to the highly interdisciplinary nature of the process, the very same problems create room for innovative approaches and the fabrication of innovative devices and concepts. Good examples include printed hierarchical silver-wire circuits [134] or self-aligned channels with resolution in the sub-100-nanometre range [67]. The inkjet printing of metal oxides has enormous potential in the fabrication of sensors, MEMS devices, display technology, photovoltaics, and several other fields.

1.6 Ferroelectric Thin Films

Ferroelectrics are electrically insulating materials in which the spontaneous polarization can be reversibly switched by an external electric field. Due to inherent non-centrosymmetric structure, all ferroelectric materials are also piezoelectric. Among all the material groups, ferroelectric perovskite oxides exhibit the highest permittivity values and piezoelectric coefficients. The basic unit cell in a perovskite crystal is ABO_3 , where A and B are cation elements. The crystal lattice of the highest symmetry is a cubic one (Figure 1.19a) with a space group $Pm\bar{3}m$ and is non-polar [135]. Most ferroelectric perovskite oxides exhibit a cubic phase at high temperature, which is often referred to as a paraelectric phase. Upon

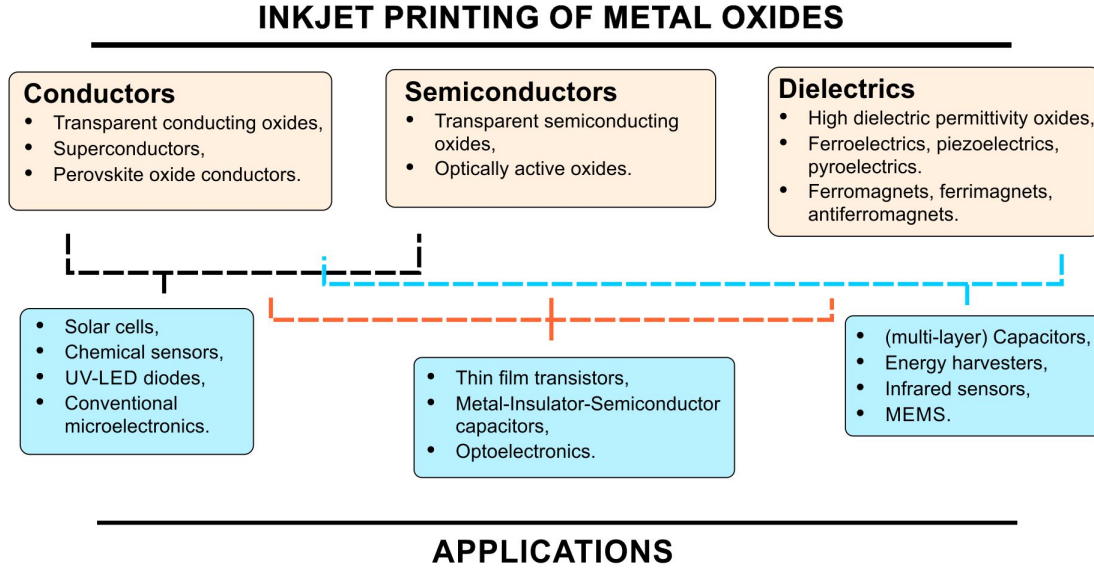


Figure 1.18: Schematic representation of selected functional properties of metal oxides and possible applications. Reproduced from [2].

cooling, the crystal undergoes a structural instability and transforms to a crystal structure of lower symmetry. Example is a tetragonal structure shown in Figure 1.19b. Due to structural frustration, the cation B is displaced from the central position and the crystal becomes polar. Several successive phase transitions to lower symmetry states are possible upon cooling, such as in BaTiO_3 .

The structural instability at the phase transition usually leads to strong anomalies in functional properties of a material, e.g. a peak in dielectric permittivity (Figure 1.19c). For applications, a strong temperature dependence of the functional properties at the classical phase transition is impractical. It has been found that some materials exhibit a morphotropic phase boundary (MPB), which is associated with large dielectric and piezoelectric properties of these materials [137]. A typical example is a solid solution of lead titanate (PbTiO_3) and lead zirconate (PbZrO_3), often abbreviated as PZT, which exhibits a MPB at around 53 mol% of PbZrO_3 . The MPB composition of PZT is relatively temperature-independent, resulting in large properties in a wide temperature range.

Usually, the spontaneous polarization is not homogeneously aligned in the same direc-

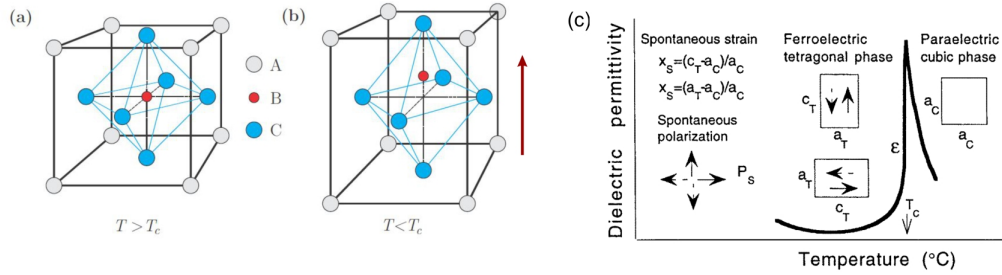


Figure 1.19: The perovskite ABO_3 unit cell in (a) cubic and (b) tetragonal phase. Net dipole moment of a crystal in (b) is shown by an arrow. (a) and (b) are from [136] and (c) is from [137].

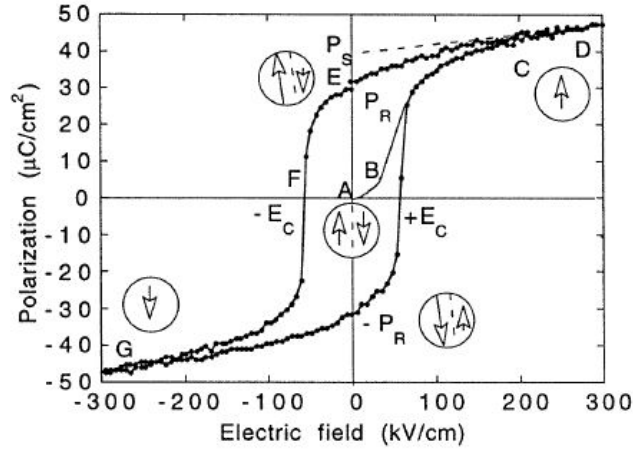


Figure 1.20: A typical polarization–electric field ($P - E$) hysteresis loop obtained for ferroelectrics. Figure was taken from [137].

tion throughout the whole crystal. The minimization of electrostatic and elastic energy leads to the formation of the so-called ferroelectric domains—regions of uniformly-oriented polarization vector. A thin region that separates two ferroelectric domains is called a domain wall (DW). DWs are classified depending on the angle between the polarization vector of two adjacent domains. The formation of 180° DWs results in minimization of the electrostatic energy, while only non- 180° DWs may reduce both electrostatic and elastic energy. The complex domain structure, that forms when a ferroelectric is cooled from paraelectric to ferroelectric phase, usually results in zero net polarization, which renders the material macroscopically non-polar. Upon the application of an electric field, the domains reorient and the material is brought into a polar state. In a polarization–electric field ($P - E$) measurements presented in Figure 1.20, the transition from a non-polar to a polar state is presented by a transition from the point A to the point D. At the point D, the majority of domains are aligned in the same direction. Upon removal of the electric field (D→E) the polarization slightly decreases due to some back-switching of domains. The polarization value at the point E is called remanent polarization, P_R . If the electric field is increased in opposite direction, the polarization will rapidly decrease and change sign at the point F. This indicates the main domain switching event and the electric field at the point F is called coercive field, E_C . Similar as for positive electric field, the polarization will reach its maximum negative value at the point G and decrease slightly upon removal of the electric field until reaching $-P_R$.

In ideal case, the $P - E$ hysteresis loops would be symmetrical and $+P_R = -P_R$ and $+E_C = -E_C$. However, many factors may influence the shape of the hysteresis loop. When the thickness of the ferroelectric decreases, the interfaces become increasingly important. Hence, thin films are prone to exhibit deviations from the ideal ferroelectric behaviour. The $P - E$ loops of ferroelectric thin films are often asymmetric and/or shifted along the field axis due to complex switching behaviour and/or presence of internal bias fields. There are many factors that cause the non-ideal behaviour of thin films: asymmetric Schottky barriers at ferroelectric-metal contacts, uncompensated electric charges in the film and interfaces, a gradient in a chemical composition, residual stress, and others [138]. Many of these factors depend on the processing of ferroelectric film as well as bottom and top electrode.

The presence of domains and domain wall displacements in ferroelectrics has been

previously associated with a large electromechanical response in ferroelectric materials [137]. While the 180° DWs are purely ferroelectric, the non- 180° DWs are both ferroelectric and ferroelastic, and can thus contribute to the piezoelectric response. When a ferroelectric is in the form of a thin film, its behaviour is essentially different from the one of a bulk material. The reason for that lies in a typically much finer grain size of a thin film and mechanical constraints imposed by the substrate. The latter can impede the non- 180° DW motion, resulting in significantly decreased piezoelectric properties of thin films [139], [140]. For example, in PZT bulk ceramics both the dielectric and piezoelectric properties peak at the compositions near the MPB because of the enhanced extrinsic and intrinsic contributions. In thin films, however, the dielectric properties peak at the MPB, while the peak in piezoelectric response is not universally present and appears to depend on the film microstructure and degree of imposed substrate clamping [141]–[143]. The DW contributions to the measured response can be probed by applying a Rayleigh law—the methodology is in detail described in Appendix C.

Chapter 2

Aims and Hypothesis

Inkjet printing has become widely recognized as the next-generation deposition technique capable of cost-effective production of electronic devices on the micrometer scale. However, due to the strongly interdisciplinary nature of inkjet printing it is still facing major problems when it comes to the realization of fully-printed devices. The layer-on-layer deposition requires full control over all process parameters, especially the wetting behaviour and the morphology of dried deposits throughout the processing.

The main aim of the first part of the thesis was to solve the fundamental issues related to wetting and drying of functional-oxide inks on inhomogeneous solid surfaces. The following methodology was used to address these issues:

- Devise a low surface-energy polymeric layer that can be easily applied to any optical grade surface.
- Treat the polymeric layer with a surface modification method to adjust the wetting.
- Optimize the processing parameters to ensure an ultimate repeatability of the wetting properties.
- Systematically study the drying of precursor inks on the surfaces with adjusted wetting properties with the aim to:
 - Relate the ink solvent composition to the shape of the dried deposit;
 - Find the physical mechanism responsible for changes in the morphology;
 - Establish a universal approach to the ink solvent design for deposition of flat and uniform layers.

The principal hypothesis was that the substrate–ink interactions strongly affect the drying process and the final morphology of the deposit. This suggests that the analysis in terms of internal liquid flows is insufficient for the explanation of the drying process and its outcome.

Once a reliable strategy of the inkjet printing of layers with uniform thickness was established, it was applied to the deposition of LaNiO_3 (LNO) and $\text{Pb}_{0.97}\text{La}_{0.02}\text{Zr}_{0.53}\text{Ti}_{0.47}\text{O}_3$ (PZT) functional structures, which is described in the second part of the thesis. It was expected that the optimization of processing conditions for each material would allow the fabrication of all-printed LNO/PZT/LNO thin film capacitors. The established process should then enable the fabrication of multilayer capacitors, i.e. structures composed of numerous LNO/PZT/LNO stacks.

The last part of the thesis explores the possibility of enhancing the piezoelectric response of ferroelectric thin films. The piezoelectric response of conventional thin films is

greatly suppressed by the substrate clamping effects. Earlier reports have shown that patterning of the films into isolated nano-islands can reduce the clamping effects and improve the piezoelectric properties. The top-down fabrication of such structures is complicated and their applicability is limited. This motivated our research toward the bottom-up approach to the synthesis of nano-structured films. The hypothesis was that the disruption of the continuity of a film by implementation of macroscopic porosity would lead to similar effects that are observed in nano-islands. This should provide a simple synthesis route to ferroelectric films with large piezoelectric properties.

Chapter 3

Materials and Methods

The experimental details are given for each chapter separately due to large variations in processing details and experimental methods used.

3.1 Materials and Equipment

The materials and equipment used in the thesis are gathered in the tables below.

Table 3.1: List of substrates used in the deposition of thin films.

Substrate	Thickness	Details	Supplier
Glass	700 μm	Eagle XG	Corning Inc.
Indium-tin-oxide-coated glass	700 μm	CEC0505	PGO GmbH
Platinised silicon wafer	625 μm	Pt(111)/TiO ₂ /SiO ₂ /Si	Sintef
Silicon wafer	500 μm	p-doped (100) Si	Prime Wafers
Polycrystalline alumina	660 μm	Superstrate, 99.6 %	Coorstek
Nickel foil	25 μm	99.98 %	Sigma Aldrich

Table 3.2: List of equipment used for processing of thin films.

Processing equipment	Model	Manufacturer
Inkjet printer	DMP 2831	Fujifilm Dimatix, Inc.
Cartridges	DMC-11610	Fujifilm Dimatix, Inc.
Spin-coater	WS-400B-6NPP/LITE	Laurell Technologies Corporation
Rapid thermal annealing (RTA) furnace	Mila-50	Ulvac, Inc.
UV/O ₃ cleaner	UV Ozone Cleaner	Ossila Ltd.

Table 3.3: List of chemicals used for the sol-gel synthesis and other experiments.

Compound	Purity	Supplier %
Poly(methyl methacrylate)	—	Alfa Aesar
Poly(vinyl alcohol)	98–99 % hydrolysed	Alfa Aesar
Poly(vinyl pyrrolidone)	—	Alfa Aesar
Anisole	99 %	Alfa Aesar
Toluene	99.5 %	Carlo Erba Reagents
2-methoxyethanol	99.8 %	Sigma Aldrich
Glycerol	99.95 %	Alfa Aesar
Benzyl alcohol	99+%	Alfa Aesar
Indium(III) nitrate hydrate	99.99 %	Alfa Aesar
Zinc(II) nitrate hydrate	99+ %	Sigma Aldrich
1,3-propanediol	98 %	Sigma Aldrich
Acetic acid	99.8+%	Sigma Aldrich
Tantalum(V) ethoxide	99.99 %	H. C. Starck
Diethanolamine	99 %	Alfa Aesar
1-octanol	99 %	Merck
Aluminum(III) sec-butoxide	97 %	Sigma Aldrich
Tetraethoxysilane	99.9 %	Alfa Aesar
Lead(II) acetate	99–103 %	Alfa Aesar
Zirconium(IV) n-butoxide	80 wt% in 1-butanol	Alfa Aesar
Titanium(IV) n-butoxide	99+%	Alfa Aesar
Lanthanum(III) nitrate hydrate	99.9 %	Sigma Aldrich
Nickel(II) acetate hydrate	99 %	Alfa Aesar
2-ethoxyethanol	99 %	Alfa Aesar
Ethanolamine	99.5 %	Sigma Aldrich
Ethylene glycol	99.5 %	Riedel-de Haen
1,2-propanediol	99.5 %	Sigma Aldrich
Diethylene glycol	99.98 %	Fisher Chemical
Octane	≥ 99.0 %	Sigma Aldrich

3.2 Tailoring Ink–Substrate Interactions (Chapter 4)

3.2.1 Materials

Poly(methyl methacrylate)–PMMA (500 kDa), poly(vinyl alcohol)–PVA (57–66 kDa), and poly(vinyl pyrrolidone)–PVP (40 kDa) were purchased from Alfa Aesar. Poly(styrene)–PS (500 kDa) was synthesized by anionic polymerization at the National Institute of Chemistry, Slovenia. 0.5 wt % polymer solutions were agitated until complete dissolution of the polymers in selected solvents: PMMA in anisole, PS in toluene, PVA in deionized water, PVP in 2-methoxyethanol. Nanotextured PMMA/PS layers were prepared by combining PMMA and PS in 1:1 weight ratio in anisole. The concentration of the PMMA/PS solution was 0.5 wt %. The liquids used for the surface-energy evaluation were water (Milli-Q, $\rho = 18.2 \text{ M}\Omega \text{ cm}^{-1}$), glycerol, benzyl alcohol and toluene.

Two inks were formulated for the inkjet printing trials. The first ink, denoted as MOE-PD, was prepared by dissolving 2890 mg of $\text{In}(\text{NO}_3)_3$ and 295 mg of $\text{Zn}(\text{NO}_3)_2$ in 20 mL of a solvent mixture of 2-methoxyethanol and 1,3-propanediol in 45:55 volume ratio. Finally, 1.14 mL of acetic acid was added. The second ink, denoted as OCT ink, was prepared by dissolving 810 mg of tantalum ethoxide and 420 mg of diethanolamine in 20 mL of 1-octanol.

Additional inks were formulated to assess the wetting of indium-tin-oxide-coated glass, platinised silicon wafer, and alumina. The tantalum-oxide-based ink (denoted as TAS ink) consisted of tantalum ethoxide, aluminum sec-butoxide and tetraethoxysilane dissolved in a solvent mixture of 2-methoxyethanol, glycerol and 1,3-propanediol in 65:25:10 volume ratio. The details of the ink preparation can be found in Refs. [19], [144]. To prepare the $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PZT) ink, dehydrated lead acetate, zirconium n-butoxide and titanium n-butoxide were first dissolved and reacted in 2-methoxyethanol, analogous to the synthetic route described in Ref. [145]. Then, 55 vol% of 1,3-propanediol was added to yield the PZT ink. The Ag ink was a commercially available silver dispersion ink, Suntronic U5714. The ink contains ethanol (~ 40 vol%) and ethylene glycol (~ 40 vol%) as the main solvents [146].

3.2.2 Preparation of thin polymeric layers

Glass substrates were cleaned by wiping them with a cloth soaked in an aqueous detergent solution, followed by a sequential ultrasonic cleaning in a detergent solution and deionized water. The substrates were dried by blowing with nitrogen gas and heating at 350 °C for 10 minutes. The polymer solutions were filtered through a 0.2 μm PTFE filter prior to spin coating. The layers were prepared by completely covering the substrate with a polymer solution and spin-coating at 3000 rpm for 30 s. Note that two different thicknesses of the PMMA layer were obtained by spin coating either the 0.5 wt% or 3 wt% PMMA solution. The samples were dried on a hotplate at 200 °C for 10 minutes immediately after spin coating. Three approaches have been used to modify the surface of PMMA and PMMA/PS layers: (i) heating on a hotplate at 350 °C in air to induce thermal decomposition of PMMA, (ii) treatment by RF oxygen plasma at 50 Pa working pressure and the power of 50 W, (iii) UV ozone treatment.

3.2.3 Inkjet printing

The inkjet printing was performed under ambient conditions using a piezoelectric printer equipped with a 10-pL cartridge. The MOE-PD and OCT inks were printed at a jetting frequency of 10 kHz with a distance between the cartridge and the substrate of 0.7 mm and a drop spacing of 20 μm . The temperature of the printer platen and nozzles was set to

ambient (22–23 °C). The printing pattern consisted of an individual line (3 mm in length) and a 500×500 μm^2 square.

3.2.4 Characterization of polymeric layers

The contact angle, θ , was measured under ambient conditions, $T = 22 \pm 1$ °C, $RH = 30 \pm 5$ %, by a sessile-drop method using a Krüss DSA20E tenziometer. The contact angle of the as-placed drops was extracted from the drop's side-view image by Young–Laplace fit for $\theta > 10^\circ$, or by circle-segment fit for $\theta < 10^\circ$. The advancing and receding contact angles were determined by pumping the liquid into or out of the drop while recording the drop from a side-view (cf. Figure 1.9b) and performing a tangent fit at the solid–liquid–vapour interface. The surface free energy and wetting envelopes were calculated using the OWRK model (see Appendix A). The surface tension of the liquids was measured by a pendant-drop method. The polar and dispersive components of the surface tension of the inks were calculated by measuring the contact angle of a selected ink on PTFE and assuming a purely dispersive character of its surface ($\gamma_S^D = 18 \text{ mJ m}^{-2}$, $\gamma_S^P = 0 \text{ mJ m}^{-2}$). The surface morphology was studied using an Asylum Research MFP-3D-STM atomic force microscope (AFM) in tapping mode using Olympus OMCL-AC240TS-R3 cantilevers. The thickness of the polymeric layers was estimated by producing a scratch with a sharp needle, recording the thickness profile across the scratch with AFM, and subtracting the height differences. The thicknesses of the thin polymeric layers deposited from the 0.5 wt% solution were: 3 nm for PVA, 5 nm for PVP, 10 nm for PMMA and 23 nm for PS.

3.3 Drying of Solution-Based Inks (Chapter 5)

3.3.1 Materials

Solutions of lanthanum nitrate hydrate and nickel acetate hydrate with concentrations in the range 0.1–0.5 mol L^{−1} were prepared by agitating the chemicals in selected solvents (ethanolamine, ethylene glycol, 1,2-propanediol) at 80 °C for 30 min. The La/Ni molar ratio was 1. Solutions of titanium n-butoxide and tantalum ethoxide with concentrations in the range 0.1–1.0 mol L^{−1} were prepared in a nitrogen dry-box. Titanium n-butoxide was combined with ethylene glycol and agitated for 24 h. The tantalum ethoxide solution was prepared in the same way, except that tantalum ethoxide was first reacted with diethanolamine (1:1 molar ratio) for 30 min before adding ethylene glycol.

In experiments of evaporation-induced wetting transitions (Section 5.2) the glass substrates were coated by a PMMA layer, following the route described in Section 3.2.2. In experiments of contact-line behaviour and deposit morphology (Section 5.3) the glass substrates were coated by a textured polymeric layer described in Section 4.5. The inks used in the same section were prepared by mixing lanthanum nitrate hydrate and nickel acetate hydrate solutions in 2-ethoxyethanol with ethylene glycol or/and ethanolamine. The concentration of these inks was 0.1 mol L^{−1}.

3.3.2 Physical properties

The viscosity of inks as a function of solute concentration was measured at 25 °C using a Physica MCR 301 rheometer. The surface tension of solutions was measured under ambient conditions, $T = 22 \pm 1$ °C, $RH = 30 \pm 5$ %, by a pendant drop method using a Krüss DSA20E tenziometer. The measurements were first done in air to measure the overall surface tension. Then the measurements were repeated in octane to assess the dispersive and polar component of the surface tension (see Appendix A for details).

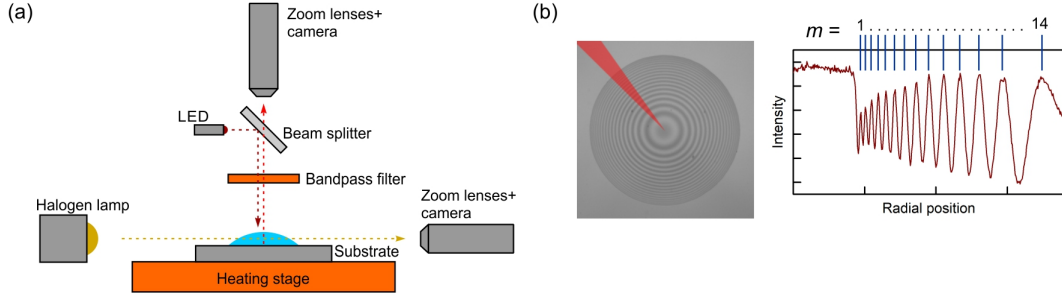


Figure 3.1: (a) The schematic drawing of the experimental set-up for observing drying drops. (b) The interference image and the intensity profile obtained by the circumferential integration.

3.3.3 Drying experiments

The drops were deposited on a substrate using a piezoelectric dispensing unit (MicroFab MJ-AL-01-50-6MX) with the orifice diameter of $50\ \mu\text{m}$. The drops were jetted at $1\ \text{kHz}$ and the waveform was adjusted for each ink separately to ensure a stable drop formation. The sessile drops studied in Section 5.3 consisted of 30 individual droplets to increase the volume of the final drop to $2 - 3\ \text{nL}$. The initial contact angle of these sessile drops corresponded to the advancing contact angle, as the jetting phase is much faster than the drop spreading phase.

The side-view images of sessile drops were recorded using a Krüss DSA20E tenziometer. The volume, diameter and contact angle were extracted by the circle-segment fit to the recorded drop profile. This method is particularly suitable for drops with large contact angles, while the quality of the fit deteriorates for thin drops ($\theta < 5^\circ$). The height profiles of thin drops were reconstructed using a thin-film interference method. The interference pattern occurs due to the phase changes of the light wave reflected at the upper boundary (liquid–air interface) and lower boundary (liquid–substrate). The phase difference is due to different path lengths of both waves with the condition for constructive interference of reflected light

$$2n_{\text{ink}}h \cos \alpha = m\lambda \quad (3.1)$$

and the condition for destructive interference

$$2n_{\text{ink}}h \cos \alpha = \left(m - \frac{1}{2}\right) \lambda. \quad (3.2)$$

n_{ink} is the refractive index of the ink, h is the local height, α is the angle of incidence of the light wave, m is the integer corresponding to the interference order and λ is the wavelength of the light. The schematic representation of the set-up is shown in Figure 3.1a. The yellow dashed line indicates the light path in cross-sectional observation of the drop and the red dashed lines show the light path for the interferometric method. The drop is illuminated by the light with a narrow bandwidth to obtain the interferometric image (right part of Figure 3.1b). The intensity profile is obtained by circumferential integration of the drop image, which reduces the noise.

The drop height profile is then reconstructed by detection of intensity maxima and counting their order from periphery toward the center (Figure 3.2a). This is performed under the assumption that the drop is the thinnest at the periphery and the thickest at

the center and that the thickness continuously increases from the edge to the center. This might not always be true as the drop can inflate in the center of the drop; however, this phenomenon is easily identifiable by tracking the changes in the interference pattern during the drying process. The parameters, such as the drop volume, diameter, contact angle and quality of the fit were determined by fitting the circular section to the experimental height profile (see Appendix B for details). To determine the quality of the fit (δ_{LF}), the last data point (adjacent to the periphery) is compared to the predicted value of the fitted function. For drops with the pinned contact line (Figure 5.13), all data points are included in the fitting process and δ_{LF} corresponds to the error in the last data point (Figure 3.2b). For the drops drying with the dynamic contact line (Figures 5.15, 5.16 and 5.17), the last three data points were excluded from the fitting process and δ_{LF} corresponds to the error of the fourth point counted from the drop edge.

The detailed height profiles presented in Figure 5.14 were determined by measuring the reflectance spectra at 0.78 μm pitch using Andor Shamrock SR-500i-D1-R spectrometer equipped with Andor Newton camera. The spectra were measured from 520.2–684.4 nm with the resolution of 0.1 nm. The drop height was calculated by fitting the Fresnel equations to each reflectance spectrum. The temperature during the drying was regulated at 40 °C using an Okolab H301-K frame and control unit.

3.4 Inkjet-Printed Functional-Oxide Multilayer Thin-Film Capacitors (Chapter 6)

3.4.1 Precursor solution synthesis

LaNiO_3 (LNO) precursor solution ($c = 1 \text{ mol L}^{-1}$) was prepared using lanthanum nitrate hydrate, nickel acetate hydrate and 2-ethoxyethanol following the route presented in Figure 3.3a. All chemicals were combined in a nitrogen dry-box and mixed at 80 °C for 1 h.

$\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PZT) precursor solution ($c = 1 \text{ mol L}^{-1}$) was prepared using dehydrated lead acetate, zirconium n-butoxide, titanium n-butoxide, and 2-methoxyethanol following the route presented in Figure 3.3b. A 10 mol% of lead acetate excess was employed to compensate for the expected lead-loss during annealing. All the chemicals were combined in nitrogen dry-box and transferred to a Schlenk line. After refluxing for 2 h

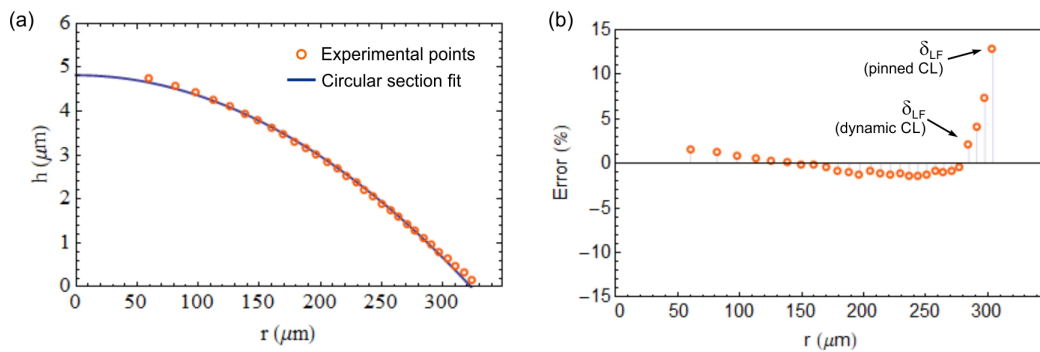


Figure 3.2: (a) The experimental height profile of a sessile drop obtained from interferometric method and the fitted circular section. (b) The deviation of experimental data points from the fitted function and estimation of the quality of the fit for drops with static and dynamic contact lines.

and distillation of by-products the solution was cooled to room temperature. Lanthanum nitrate hydrate was added to PZT solution in the case of lanthanum-doped PZT to achieve 2 mol% dopant concentration ($\text{Pb}_{0.97}\text{La}_{0.02}\text{Zr}_{0.53}\text{Ti}_{0.47}\text{O}_3$).

PbTiO_3 (PT) precursor solution ($c = 0.4 \text{ mol L}^{-1}$) was prepared using dehydrated lead acetate, titanium n-butoxide and 2-methoxyethanol following the similar route as described above. A 100 mol% of lead acetate excess was employed to compensate for the expected lead-loss during annealing. All the chemicals were combined in nitrogen dry-box and transferred to a Schlenk line. After refluxing for 2 h and distillation of by-products, the solution was cooled to room temperature and diluted to adjust the concentration to $0.0625 \text{ mol L}^{-1}$.

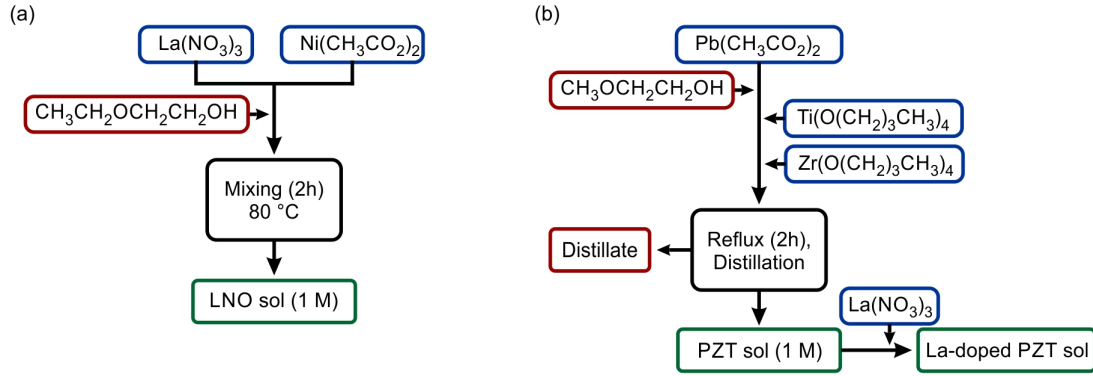


Figure 3.3: Schematic presentation of the synthesis of (a) $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PZT) and La-doped PZT precursor solutions and (b) LaNiO_3 (LNO) precursor solution.

3.4.2 Ink synthesis

LNO and PZT inks for inkjet printing were synthesized by mixing LNO and PZT precursor solutions (both of 1 mol L^{-1} concentration) with ethanolamine and ethylene glycol in 64:14 volume ratio. Additional inks that were synthesized for a study on the morphology of dried deposits contained varying fractions of 1,2-propanediol. The inks were filtered through a $0.2 \mu\text{m}$ PTFE filter prior to filling the cartridges.

The LNO structures reported in Section 6.1 were printed from the 0.1 mol L^{-1} ink. For the fabrication of all-printed capacitors the concentrations of the LNO and PZT inks were fixed at 0.2 mol L^{-1} and 0.15 mol L^{-1} , respectively.

3.4.3 Processing details

3.4.3.1 Printed lanthanum nickelate (LNO) electrodes

LNO structures in Section 6.1 were printed onto about 280-nm thick $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PZT) thin films, which were deposited onto platinised silicon substrates by spin coating 0.5 mol L^{-1} precursor solution. Prior to deposition of the PZT film, a thin PbTiO_3 seed layer was spin coated from a $0.0625 \text{ mol L}^{-1}$ PT solution (see Section ??) onto a platinised silicon substrate and annealed at 500°C for 15 min. PZT solution was then spin-coated on the PbTiO_3 layer and heated at 150°C and 350°C for 2 min at each temperature. The deposition was repeated until four layers were deposited. The films were then annealed in air at 650°C for 15 min at 10°C s^{-1} heating rate in an RTA furnace.

Prior to inkjet printing, the samples were coated by a thin layer of poly(methyl methacrylate) and treated by UV/O_3 to regulate the wetting—a similar approach is described in

Ref. [40]. This enabled reproducible printing of laterally well-defined structures on PZT films. The printing pattern consisted of squares with $250 \times 250 \mu\text{m}^2$ sides. The layers were printed using a drop spacing of $20 \mu\text{m}$ and afterwards subsequently dried/heated on hot plates set at 70°C , 150°C and 350°C . Finally, the samples were annealed in oxygen at 650°C in an RTA furnace for 5 min.

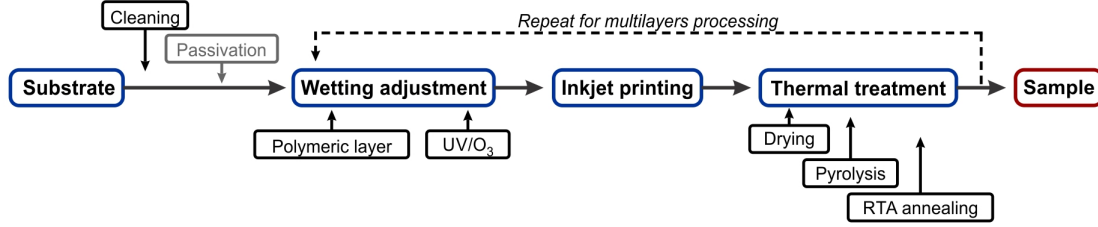


Figure 3.4: Schematic presentation of the sample preparation by inkjet printing.

3.4.3.2 Printed lead zirconate titanate (PZT) ferroelectric layers

PZT structures in Section 6.2 were printed onto about 100-nm thick LNO thin-film electrode, which was deposited onto SiO_2/Si wafers by spin coating of 0.5 mol L^{-1} LNO precursor solution. The spin-coated films were heated to 150°C and 350°C for 2 min at each temperature and annealed at 700°C in oxygen in RTA furnace after each deposition. The process was repeated until three layers were deposited.

Prior to inkjet printing, the samples were coated by a thin layer of poly(methyl methacrylate) and treated by UV/O_3 to adjust the wetting. The pattern dimensions and drop spacing were varied to investigate its effect on the morphology of the dried deposits. After printing, the patterns were dried at 70°C for 30 s, and heated to 150°C and 350°C , 2 min each. Finally, the layers were annealed in air in an RTA furnace at 650°C .

3.4.3.3 Fully-printed capacitors/transducers

A typical capacitor fabrication process consisted of several steps: (i) The thermally oxidized silicon wafer (oxide thickness of 450 nm) was passivated by an about 30 nm thick Al_2O_3 layer deposited by spin coating to prevent the reaction between PbO and SiO_2 [147]; (ii) The passivated wafers were coated with an about 8 nm thick polymeric layer, which undergoes a phase separation upon drying to produce a nano-textured surface. The as-prepared surface has a low surface energy and consequently a large contact angle of the ink, $\theta = 45^\circ$. Thus, the polymer-coated sample was treated by UV/O_3 prior to printing to adjust the contact angle to 16° ; (iii) The inkjet printing was performed under ambient conditions using a piezoelectric printer equipped with a 10-pL cartridge. The inks were printed at a jetting frequency of 20 kHz and the drop spacing of $25 \mu\text{m}$ for LNO and $20 \mu\text{m}$ for PZT. (iv) Immediately after printing, the sample was dried at 70°C for 1 min and subjected to sequential treatments at 150°C , 250°C and 350°C on hotplates, for 2 min at each temperature. The layer was then crystallized at 700°C for 5 min in an RTA furnace with the heating rate of 7.2 K s^{-1} for LNO and 10.8 K s^{-1} for PZT. The steps (ii) to (iv) were repeated several times to gradually build up the desired multi-layer structure.

A spin-coated reference sample was prepared by spin coating the 1 mol L^{-1} PZT precursor solution onto pre-printed LNO bottom electrodes with the dimensions of $0.3 \times 10 \text{ mm}^2$. A part of the sample was masked with a scotch tape to avoid coating a part of the LNO

bottom electrode. The spin-coated layer was heat treated identically to the printed samples and the spin coating was repeated three times. Finally, the top LNO electrodes were printed on the spin-coated PZT layer.

The fabrication of capacitors on alumina plates and nickel foils followed the same methodology. The polished polycrystalline alumina substrates exhibited a relative density above 97 % and a grain size below 1 μm . The Ni-foils were 25 μm thick and were first polished with alumina powder in order to reduce the surface roughness. They were then pre-annealed at 900 $^{\circ}\text{C}$ in H_2/N_2 mixture to remove any surface oxide. Then, 100 nm of HfO_2 buffer layer was grown by atomic layer deposition (ALD, Cambridge Nanotech Savannah 200 ALD System).

3.4.4 Structural and electromechanical characterization

The morphology of thin films was investigated using an Asylum Research MFP-3D-STM atomic force microscope, a JEOL JSM-7600F Field-Emission Scanning Electron Microscope, a Bruker Dektak XT profilometer and an Asylum Research MFP-3D-STM atomic force microscope. For the transmission electron microscopy (TEM) observation, a sandwich cross-section preparation technique was employed. Samples were mechanically thinned, dimpled and then finally thinned down to electron transparency using a Gatan PIPS ion-milling system. TEM studies were carried out using a JEOL JEM-2010F and a probe Cs-corrected JEOL ARM 200 CF STEM, both operated at 200 kV. EELS experiments were performed using a GATAN Quantum ER Dual EELS electron energy loss spectrometer in STEM mode. The time-of-flight secondary ion mass spectrometry was performed using a ToF-SIMS 5 instrument (ION-TOF, Germany). The Bi_1^+ ions were used as an analytical beam and O_2^+ ion beam was used for sputtering in the case of LNO electrodes (Section 6.1), while Cs^+ beam was used for sputtering in the case of all-printed capacitors (Section 6.3). X-ray diffraction was performed using a Bruker-Nonius X8 Kappa diffractometer with $\text{Mo K}\alpha$ radiation ($\lambda = 0.7107$) and an APEXII (CCD) detector. The X-ray beam was 250 μm in diameter and centred in the middle of capacitors active area.

The dielectric response was measured using a Novocontrol Alpha High Resolution Dielectric Analyzer, with the signal amplitude of 50 mV. The ferroelectric hysteresis loops in Sections 6.1 and 6.2 were measured with a triangular test signal with the frequency of 100 Hz using a Radiant Precision Premier 2. Fatigue measurements were performed using an AixACCT TF2000FE system with a sinusoidal signal (100 Hz, 300 kV cm^{-1}) being applied to the sample for 10^7 cycles. The same signal was used to measure P-E loops during the field cycling. The $P - E$ and $S - E$ hysteresis loops in Section 6.3 were measured at 100 Hz using an AixACCT TF2000FE system equipped with a double-beam laser interferometry module. The longitudinal piezoelectric coefficient was measured by applying a sinusoidal signal with 500 mV amplitude and frequency of 1 kHz and measuring the mechanical displacement using double-beam laser interferometry. A dc bias field of 100 kV cm^{-1} was superimposed on the sinusoidal signal during the piezoelectric measurements. The active area of the capacitors was 0.1 μm^2 .

3.5 Nanostructured Ferroelectric Films with a Greatly Enhanced Piezoelectric Response (Chapter 7)

3.5.1 Solution synthesis and film deposition

The $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PZT) coating solution of 1 mol L^{-1} concentration was synthesized as described in Section 3.4.1. To deposit nanostructured films, polyvinylpyrrolidone (PVP) with the molecular weight of 360 kDa was added to the PZT precursor solution in the

ratio PVP:(Zr+Ti)=1:2. After the dissolution of the PVP, a viscous coating solution ($\eta = 87$ mPa s; measured with an Anton Paar Physica MCR 301 rheometer) was obtained. All the PZT films were deposited on platinised silicon substrates by spin coating for 30 s at 3000 rpm. The samples were heated on hot plates set at 150 °C and 350 °C for 2 min each, and crystallized at 650 °C for 15 min in an RTA furnace. Nanostructured films were deposited in a single coating step, while for dense films the deposition process was repeated 10 times to achieve the desired film thickness. The nanostructured films were about 1.3 μm thick and the dense films were 1.55 μm thick (evaluated from cross-sectional SEM images). To facilitate the (100) texture of the PZT film a thin PbTiO_3 seed layer was spin coated from a 0.0625 mol L^{-1} solution (see Section 3.4.1 for synthesis details) before the deposition of the PZT and annealed at 500 °C for 15 min.

3.5.2 Device fabrication and characterization methods

The pores in the nanostructured films were filled with epoxy resin (Microchem SU-8 3010, diluted to 40 w/w%) by spin coating. The epoxy was cured at 90 °C and cross-linked under UV illumination (Lot Oriel Gruppe LS0212 UV lamp) before hard-baking at 150 °C and 250 °C. The top electrodes were patterned by laser direct photolithography with an LPKF Protolaser LDI laser writer. About 100 nm of gold was deposited by rf-sputtering (Auto 306, 5Pascal) and patterned by lift-off of the photoresist layer. The epoxy resin was then burned out by heating samples to 450 °C with a heating rate of 50 °C min^{-1} . The morphology of the thin films was investigated using a JEOL JSM-7600F Field-Emission Scanning Electron Microscope (FE-SEM) and an Asylum Research MFP-3D-STM atomic force microscope (AFM). X-ray diffraction patterns were obtained with a Panalytical X'Pert Pro X-ray diffractometer with $\text{Cu-K}\alpha_1$ radiation. Fourier-transform infrared-spectroscopy measurements were performed using a Perkin Elmer Spectrum 100 with an installed attenuated total-reflectance (ATR) module. Thermal analyses were made using a simultaneous thermogravimetry/differential thermal analysis (TG/DTA) system (Netzsch STA 409) with a heating rate of 10 °C min^{-1} in a flowing-air atmosphere using alumina crucibles. The samples were dried prior to the analysis at 80 °C for 12 h.

3.5.3 Piezoelectric and polarization measurements

The ferroelectric hysteresis loops were measured with a sinusoidal test signal (100 Hz) using Aixacct TF2000FE. Simultaneously, double-beam laser interferometry was used to record the field-induced displacements and extract the longitudinal piezoelectric coefficient d_{33} . The double-beam laser interferometry effectively removes the influence of sample bending [148]. All the small-signal measurements and Rayleigh parameters were measured at 1 kHz. The bias field dependence of d_{33} shown in Figure 7.7e was measured using an AC signal of 3.5 kV cm^{-1} for thin films and 1 kV cm^{-1} for bulk PZT. For the measurements of the piezoelectric Rayleigh parameters the samples were hot-poled at 150 °C using a DC field of 100 kV cm^{-1} applied for 5 min. The error bars shown in Figure 7.5c,d were determined by performing 10 measurements for every DC bias field. The dielectric response was measured using an Agilent E4980A Precision LCR Meter. The bulk $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ was synthesized using a conventional mixed-oxide route [149] and exhibited a relative density of 98 % and a grain size of $13.5 \mu\text{m} \pm 5.7 \mu\text{m}$.

3.5.4 Finite-element modelling

The models of the dense and porous PZT films were built with commercial software COMSOL Multiphysics version 5.2 in combination with a MEMS module and Matlab LiveLink.

The geometry of the nanostructured film was obtained from a SEM cross-sectional image of the porous sample. The image was converted to black and white and indexed with the GNU Image Manipulation Program (GIMP). Regions corresponding to pores and bulk PZT were isolated. The as-obtained structure was multiplied $10\times$ in the lateral direction, which gave a $31\text{-}\mu\text{m}$ -wide structure that was used in the model. The dense film was modelled using a similar geometry as for the porous film, except that the PZT layer was simplified to a rectangular object without any pores. In both models the thickness of the PZT film was $1.3\text{ }\mu\text{m}$, the Au electrode was 100 nm thick and the Si substrate was $625\text{ }\mu\text{m}$ thick. The material properties of air were assigned to the pores, while the PZT was described as PZT-4D (Navy Type I). The properties of the Si substrate and the Au electrode were found in the literature [150]. An electric field of 20 kV cm^{-1} was applied to the PZT in a parallel polarization vector. The structure was mechanically constrained across the bottom edge of the silicon substrate.

Chapter 4

Tailoring Ink–Surface Interactions

The surface properties of a substrate are among the most important parameters in the printing technology of functional materials, determining not only the printing resolution but also the stability of the printed features. This chapter addresses the wetting difficulties encountered during inkjet printing on homogeneous solid substrates as a result of improper surface properties. It is, in fact, uncommon that the surface properties of an ink and a substrate are balanced in such a way that the wetting is optimal for inkjet printing. Rather than that, the ink frequently completely wets the substrate or exhibits a too large contact angle. To overcome this difficulty, a few-nanometres-thick polymeric layers were used to mediate the wetting between the ink and the substrate. For a particular ink formulation, the surface-energy matching proved insufficient as the contact line recedes during drying. These inks required an additional control over the surface topography of the polymeric layer, with the aim to increase the pinning energy.

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4.1 Surface Free Energy of Glass and Polymeric Layers

Surface free energy (SFE) of the investigated surfaces was calculated via the OWRK model (Appendix A) using contact-angle measurements of water, glycerol, benzyl alcohol and toluene. Uncoated glass substrates exhibit a large SFE and a high surface polarity (see Table 4.1). According to the OWRK model, most of the solvents (except those that are highly nonpolar) would wet the glass substrate completely. Such wetting behaviour is desirable in some applications; however, it represents a large impediment to the patterning of well-defined structures using inkjet printing.

Coating a glass substrate with a thin polymeric layer affects its SFE, which depends on the chemical nature of the polymer, while the surface morphology (and surface roughness) remained unaffected. PVA and PVP exhibit a hydrophilic character and the layers accordingly exhibit a high surface polarity of about 90 %, as well as a high overall SFE (Table 4.1). In contrast, PMMA and PS are hydrophobic, thus the respective layers exhibit a low surface polarity and a significantly reduced overall SFE when compared to the bare glass. The zero polarity of a PS-coated substrate layer implies that such a surface is incapable of forming any polar interactions with the liquids used in this study.

Large differences in the surface properties of glass and polymeric layers are expected to significantly impact on the wetting behaviour of a particular liquid. To assess these differences, we formulated two inks—a moderately polar MOE-PD ink and a non-polar OCT ink (see Table 4.2)—and compared the printing outcome to the wetting diagrams. The results for the PVA layers are not reported here as they exhibited nearly identical

Table 4.1: Surface free energy (SFE) of bare glass substrate and glass substrate coated with thin polymeric layers used in the printing trials.

Sample	γ_S mJ m ⁻²	γ_S^D mJ m ⁻²	γ_S^P mJ m ⁻²	Polarity %
Bare glass	82	7	75	91
Glass/PVA	78	6	72	92
Glass/PVP	75	9	66	88
Glass/PMMA	33	26	8	23
Glass/PS	36	36	0	0

Table 4.2: Surface tension of the inks used in the printing trials.

Ink	γ_L mN m ⁻¹	γ_L^D mN m ⁻¹	γ_L^P mN m ⁻¹	Polarity %
MOE-PD	38.7	27.8	10.9	28
OCT	26.9	25.2	1.7	6.3

surface properties to glass. The position of the $\gamma_L^D - \gamma_L^P$ point of the MOE-PD ink inside the 0° wetting envelopes of the glass and the PVP layer implies that the ink wets these surfaces completely, which is reflected in the large width of the printed lines (first row, Figure 4.1) and has also been confirmed by the contact angle measurements ($\theta \approx 0^\circ$, see Table 4.3).

According to the wetting diagram the same ink should only partially wet the PMMA and PS layers. This correlates well with the printing results, where a small width of the printed lines corresponds to a large contact angle [73]. The advancing contact angles measured by a modified sessile drop method were 37° and 60° for PMMA and PS layers, respectively, which is in accordance with the predicted values from the wetting diagrams. In the case of PS-coated glass, continuous lines could not be printed; instead, the lines broke into individual large drops (bottom-right part of Figure 4.1). It is known that stable and continuous lines can be printed only when the receding contact angle is zero, or close to zero if there is a large contact angle hysteresis [69]. In the case of non-zero receding contact angle—and hence, unfixed contact line—the liquid bead breaks into separate drops due to the Rayleigh instability. As the receding contact angle of MOE-PD ink on PS was 56°, this is probably the reason why stable lines did not form on those samples. All the other samples exhibited approximately zero receding contact angle.

Due to the lower OCT ink polarity, the predicted wetting behaviour is different from that of the MOE-PD ink. The printing of the OCT ink on glass produced narrow lines, which is in accordance with the large contact angle predicted by the wetting diagram (inset of Figure 4.1, glass). Due to the slightly stronger dispersive character of the PVP, printing the OCT ink yielded broader lines than for the bare glass. The measured advancing contact angles on glass and PVP substrates were 35° and 15°, which also fits well with the predictions of the OWRK model. For both the PMMA and PS layers the $\gamma_L^D - \gamma_L^P$ of the

Table 4.3: The advancing and receding contact angles of the inks on bare glass and glass coated with thin polymeric layers. CW denotes the complete wetting, i.e., $\theta \approx 0^\circ$.

Ink	MOE-PD		OCT	
	θ_A	θ_R	θ_A	θ_R
Bare glass	CW	CW	35°	CW
Glass/PVP	CW	CW	15°	CW
Glass/PMMA	37°	CW	CW	CW
Glass/PS	60°	56°	CW	CW

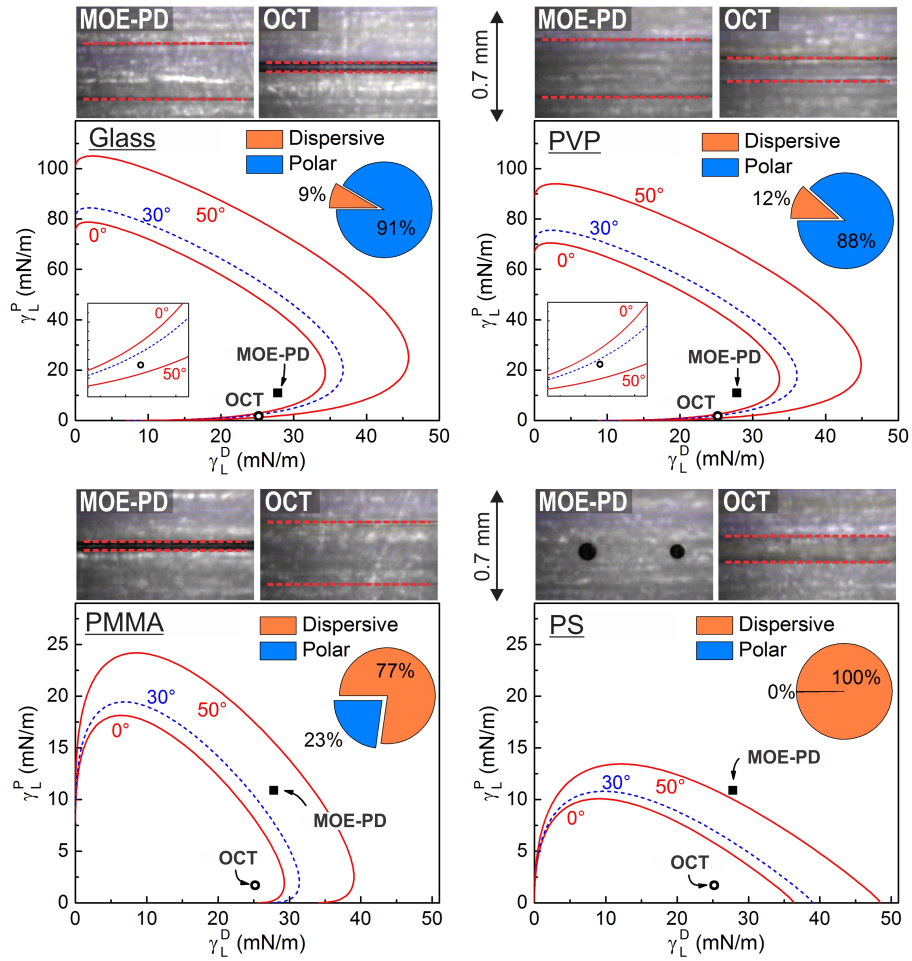


Figure 4.1: Wetting envelopes represented as $\gamma_L^D - \gamma_L^P$ plots (designed with two different y -axes scales) and optical micrographs of printed lines of two ink formulations on glass, and PVP-, PMMA- or PS-coated glass. Scale bars in optical micrographs correspond to 200 μm . Pie charts show the fractions of polar and dispersive contributions to the SFE of glass and polymeric layers. The red dotted lines in the optical micrographs mark the edges of the printed lines; however, in the case of PS-coated glass, the contact angle of the MOE-PD was too large to print a continuous line. Reproduced from [40].

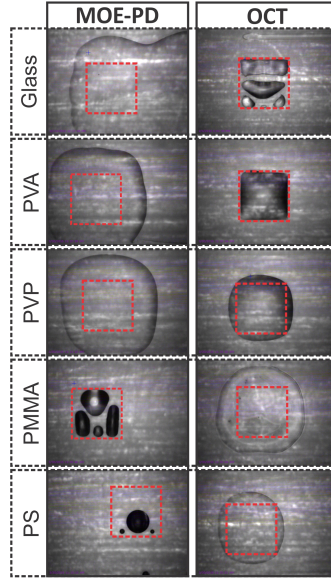


Figure 4.2: Printed square patterns of MOE–PD and OCT inks on a bare glass and glass substrates coated with thin polymeric layers. The user-defined $500 \times 500 \mu\text{m}^2$ square pattern is marked in red. Reproduced from [40].

OCT ink lies inside the 0° wetting envelopes, and accordingly, the printing of the OCT ink produced wide lines (bottom row of Figure 4.1).

The results presented above clearly demonstrate that two-component model of SFE is required to explain the wetting of the inks. For example, SFE of glass is much higher than that of PMMA layer (see Table 4.1), however, the OCT ink wets the glass better. In this case, a direct comparison of overall SFE leads to a wrong prediction of the wetting. The same occurs when comparing the wetting of OCT and MOE–PD ink on the glass, whereas the MOE–PD ink has a larger SFE but exhibits a lower contact angle than OCT ink. The presence of a solute and additives, such as acetic acid in the OCT ink or diethanolamine in the MOE–PD ink, could also affect the wetting behaviour. More sophisticated models, e.g., the van Oss–Good–Chaudhury model, could be used to distinguish between the Lewis acid–base contributions; however, a higher complexity of the model makes the analysis in terms of wetting diagrams impossible. Even though OWRK model provides only approximation of the SFE, a good correlation to the experimental results was found for all investigated combinations.

The ability to deposit well-defined patterns is a prerequisite for the realization of electronic devices by printing technology. Patterns often consist of different geometrical shapes, such as dots, lines and rectangles. While the drops are always stable, the lines and the squares may exhibit instabilities. The bulging of lines is promoted by a large contact angle, low printing speed and small drop spacing, while breaking of lines appears due to Rayleigh instability caused by a non-zero receding contact angle [9]. Similarly to lines, rectangular patterns also exhibit instabilities, such as the breaking of continuous structures into separate droplets and rounding of the corners, which are often related to a non-zero receding contact angle [74], [151].

Our experiments show that the stability of 2-dimensional patterns, i.e., $500 \times 500 \mu\text{m}^2$ squares, is even more sensitive to the surface properties than the stability of the lines. Even though the lines were continuous when printing the OCT ink on glass (or similarly the MOE–PD on PMMA, see Figure 4.1), the continuity of the square patterns broke for

the same ink–substrate combinations (Figure 4.2). On the other hand, the ink–substrate combinations that produced wide lines formed undefined shapes when printing a square pattern, e.g., MOE-PD on the glass. The deterioration of the square shape is a consequence of the ink overspreading driven by a small contact angle. The overspreading could, to some degree, be minimized by increasing the drop spacing, e.g., in the cases of printing OCT on PVP and PS layers. However, for the MOE-PD ink on the glass, PVA or PVP layers, as well as the OCT ink on the PMMA layer, the over-spreading is too extensive and inhibits the deposition of well-defined patterns.

The results clearly reveal that the ink–substrate interactions are a key factor in high-quality printing. The wetting behaviour of the thin polymeric layers on a glass substrate is determined by the intrinsic properties of the polymer. However, printing geometrically more complex objects, such as those shown in Figure 4.2, requires a precise adjustment of the substrate surface properties. In the following sections we describe simple approaches to the precise modification of the surface properties by the surface treatment of the PMMA layers.

4.2 Thermal Decomposition of PMMA Layers

Upon heating PMMA degrades almost completely into its monomeric units [152]. The decomposition temperature is strongly affected by the atmosphere in which the degradation occurs as well as by the polymerization method and the molecular weight of the polymer [153]. In air, the onset of the thermal decomposition of the PMMA powder is typically at ~ 250 °C [154]. The decomposition of thin layers, however, is expected to differ somewhat from the decomposition of powder [155]. Isothermal heating of a PMMA layer on glass at 350 °C resulted in a steady decrease of its thickness (Figure 4.3) due to evaporation of the decomposition products and densification of the layer. The thickness of the initially 175-nm-thick layer decreases to zero after 20 min of heating at 350 °C, indicating a complete decomposition of the polymer.

The impact of thermal decomposition of the PMMA layer on its surface properties was evaluated by measuring the advancing contact angle of MOE-PD ink on a PMMA layer that was heated at 350 °C for different times and afterwards cooled to room temperature. Figure 4.3 presents the contact angles of the MOE-PD ink on these substrates. For heating times up to about 15 min the contact angle remains almost unchanged at about 35°. However, when the PMMA layer thickness approaches zero (this region is indicated by the vertical dashed lines in Figure 4.3) we observe a rapid reduction in the contact angle of the MOE-PD ink.

To provide a better insight into the origins of the observed wetting transition we performed a surface-energy analysis of the PMMA layers heated for different times at 350 °C. Note that in these experiments the polymer concentration was 0.5 wt%, which strongly reduced the initial layer thickness to about 10 nm. Although the same experiment could be performed with thicker layers, it is easier and more elegant to control the wetting transition of the thinner layers. Due to a lower thickness, the layer decomposes at shorter heating times. As shown in Figure 4.4a, polar and dispersive contributions to the SFE of the initial 10-nm-thick and 1-minute heated PMMA layer are very similar, while 4 min of heating already initiates the wetting transition. For $t \geq 4$ min, the polar component of the SFE strongly increases and, simultaneously, the dispersive component decreases. After 20 min of heating, the SFE becomes similar to that of bare glass. The evolution of the wetting envelopes with the heating time of the PMMA layer is shown in Figure 4.4b. As expected from the surface-energy analysis, the wetting envelopes drastically change with the degree of the layer decomposition. The most pronounced change in wetting envelopes

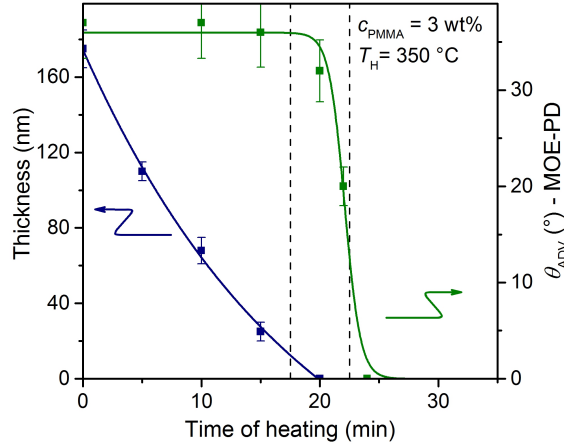


Figure 4.3: Thermal decomposition of PMMA layer at 350 °C in air. The layer was deposited from a 3 wt% PMMA solution. The plot shows the thickness of the layer and the advancing contact angle of the MOE–PD ink as a function of the heating time. Reproduced from [40].

is the upward stretch due to a strong increase in the polar contributions with the heating time. This stretching is accompanied by a slight shift of the wetting envelopes to the left—a consequence of the dispersive component reduction. The left-shift can be clearly observed when comparing the layers heated for 0 and 4 min. The inset of Figure 4.4b shows that additional heating shifts the wetting envelopes even more to left. Both the upward stretching and left-shift of the wetting envelopes have a large impact on the wetting behaviour, which will be discussed in the following paragraphs.

The transition of the surface properties upon heating—from PMMA-like toward glass-like—can be explained by a situation in which the glass substrate percolates in random small spots through a decomposing PMMA layer. In such spots the surface properties correspond to the ones of the glass substrate, while the total area of the exposed spots determines the macroscopic properties. We thus express the surface concentration of polymer molecules on the substrate as the surface coverage, n , which is the area covered by polymer molecules divided by the total area. For $n = 1$, the surface is completely covered by the polymer molecules and the surface properties correspond to those of the polymer (exemplified by Stage 1 in Figure 4.5). For $n = 0$, there are no polymer molecules at the surface–air interface and the properties correspond to those of the substrate, see Stage 3, Figure 4.5. For $0 < n < 1$, the properties strongly depend on the value of n . The polar and dispersive components relate to the surface coverage with

$$\gamma^P(n) = (\gamma_p^P - \gamma_s^P) n + \gamma_s^P, \quad (4.1)$$

$$\gamma^D(n) = (\gamma_p^D - \gamma_s^D) n + \gamma_s^D. \quad (4.2)$$

Equations 4.1 and 4.2 are valid in the case of non-interacting percolative spots that are much smaller than the liquid feature wetting the substrate. Inserting the boundary conditions ($n = 1$ or 0) into the equations shows a clear transition from polymer-like toward substrate-like surface properties. The situation is schematically represented by Stage 2 in Figure 4.5.

Printing a square pattern on the PMMA layers after different stages of the thermal decomposition assessed the viability of the approach. Printing on the as-deposited PMMA

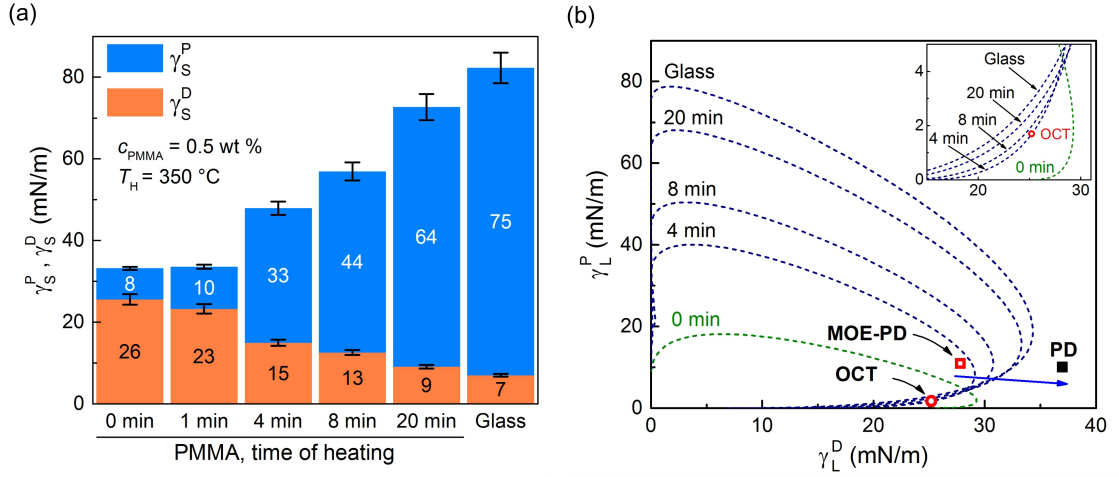


Figure 4.4: (a) Polar and dispersive contributions to SFE of the 10-nm-thick PMMA layers that were heated for different times at 350 °C. The layer was deposited from a 0.5 wt% PMMA solution. (b) Wetting envelopes calculated for 0° contact angle. The wetting envelope of the sample heated for 1 min is similar to that of the initial PMMA layer and is not shown. The inset shows the evolution of wetting envelopes near the γ_L^D -axis. In both plots the data for the glass substrate are included for comparison. The $\gamma_L^D - \gamma_L^P$ points of MOE-PD, OCT and 1,3-propanediol (PD) are included and the change of the SFE due to evaporation of the MOE-PD ink is indicated by a blue arrow towards the point PD. Reproduced from [40].

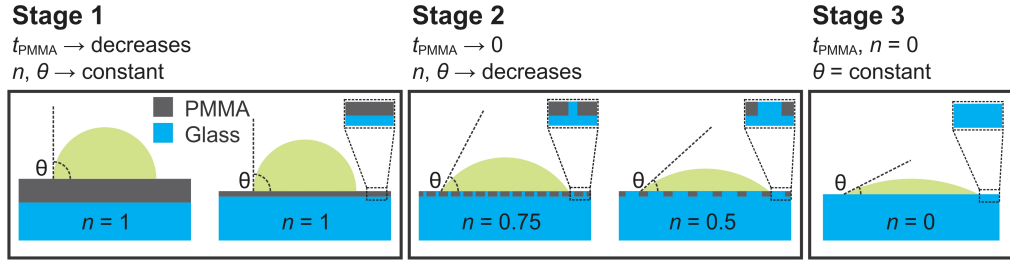


Figure 4.5: Schematic presentation of the wetting transition for the PMMA layer depending on its coverage (n) of the glass substrate from $n = 1$ in Stage 1 to $n = 0$ in Stage 3. The contact angle of the liquid (marked in green) on the PMMA layer is much higher than on the glass. The drop, PMMA layer and glass substrate are not in scale for a better visualization of the decomposition process.

layers results in a discontinuous layer of the MOE-PD and over-spreading of the OCT ink, as already discussed in the previous section. Isothermal heating of the PMMA layer for 4 min changed the surface properties and also the morphology of the square pattern printed from the MOE-PD ink. The poorly defined edges of the printed square (left column in Figure 4.6) suggest that further heating is required to create optimal patterning conditions. Upon heating for a total of 8 min the deposition of well-defined structures of MOE-PD ink was enabled, whereas longer heating times decreased the printing resolution and resulted in over-spilling of the ink. The printing results (Figure 4.6) show some inconsistency with the wetting envelopes presented in Figure 4.4b. Although the position of the MOE-PD

$\gamma_L^D - \gamma_L^P$ point in the wetting envelope of the layer heated for 4 and 8 min indicates that the ink should completely wet the substrate, the printing resulted in a partial wetting. This inconstancy is probably related to preferential evaporation of MOE during the printing process, which induces a shift from the MOE-PD toward the PD $\gamma_L^D - \gamma_L^P$ point in the wetting diagram (indicated by a blue arrow in Figure 4.4b)—a consequence of such a shift is a larger actual contact angle for the printed ink [146].

A different wetting situation was observed in the case of the OCT ink. A 4-minute heating at 350 °C already resulted in optimal surface properties for the layer and enabled patterning of well-defined squares (right column in Figure 4.6). Any additional heating of the PMMA layer resulted in a degradation of the print quality caused by a too large contact angle. The printing results are in good correlation with the wetting envelopes presented in Figure 4.4b, whereas a right shift of the wetting envelopes with the heating time indicates an increase in the contact angle. The results presented above show that heating the PMMA layer at 350 °C produces a smooth transition from a large to a small contact angle for the MOE-PD ink (and vice versa for the OCT ink), which can be exploited for a precise tailoring of the wetting of glass substrates.

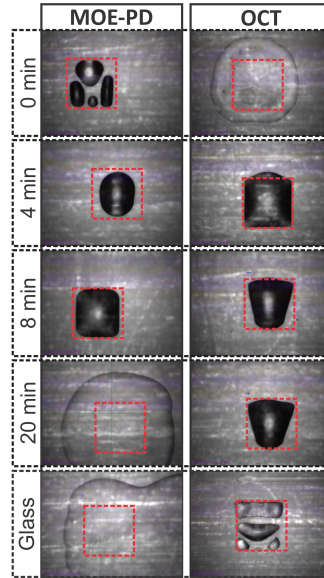


Figure 4.6: Printed square pattern of MOE–PD and OCT inks on as-deposited and partially thermally decomposed PMMA layers. The user-defined $500 \times 500 \text{ } \mu\text{m}^2$ square pattern is marked in red. Reproduced from [40].

4.3 O₂ Plasma and UV/O₃ Treatment of Polymeric Layers

Although thermal decomposition of the PMMA layer proved highly efficient for wetting adjustment on several homogeneous substrates, it cannot be applied for partially inhomogeneous surfaces, such as substrates with pre-deposited structures. This is exemplified by printing the MOE–PD ink on a glass substrate with sputtered Au stripe electrodes—different surface properties of both materials result in inhomogeneous wetting of the ink (Figure 4.7a). Coating with PMMA decreases the SFE and the contact angle becomes too large for reliable printing of lines (Figure 4.7a). Heating the PMMA coated sample to 350 °C results in the decomposition of the polymer; however, the decomposition rate depends on the underlying surface: it is more rapid in the Au-coated areas. As the wetting of a

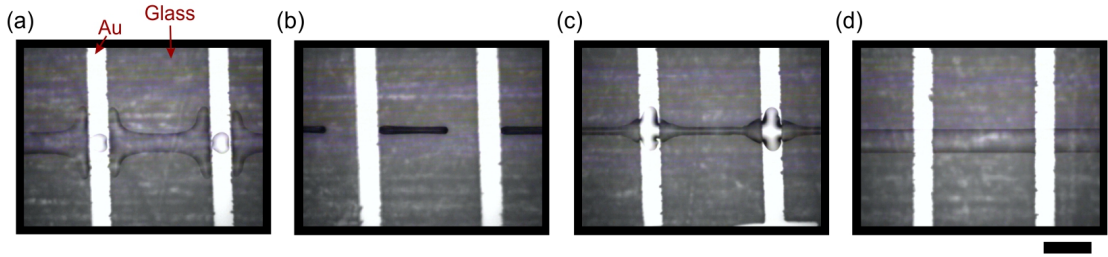


Figure 4.7: Inkjet printed line of MOE-PD ink over a partially inhomogeneous surface: glass substrate with sputtered gold stripes. (a) Untreated sample, (b) PMMA coated sample, (c) PMMA coated sample heated 5 min at 350 °C, (d) PMMA coated sample treated with O₂ plasma for 0.5 s. The scale bar is 200 μm .

partially decomposed layer strongly depends on its surface coverage (see 4.2), the heating thus produces inhomogeneous wetting behaviour of the ink (Figure 4.7a).

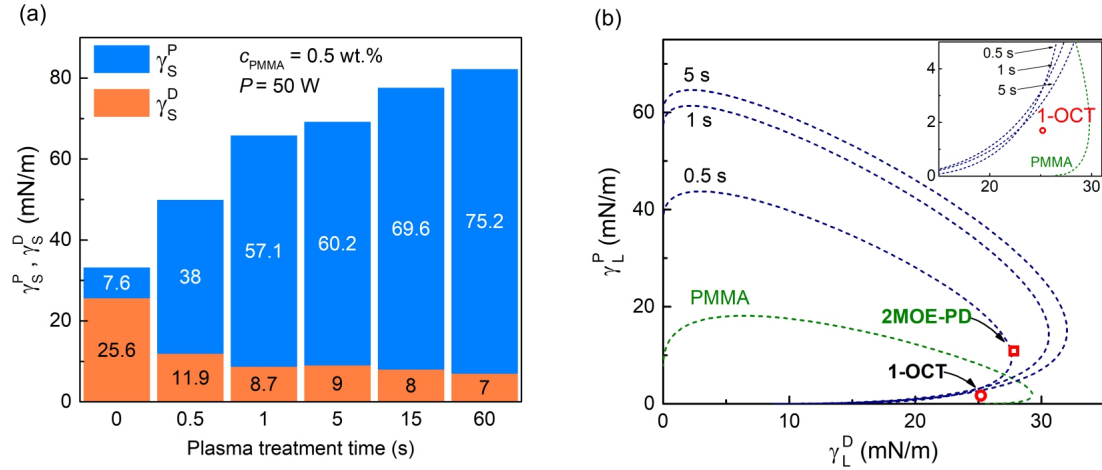


Figure 4.8: (a) Polar and dispersive contributions to SFE of the 10-nm-thick PMMA layers that were treated by O₂ plasma. The layer was deposited from a 0.5 wt% PMMA solution. (b) Wetting envelopes calculated for 0° contact angle. The inset shows the evolution of wetting envelopes near the γ_L^D -axis. The bottom plot also includes the $\gamma_L^D - \gamma_L^P$ points of MOE-PD and OCT inks.

A fundamentally different approach of the wetting adjustment is based on treating the PMMA layer with oxygen plasma [156] or UV/O₃ [157]. Both methods produce highly reactive oxygen species that react with the surface of PMMA layers, leading to the increase in the surface polarity [158]. By adjusting the time of exposure to reactive oxygen species it is possible to continuously tailor the SFE of the PMMA layer (Figure 4.8a). A gradual increase in a polar component accompanied by a decrease in a dispersive component has a large effect on the wetting envelopes (Figure 4.8b), which provides a way to adjust the wetting of a given ink. In contrast to the thermal decomposition of the PMMA layer, SFE for O₂ plasma treated PMMA layer is independent of the underlying surface. This is exploited for adjusting wetting of partially inhomogeneous surfaces, such as the pre-deposited structures (Figure 4.7d). Exposing the PMMA layer to UV/O₃ produces similar results as O₂ plasma treatment, while the equipment for UV/O₃ treatment is much simpler than for generating O₂ plasma.

4.4 Adjusting the Wetting of Different Substrates

The possibility to select a substrate without concern for its wetting properties is beneficial in printing technology. In this section we demonstrate how the wetting for the three ink–substrate systems can be adjusted using the thin polymeric layers.

The indium–tin–oxide-coated glass (ITO/glass) is used in applications that require a transparent electrode, such as photovoltaics and displays. We highlight the inkjet printing of thin dielectric structures from tantalum-oxide-based (TAS) ink [19]. Printing on bare ITO/glass results in extensive spilling of the ink, which hinders the possibility of patterning (Figure 4.9, top left). The deposition of a 10 nm thick PMMA layer and partially decomposing it by heating at 350 °C for 8 min improves the wetting behaviour and enables the deposition of well-defined patterns with a high resolution (Figure 4.9, top right).

The second example is printing ferroelectric lead zirconate titanate (PZT) onto a platinumized silicon wafer (Pt/Si). The patterning of PZT ink is already possible on bare Pt/Si substrates; however, the printing results in some over-spilling of the ink and a large width of the printed lines (Figure 4.9, middle left). Coating the surface of the Pt/Si substrate with a 10-nm-thick PMMA layer improved the printing resolution (Figure 4.9, middle right). The increase in the contact angle is furthermore reflected in a reduction in the line width from 230 μm to 60 μm for the uncoated and the PMMA-coated Pt/Si substrate, respectively.

Another possible application for thin polymeric layers is the promotion of ink spreading on the substrate. An example is the deposition of large-area electrodes by inkjet printing commercially available silver nanoparticle ink (Ag ink) onto alumina (Al_2O_3) substrates. In this particular case the ink was printed with a relatively large drop spacing of 40 μm , which resulted in a non-uniform layer with a broken continuity (Figure 4.9, bottom left). Coating Al_2O_3 with a hydrophilic PVP layer promoted the spreading of the ink and ensured a stable coalescence of the drops (Figure 4.9, bottom right).

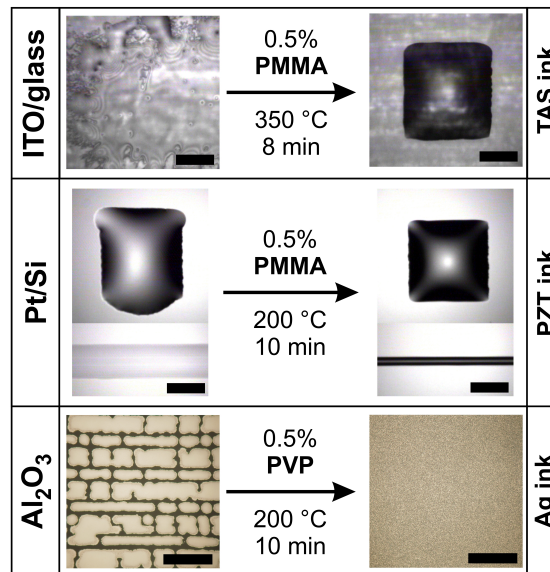


Figure 4.9: Inkjet printing of different inks on bare substrates (left) and substrates coated with a thin polymeric layer (right). Scale bars correspond to 250 μm . Reproduced from [40].

4.5 Promoting Contact Angle Hysteresis

While the polymeric layers discussed above provide an excellent control over the SFE, they show a relatively small contact angle hysteresis (CAH) due to the absence of topographical features and, consequently, very low surface roughness (Figure 4.10a, see Section 1.3.3). Although CAH is sufficient for printing of stable patterns, the instabilities may occur during the drying of printed features. This is exemplified by printing of lanthanum nickelate precursor ink with the ternary solvent composition of 2-ethoxyethanol (2EE), ethylene glycol (EG) and ethanolamine (EA) on PMMA layers treated by UV/O₃ for 150 s [159]. The advancing contact angle of the ink on such layer is 10°. Despite the low advancing contact angle of the UV/O₃-treated PMMA layer the drying results in de-pinning of the contact-line (CL), which is marked by an inward motion of the CL upon evaporation (Figure 4.10b).

To increase the CAH, the PMMA was combined with PS to induce a phase separation

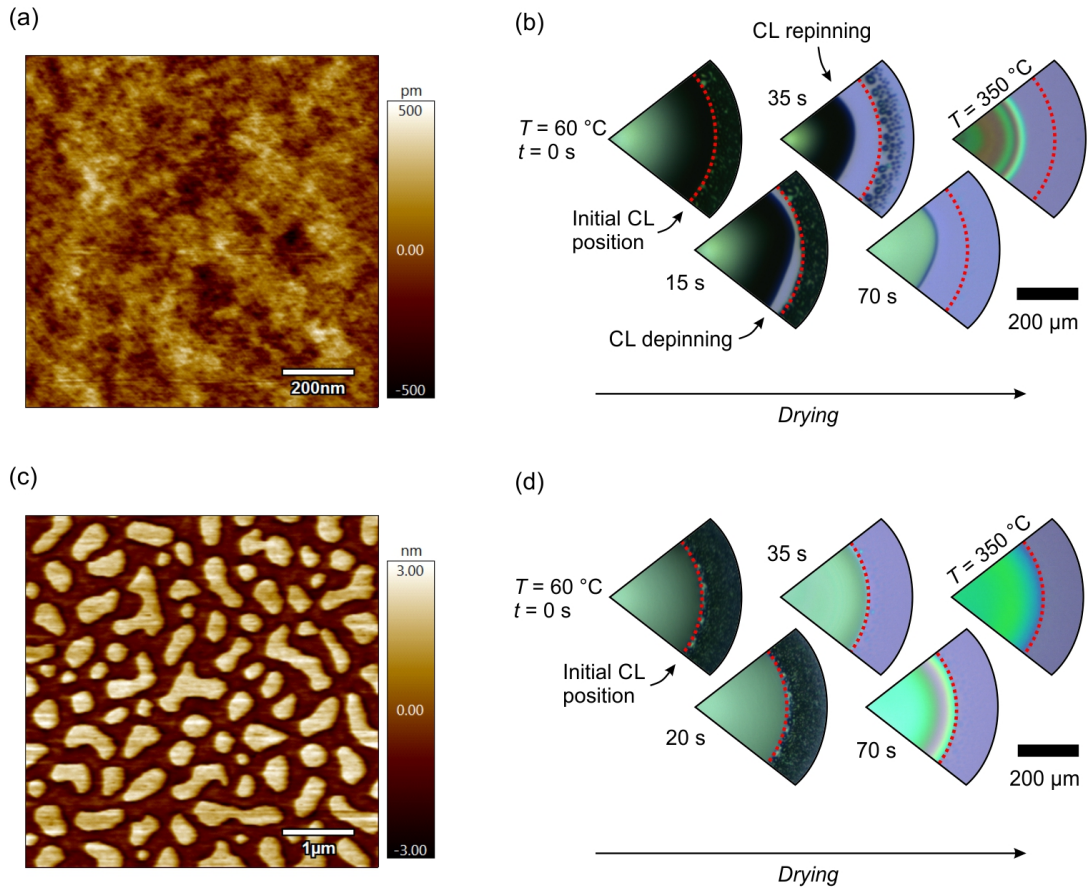


Figure 4.10: Wetting behaviour on smooth PMMA and nanotextured PMMA/PS polymeric layers. (a) AFM topography scan of a PMMA polymeric layer. (b) Optical images of the sessile drop upon drying acquired at major wetting transitions. (c) AFM topography scan of a textured PMMA/PS polymeric layer. (d) Optical images of the sessile drop acquired upon drying on PMMA/PS layer. The original contact-line (CL) position in (b) and (d) is marked by the red dotted lines. The polymeric layer was treated by UV/O₃ for 150 s prior to printing to facilitate the wetting and the ink used was LNO-64EA (see Table 6.2).

during deposition process and deposit polymeric layer with textured morphology. These layers exhibit periodic topographical features about 400 nm wide with a 4 nm peak-to-valley height (Figure 4.10c). Each feature acts as a topographical defect and effectively increases the pinning energy of the wetting liquid and its contact line hysteresis [58], [160]. In contrast to a smooth surface which is characterized by the dynamic contact-line behaviour of the drying drop (Figure 4.10b), the textured surface does not exhibit any wetting instability (Figure 4.10d). The developed polymeric layers have five key attributes: (i) they can be easily applied on almost any surface, (ii) the surface properties are reliably reproduced, (iii) the as-deposited layers have low surface free energy which can be increased by UV/O₃ treatment, (iv) they readily decompose at temperatures higher than 350 °C and (v) are sufficiently thin (~ 8 nm) to prevent cracking and minimize its effects on the adhesion of the functional oxide layer, and reduce the amount of residual carbon at the interface.

Chapter 5

Drying of Solution-Based Inks

A well known issue in printing technology is the ring-like deposit morphology (coffee stain effect) which occurs after the printed feature is dried. Up to now there has been no universal solution or approach to printing of uniform structures. Commonly, the coffee stain effect is suppressed by employing a specific solvent mixture, which induces a Marangoni flow as the drying proceeds. However, the experiments indicate that the deposit morphology depends strongly on the wetting conditions, drop spacing, feature size, drying temperature and micro-environment. It is thus unlikely that the internal liquid flows alone determine the shape of a dried deposit.

In this chapter the drying of solution-based inks is discussed in detail. First, the basic view of a drying drop is established. In the second part, the impact of the solvent composition on the evaporation-induced wetting transitions is discussed. The third part then focuses on the drying of two inks, among which one produces a ring-like deposit and the other a dome-like deposit. The correlation between the contact line (CL) dynamics at low contact angles and the final deposit morphology is established.

5.1 Definition of a Drying Sessile Drop

5.1.1 Single Solvents Without a Solute

In the most basic scenario a single-solvent drop dries on a solid substrate. The drops discussed here are sufficiently small that they assume the shape of a spherical cap due to the surface tension forces. The flattening of a drop due to the gravity occurs only when the Bond number ($Bo = g\rho R^2/\gamma$) becomes comparable or greater than 1. For solvents used in the thesis, the drops with a diameter smaller than ~ 1.4 mm have $Bo \ll 1$ and can be considered as ideal.

Depending on the dynamics of the contact line (CL), two main modes of evaporation exist: a constant drop radius (CDR) mode (Figure 5.1a) and a constant contact angle (CCA) mode (Figure 5.1b). In the CDR mode the CL is pinned and remains stationary throughout the drying process, while the contact angle decreases due to the loss of solvent. A pinning of the drop generally occurs for the ink–substrate combinations with a small θ_{eq} and a sufficiently large contact angle hysteresis ($\theta_R = 0$). On the contrary, the CCA mode is characteristic for non-wetting combinations, or systems with CL destabilized by an external modulation (e.g. electrowetting or surface acoustic waves). The CCA mode has often been advertised as the method for successful suppression of the coffee stain effect; however, it is important to realize that at large θ_R the CL recedes almost exclusively without the deposition of the solute. In practice such behaviour results in a loss of the pattern definition—often producing a circular deposit regardless of its initial shape.

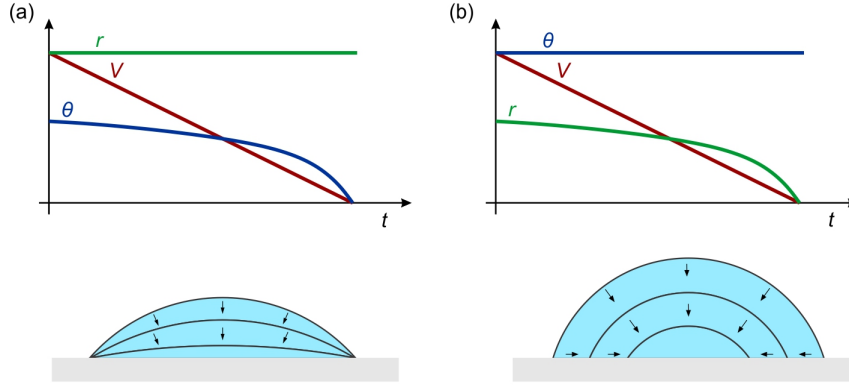


Figure 5.1: The main modes of drop evaporation depending on the contact line (CL) dynamics: (a) constant drop radius (CDR) mode and (b) constant contact angle (CCA) mode. The bottom part shows a cross-sectional illustration of the drying drop in a particular mode. V , r and θ are the drop volume, radius and contact angle, respectively.

The drop may transit between both modes, e.g. it first dries in the CDR mode and at a certain moment it undergoes CL depinning and later exhibits the CCA behaviour. A special case of periodic and rapid transitions between both modes is a "stick-slip" motion of the CL. In this case the drop is mostly in a CDR mode with occasional discrete jumps to the CCA mode. The stick-slip mode rarely occurs for solution-based inks and is more common for dispersion inks [161].

Under standard conditions the evaporation rate along the liquid–air interface of a spherical drop is not uniform. For drops with small contact angles ($\theta \ll 90^\circ$) the evaporative flux J is limited by the vapour diffusion and equals $J = -D\nabla c$, where D is the diffusion coefficient and c is the solvent vapour concentration. As originally proposed by Deegan et al. [12], the evaporation field can be found by solving the analogous electrostatics problem. Under assumptions that the evaporation is not influenced by the solute and that the enough solvent can be supplied to all regions of a drop, Popov [162] derived an expression for the evaporation flux of a thin drop

$$J(r) = \frac{2D(c_s - c_\infty)}{\pi\sqrt{R^2 - r^2}}, \quad (5.1)$$

where c_s is the concentration of a saturated vapour just above the liquid–air interface, c_∞ is the ambient vapour concentration, R is the radius of the drop and r is the distance from the drop center. It can immediately be seen that J diverges on r approaching R , i.e. near the periphery of a drop, which indicates that the evaporation is much stronger near the CL. There are several direct and indirect consequences of a higher evaporative flux at the periphery of a drying drop. For drops with the pinned CL this leads to the inevitable outward liquid flow from the center of the drop to replenish for the evaporated solvent and maintain the spherical shape of a drop. This so-called capillary flow has been associated with the accumulation of the material at the edge, i.e. coffee stain effect [12]. The second consequence of a non-uniform evaporation flux is the appearance of a temperature gradient inside the drop (and the substrate) due to the evaporative cooling. The temperature gradient can be significant and can produce a surface tension gradient, which results in a thermal Marangoni flow [163].

5.1.2 Solute effects

There are two major approaches to the formulation of inks based on the physical state of the solute/solid content: solution-based inks and dispersion-based inks. The solution-based inks consist of only one phase as the solute is homogeneously dissolved in the solvent. The inks discussed in this thesis are all solution-based.

The presence of a solute strongly impacts the drying of a drop. Physical properties of a solution differ from that of a pure solvent and depend on the solute concentration. The increase in the solute concentration of a polymer solution typically produces an exponential increase in its viscosity [164]. Similarly, the viscosity increases with the concentration of organometallic precursors dissolved in organic solvents (Figure 5.2a). The evaporation of the solvent during drying increases the solute concentration, especially at the periphery (Figure 5.2b). The concentration eventually becomes sufficiently large to form a gelled region where the solute transport becomes negligible. The characteristics of a gelled region (gelation concentration, pinning energy, solubility) relate to the chemistry of a solute in a solution. For many polymers the transformation to a gelled state is reversible and the gelled region can redissolve in the solvent; for example, by switching between evaporation and condensation [165]. In sol-gel inks, the formation of the gelled region is irreversible and the precipitate cannot redissolve.

In many experimental and theoretical studies on drying, the presence of solute was assumed to affect only the viscosity, while the surface tension was considered to be constant. It has been shown that the surface tension of a polymer solution actually depends on the attractive or repulsive interaction between the polymer molecules and the solvent [166]. The change in the surface tension with the solute concentration ($d\gamma/dc$) can be both positive or negative. Much less is known about the surface tension behaviour of solutions of transition metal alkoxides and salts in organic solvents. Aqueous solutions of inorganic salts typically exhibit a positive $d\gamma/dc$ coefficient [167]. Similarly, the surface tension of lanthanum nitrate and nickel acetate (precursor solution for LaNiO_3 , LNO) dissolved in organic solvents increases with the solute concentration (Figure 5.3a). The $d\gamma/dc$ coefficient is 6.8×10^{-3} for ethylene glycol (EG), 5.8×10^{-3} for ethanolamine (EA) and 5.7×10^{-3} for 1,2-propanediol (12PD) in the $0.1 - 0.5 \text{ mol L}^{-1}$ concentration range. The measurement of the interfacial tension with octane (non-polar solvent) was used to estimate the polar

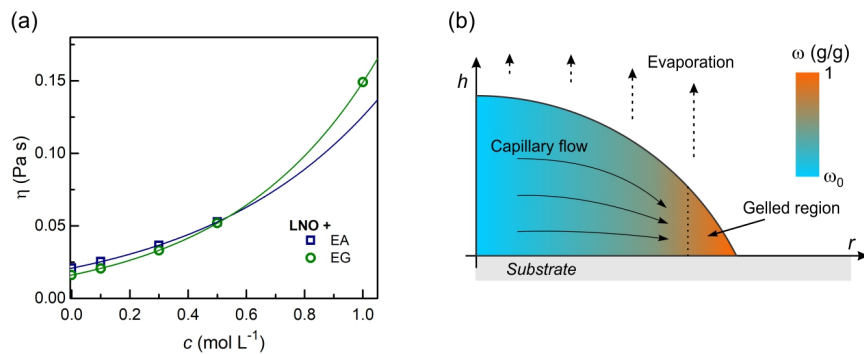


Figure 5.2: (a) The viscosity of lanthanum nitrate and nickel acetate solutions (LNO) in ethylene glycol (EG) and ethanolamine (EA). (b) A cross-sectional illustration of a drying drop containing solute in the CDR mode. Upon drying the solute concentrates at the edge of the drop due to the capillary flow to the CL. ω corresponds to the mass concentration of the solute.

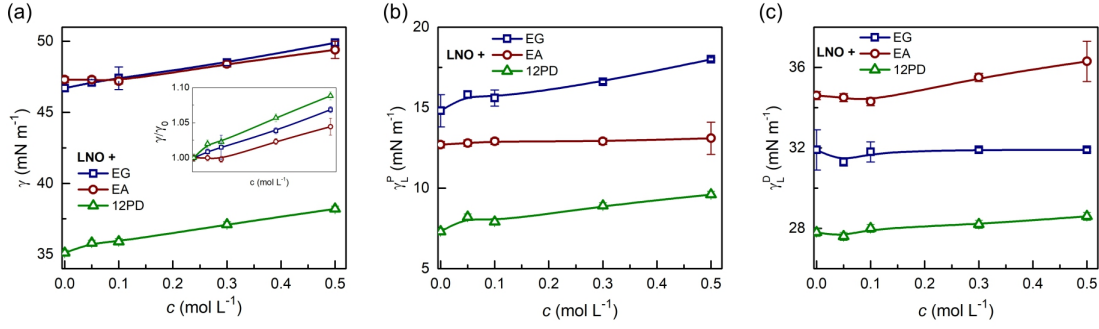


Figure 5.3: The surface tension of lanthanum nitrate and nickel acetate (LNO) solutions in ethylene glycol (EG), ethanolamine (EA) and 1,2-propanediol (12PD). (a) The total surface tension, its (b) dispersive component and its (c) polar component. Inset in (a) shows the relative changes in the surface tension (γ/γ_0) of the solutions.

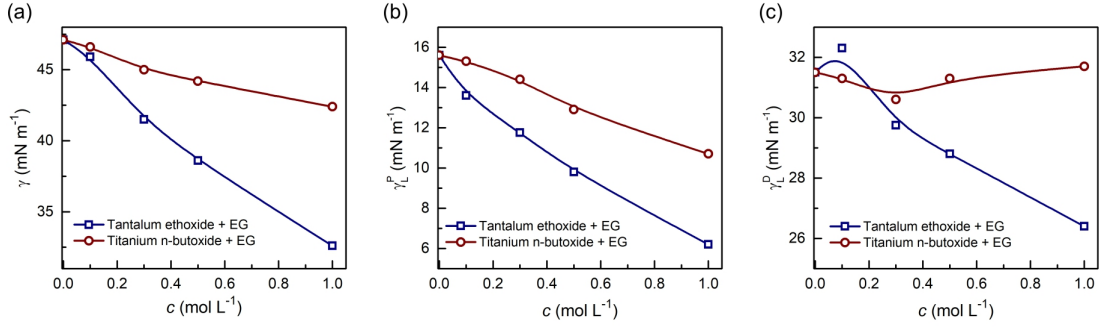


Figure 5.4: Surface tension of titanium n-butoxide and tantalum ethoxide solutions in ethylene glycol (EG). (a) The total surface tension, and its (b) dispersive component and its (c) polar component.²

and dispersive components of the surface tension (see Appendix A). The polar component of the surface tension increases for EG and 12PD solutions, while it is constant for the EA solution (Figure 5.3b). On the other hand, the dispersive component is constant for EG and 12PD solutions and increases for EA solutions (Figure 5.3c).

An opposite behaviour is observed for metal alkoxide solutions (Figure 5.4a). Both tantalum ethoxide and titanium n-butoxide solutions in EG show a decrease in overall surface tension with concentration. The change in surface tension is not linear and $d\gamma/dc$ coefficient varies between -2.2×10^{-2} and -1.2×10^{-2} for tantalum ethoxide solutions and -8×10^{-3} and -3.6×10^{-3} for titanium n-butoxide solution. Both solutions show a pronounced decrease in the polar component of surface tension (Figure 5.4b), while the dispersive component decreases for tantalum ethoxide solution, but remains constant for titanium n-butoxide solution (Figure 5.4c).

It is clear that the surface tension is a strong function of the solute concentration and—depending on the chemical nature of the solute—it can either decrease or increase with the concentration. The accumulation of a solute at the edge of a drop is thus expected to produce a surface tension gradient (and related Marangoni flow [89]), and additionally influence the CL stability. For moderately polar solvents (e.g., ethylene glycol, ethanolamine)

² Tantalum ethoxide solution was stabilized with diethanolamine.

on partially polar surfaces (e.g., O₂-treated PMMA), the presence of metal salts will tend to destabilize the CL, while metal alkoxides will stabilize it.

5.1.3 Solvent mixtures

A common approach to the ink synthesis is by combining two or more solvents to adjust the ink's physical properties (viscosity, volatility, surface tension). Recently, it has been proposed that a combination of solvents with different volatilities and surface tensions can suppress the coffee stain effect via solvent-induced Marangoni flows (see Section 1.4.1). The basis of this method is a depletion of a more-volatile solvent at the drop periphery due to the enhanced evaporation from that region. Depending on the surface tension of a less-volatile solvent, the periphery can be at the lower or higher surface tension than the bulk of the drop. This—in addition to the appearance of the Marangoni flow—can impact also the wetting behaviour. In an idealized case the surface tension of a two-solvent-mixture exhibits a linear relationship with the composition

$$\gamma_{\text{SM}} = (\gamma_1 - \gamma_2)x_1 + \gamma_2. \quad (5.2)$$

In the frame of the OWRK model, the dispersive and polar parts are also linear functions of the composition (similar to Equations 4.1 and 4.2)

$$\gamma_{\text{SM}}^{\text{D}} = (\gamma_1^{\text{D}} - \gamma_2^{\text{D}})x_1 + \gamma_2^{\text{D}} \quad (5.3)$$

and

$$\gamma_{\text{SM}}^{\text{P}} = (\gamma_1^{\text{P}} - \gamma_2^{\text{P}})x_1 + \gamma_2^{\text{P}}. \quad (5.4)$$

For a surface with known $\gamma_{\text{S}}^{\text{D}}$ and $\gamma_{\text{S}}^{\text{P}}$, Equations 5.3 and 5.4 predict the wetting behaviour of a solvent mixture at any solvent composition. It will be shown in the following section that the evaporation-induced changes in the solvent composition can lead to major wetting transitions, i.e. displacements of the CL.

5.2 Evaporation-Induced Wetting Transitions

When a solvent mixture evaporates, the solvent composition changes accordingly to the partial vapour pressures of the solvents. For ideal solvent mixtures the Raoult's law applies:

$$p_{\text{tot}} = p_1^{\circ}x_1 + p_2^{\circ}x_2, \quad (5.5)$$

where p_{tot} is the total vapour pressure above the solvent mixture, $p_{1,2}^{\circ}$ are the partial vapour pressures of solvent 1 and 2 and $x_{1,2}$ are their mole fractions. If the solvents 1 and 2 have different vapour pressures and surface properties, the evaporation of a mixture can trigger a wetting transition. The equilibrium contact angle at different compositions can be calculated by considering the polar and dispersive contributions of the solvent mixture and the surface properties of the substrate as

$$\theta_{\text{eq}} = \arccos \left(\frac{2\sqrt{\gamma_{\text{SM}}^{\text{P}}\gamma_{\text{S}}^{\text{P}}} + \sqrt{\gamma_{\text{SM}}^{\text{D}}\gamma_{\text{S}}^{\text{D}}}}{\gamma_{\text{S}}^{\text{D}} + \gamma_{\text{S}}^{\text{P}}} - 1 \right), \quad (5.6)$$

where $\gamma_{\text{SM}}^{\text{P}}$ and $\gamma_{\text{SM}}^{\text{D}}$ are the polar and dispersive contributions to the surface tension of a solvent mixture and $\gamma_{\text{S}}^{\text{P}}$ and $\gamma_{\text{S}}^{\text{D}}$ are the polar and dispersive contributions to the surface free energy (SFE) of a substrate.

Such wetting analysis is over-simplified and does not take into account the contact angle hysteresis (CAH). It is currently impossible to adequately account for the CAH as

the existing models fail to provide a good agreement to the experimental data. Regardless, the wetting analysis predicts the behaviour of solvent mixtures remarkably well and is useful for the establishment of general guidelines in the design of the ink.

5.2.1 De-wetting transition

A transition from a wetting to a non-wetting state (a de-wetting transition) can occur if a solvent mixture contains a less-volatile solvent with a much larger contact angle on a given surface than a more-volatile solvent. In fact, this is a common situation for sol-gel inks, where the main solvent (e.g. 2-methoxyethanol) is combined with a less-volatile viscous solvent. The less-volatile solvents used in these inks (diols, polyols and alkanolamines) generally also exhibit a large surface tension.

We consider two solvent mixtures that are used in experiments described in the thesis:

- 2-ethoxyethanol (2EE) and ethylene glycol (EG)
- 2-ethoxyethanol (2EE) and ethanolamine (EA)

The physical properties of the solvents are summarized in Table 5.1. The wetting diagrams as a function of the composition ($\theta_{\text{eq}} - \phi$) were constructed for a solvent mixture using Equations 5.3, 5.4 and 5.6. To provide a more general description of the solvent mixture wetting behaviour, each $\theta_{\text{eq}} - \phi$ diagram contains calculations for three different surfaces: PMMA, PMMA treated with O_2 plasma for 0.5 s, and glass.

The $\theta_{\text{eq}} - \phi$ diagram of 2EE–EG solvent mixture is presented in Figure 5.5. While pure 2EE exhibits a complete wetting on all surfaces, pure EG exhibits a partial wetting on PMMA and O_2 -treated PMMA (θ_{eq} of 47° and 31° , respectively) and a complete wetting on glass. The solvent mixture exhibits a transition from a complete to a partial wetting at 37 vol% of EG on PMMA. The same wetting transition occurs for the O_2 -treated PMMA at 63 vol% EG fraction. Due to a higher boiling point of EG it is expected that the solvent composition will shift toward higher EG concentration during the drying of a solvent mixture.

The impact of the initial solvent composition on the evaporation-driven wetting transitions was investigated by observing the side profile of a sessile drop upon drying on a PMMA-coated glass substrate. The volume, diameter and contact angle were extracted by performing a circular fit to the drop profile at each frame acquisition. Figure 5.6 shows the time evolution of the drop parameters for three solvent mixtures with 80/20, 45/55 and 20/80 initial volume ratios of 2EE and EG. According to the $\theta_{\text{eq}} - \phi$ plot (Figure 5.5), the 20/80 solvent mixture will initially exhibit a complete wetting and transit into a partial-wetting state upon drying (when the EG fraction becomes larger than 37 vol%). Indeed,

Table 5.1: Surface tension and boiling point (T_{B}) of 2-ethoxyethanol, ethanolamine and ethylene glycol. The physical data were extracted from Tables 1.1 and 1.2.

Ink	γ_{L}	$\gamma_{\text{L}}^{\text{D}}$	$\gamma_{\text{L}}^{\text{P}}$	T_{B}
	mN m ⁻¹	mN m ⁻¹	mN m ⁻¹	°C
2-ethoxyethanol (2EE)	28.6	23.6	5.0	135
Ethanolamine (EA)	47.3	34.6	12.7	171
Ethylene glycol (EG)	46.7	31.9	14.8	197

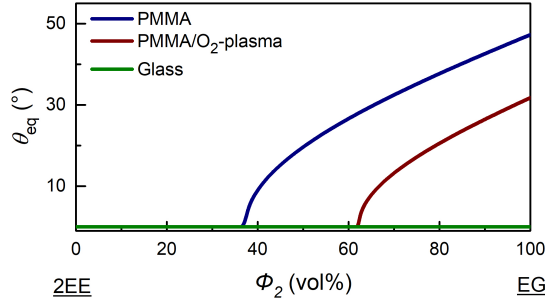


Figure 5.5: Equilibrium contact angle of 2EE–EG solvent mixture on selected surfaces. The O₂-treated PMMA surface corresponds to the PMMA sample subjected to oxygen plasma for 0.5 s. The SFE data are presented in Chapter 4.

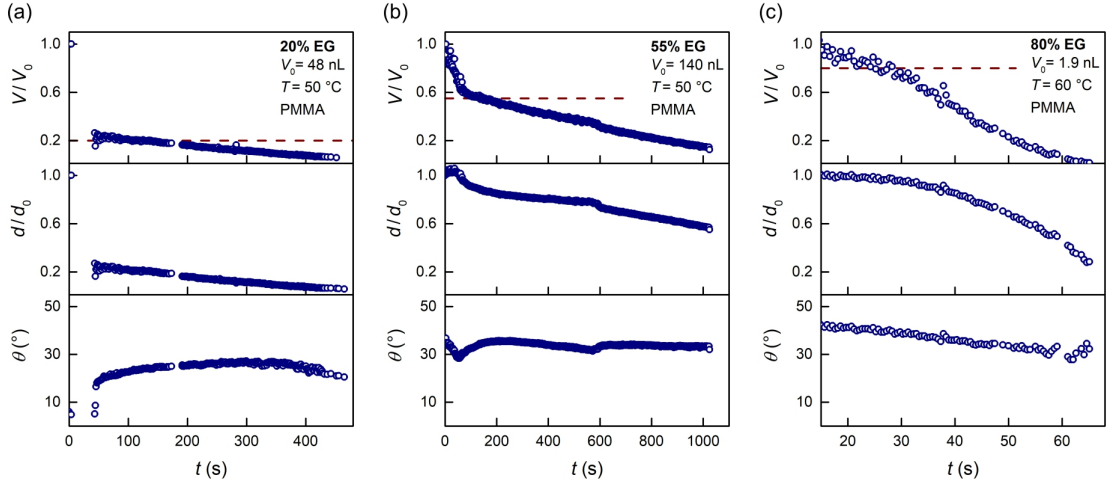


Figure 5.6: Time evolution of the volume, diameter and contact angle of drying drops with 2EE/EG volume ratio of (a) 80/20, (b) 45/55 and (c) 20/80. The initial EG solvent fraction in a solvent mixture is marked by a red dashed line in the V/V_0 plots. PMMA-coated glass substrates were used in all the experiments.

such a wetting transition occurs shortly after the onset of drying ($t = 45$ s) and is marked by a sharp decrease in the drop diameter in parallel with an increase in the contact angle to 26° (Figure 5.6a). In this initial moments, the V/V_0 ratio rapidly decreases until reaching ~ 0.2 , which corresponds to the initial volume fraction of EG. The 45/55 solvent mixture initially exhibits a partial wetting with $\theta = 37^\circ$. As the initial contact angle of a printed drop typically corresponds to the advancing contact angle [14], the drop dries in the CDR mode for initial 50 s. At 52 s the contact angle reaches its minimum value (28°) and becomes equal to the receding contact angle. Afterwards, the contact angle starts to increase and the diameter decreases—marking a de-wetting transition. Shortly after the de-wetting transition the V/V_0 ratio reaches about 0.55 and its slope changes, suggesting that most of 2EE evaporated from the drop. For the rest of the drying process the drop remains in CCA mode with $\theta = 35^\circ$. The 20/80 solvent mixture exhibits no wetting transition upon drying and remains always in the CCA mode. Although the diameter constantly decreases upon drying, the contact angle also slowly decreases from 42° to 31° .

The 2EE–EA solvent mixture exhibits a similar wetting diagram (Figure 5.7) to the

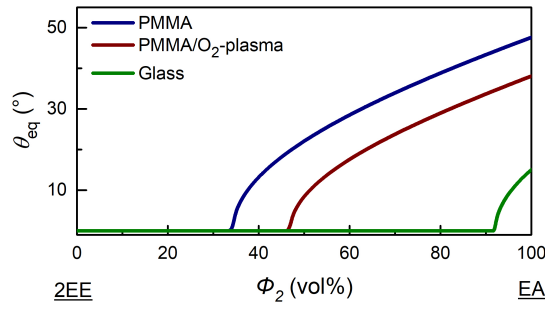


Figure 5.7: Equilibrium contact angle of 2EE–EA solvent mixture on selected surfaces. The O_2 -treated PMMA surface corresponds to the PMMA sample subjected to oxygen plasma for 0.5 s. The SFE data are presented in Chapter 4.

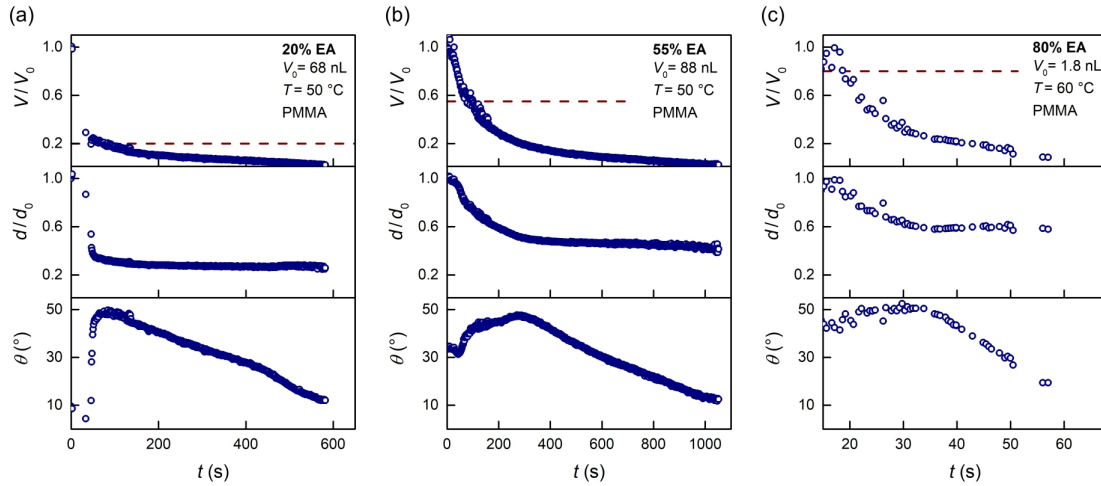


Figure 5.8: Time evolution of the volume, diameter and contact angle of drying drops with 2EE/EA volume ratio of (a) 80/20, (b) 45/55 and (c) 20/80. The initial EA solvent fraction in a solvent mixture is marked by a red dashed line in the V/V_0 plots. PMMA-coated glass substrate was used in all the experiments.

2EE–EG solvent mixture. The wetting on PMMA-coated glass substrate is almost identical for both systems. On the O_2 -treated PMMA the transition from complete wetting to partial wetting occurs at a lower volume fraction (47 vol%) due to a slightly stronger dispersive character of EA as compared to EG. An additional feature in the wetting diagram of the 2EE–EA solvent mixture is the non-zero contact angle of the EA-rich compositions on glass. This indicates that the EA-based solvent mixture has a larger tendency toward the de-wetting transition on polar substrates than the EG-based solvent mixture.

The time evolution of volume, diameter and contact angle of a drying drop of 2EE–EA solvent mixtures is shown in Figure 5.8. A sharp decrease in the drop diameter and simultaneous increase in the contact angle is observed for the 80/20 composition similar as in the case of 2EE–EG. For all the solvent compositions the contact angle reaches its maximum value of $\sim 50^\circ$ after the wetting transition. This is somewhat different from the 2EE–EG system for which the maximum contact angle depends on the initial fraction of EG. Interestingly, shortly after the de-wetting transition the CL pins for the 2EE–EA mixtures and the drops transit from the CCA to the CDR mode for the rest of the drying.

It is important to realize that the wetting transitions described in this section occur at a large receding contact angle and result in deterioration of a printed pattern definition upon drying. This is exemplified by Figure 5.9 which shows a square pattern undergoing an evaporation-induced de-wetting transition. The depinning of the CL first occurs at the edges of a square pattern—the region of the highest surface curvature (small contact angle) and the highest evaporation rate. The surface tension forces eventually drive the drying pattern into an energetically most favourable circular shape.

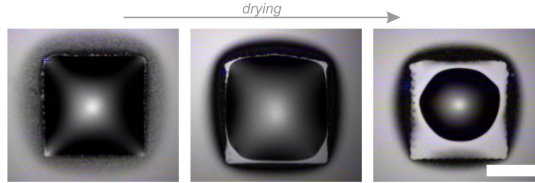


Figure 5.9: A printed square pattern undergoing a de-wetting transition upon drying. The scale bar is 250 μm .

5.2.2 Spreading transition

While de-wetting transitions are rather common, the transition from a non-wetting to a wetting state (a spreading transition) is more exotic. The spreading transition occurs if the less-volatile solvent wets the surface better than the more-volatile solvent. This situation is exemplified by 1-octanol (OCT)–diethylene glycol (DEG) solvent mixture (see Table 5.2).

Table 5.2: Surface tension and boiling point (T_B) of 1-octanol and diethylene glycol.

Ink	γ_L	γ_L^D	γ_L^P	T_B
	mN m^{-1}	mN m^{-1}	mN m^{-1}	$^{\circ}\text{C}$
1-octanol (OCT)	26.9	25.2	1.7	196
Diethylene glycol (DEG)	44.4	34.0	10.4	244

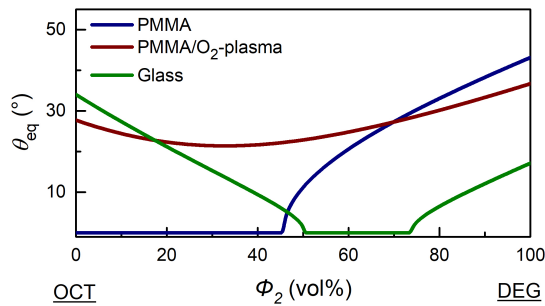


Figure 5.10: Equilibrium contact angle of OCT–DEG solvent mixture on selected surfaces. The O_2 -treated PMMA surface corresponds to the PMMA sample subjected to oxygen plasma for 0.5 s. The SFE data are presented in Chapter 4.

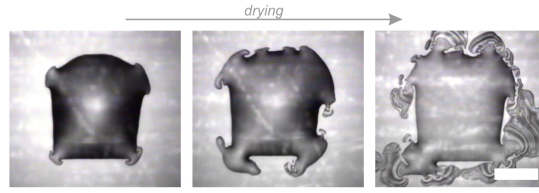


Figure 5.11: A printed square pattern undergoing a spreading transition upon drying. The scale bar is 250 μm .

According to the wetting diagram of OCT–DEG (Figure 5.10), OCT-rich compositions exhibit a de-wetting transition on a non-polar PMMA surface and a spreading transition on a polar glass surface. The solvent mixture composed of 80 vol% of OCT and 20 vol% of DEG indeed shows a spreading transition on glass. A spreading transition was difficult to observe by a side-view method that was used to follow the de-wetting transitions. Instead, we followed the drying of a square pattern printed on a glass substrate from a top-view (Figure 5.11). Similar as in Figure 5.9, the wetting transition first occurs at the corners of the pattern. This leads to spreading and outward spilling of the liquid at the corners, which results in an extremely small contact angle ($\theta \approx 0$) at the spilled areas, while the bulk of the feature remains relatively thick and has large contact angle at the sides.

5.3 Contact-Line Dynamics at a Small Receding Contact Angle

We have demonstrated that the solvent mixtures with a large fraction of a less-volatile solvent are less prone to major wetting transitions upon drying. In this section the solvent mixtures 2EE–EG and 2EE–EA with 20/80 composition are considered in a greater detail. The solute is introduced to the solvent mixture by dissolving lanthanum nitrate and nickel acetate, and these solutions are referred to as LNO-80EG and LNO-80EA inks. Nanolitre droplets of the ink were printed by a piezoelectric dispensing unit onto nanotextured polymeric layers treated by UV/O₃ (see Section 4.5). Nanotextured layers were selected over the smooth layers to enlarge the contact angle hysteresis.

In the first set of experiments, the polymeric layers were exposed to UV/O₃ for 150 s. The initial contact angle (θ_i) of the LNO-80EG ink was 16° and was somewhat larger than that of the LNO-80EA ink ($\theta = 5^\circ$). After deposition on the substrate, the droplets were heated to 60 °C and observed from a side-view to extract their volume, diameter and contact angle. A constant diameter in parallel with a decreasing contact angle indicate that both inks dry in a CDR mode and exhibit no major evaporation-induced wetting transition (Figure 5.12a,b). This is confirmed by the optical images of the drops before and after drying (Figure 5.12c,d). Both inks, however, show drastically different deposit morphologies after drying: the LNO-80EG ink produces a ring-shaped deposit (Figure 5.12e) and the LNO-80EA ink produces a dome-shaped deposit (Figure 5.12f).

Clearly, there are some control parameters that are responsible for different morphologies obtained from both inks. A recent study on simulations of thin, binary solvent droplets containing a polymeric solute³ identified several control parameters which contribute to the uniformity of the final deposit and minimization of the coffee stain effect [168]:

- Large difference in the volatility of solvents,

³ The authors assumed that the gelled region forms when the local concentration of the polymer exceeds its gelation concentration, which seems a reasonable assumption also for sol-gel precursors.

- Large initial fraction of a more-volatile solvent,
- High initial solute concentration or low gelation concentration,
- Suppressed liquid-to-liquid diffusion,
- Strong solute diffusion.

However, these control parameters are obviously inconsistent with the experimental data presented above. For example, the volatility difference is larger for 2EE–EG than for 2EE–EA; yet, the LNO-80EA deposit is flatter. Both inks have a large fraction of the less-volatile solvent, while the systems with a small fraction of less-volatile solvent are unstable upon drying.⁴ The acceptable initial concentration of the solute is limited by the layer thickness and its tendency to crack at a large thickness. The reports also show that the liquid-to-liquid diffusion is large and is further enhanced by the Marangoni flow, which develops due to the surface tension gradients [59]. On the other hand, the solute diffusion is significant only in the presence of a strong Marangoni flow and is otherwise negligible.

In many theoretical studies the drops were assumed to dry either completely in CDR mode or CCR mode, which is not always the case. The colloidal drops undergoing several pinning–depinning transitions have been studied by R. Deegan [78]. He showed that the

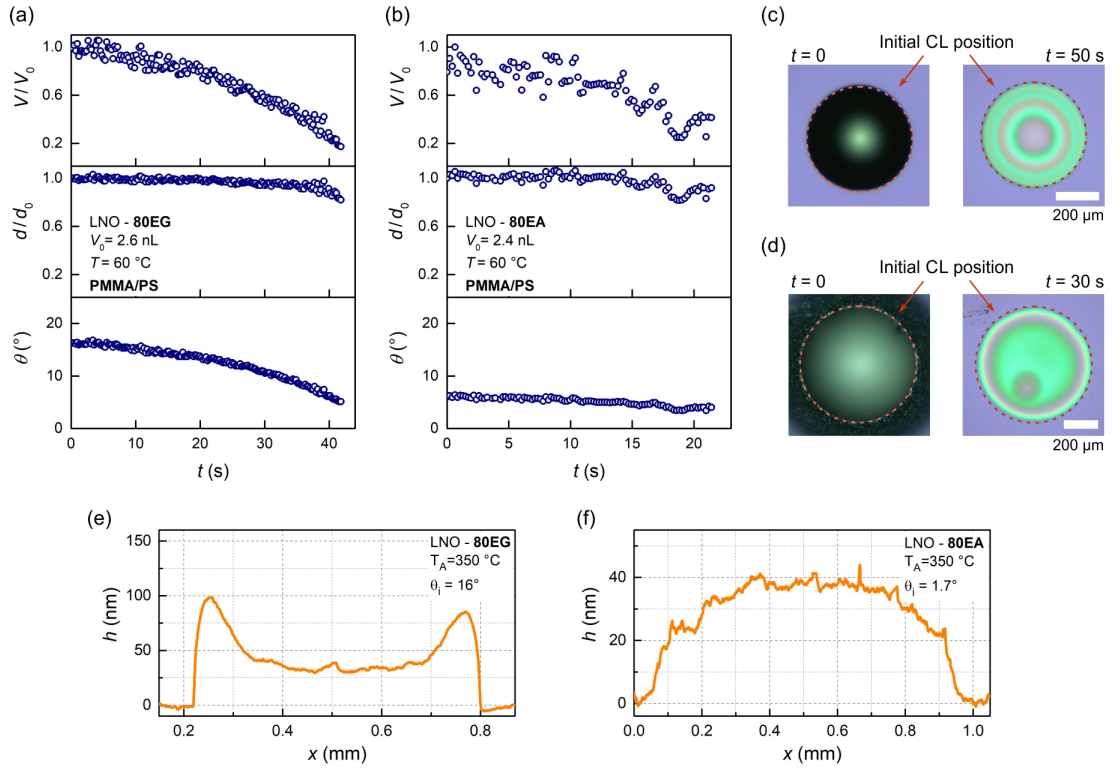


Figure 5.12: The time evolution of volume, diameter and contact angle of (a) LNO-80EG and (b) LNO-80EA drops drying at 60 °C. The parameters were extracted by a circular fit to drop profiles observed from a side-view. The optical images of the drops before and after drying for (c) LNO-80EG and (d) LNO-80EA inks. The thickness profile of the dried drops heated at 350 °C for (e) LNO-80EG and (f) LNO-80EA inks.

⁴ Early experiments were done on the inks with only 20 vol% of a less-volatile solvent. Even for these, a pronounced coffee stain effect was observed after drying on hydrophilic glass substrates.

competition between self-pinning and de-wetting produces a rich variety of particle patterns inside a dried drop. Yet, particle dispersions are fundamentally different from the solutions due to a much larger physical size of the solid phase in the ink. The solid particles (typically 0.1–10 μm large particles are used in the drying experiments) are comparable to the local height of the drop at its periphery and affect the CL behaviour. A typical example is sorting of a particles by their size near the CL of an evaporating drop [169]. On the contrary, the size of a dissolved solute is on the molecular level.

The interferometric method was used to follow the height evolution and CL dynamics of the drops at a low contact angle. The drops were illuminated by a narrow-bandwidth light and imaged in the reflectance mode to obtain an interferometric image. This method provides the information about the drop height (h) as a function of the radial position (r) once the drop becomes too thin for the side-view observation. Figure 5.13a shows the time evolution of the drop volume, diameter and contact angle of the LNO-80EG ink, obtained by a circular fit to the drop profile that was calculated from the interferometric images. The initial contact angle is 16° and is the same as in Figure 5.12a. For drying times shorter than 415 s, d/d_0 and θ behave accordingly to the CDR mode and the quality of the fit, δ_{LF} , is close to 0 (see Section 3.3.3 for details). For longer times the quality of the fit deteriorates. The drop profiles acquired at different times (Figure 5.13b,c) reveal that the drop shape starts to deviate from the spherical cap shape in the last moments of the evaporation. The deviations from the ideal shape can be better seen by looking at the local slope of the profile, i.e. dh/dr . As shown in Appendix B, dh/dr of a thin drop is a linear function of r and any non-linear deviations (sub-linear or super-linear) are due to distortion of the spherical cap shape. Figure 5.13d,e shows that dh/dr is initially a linear function; however, it becomes super-linear at times longer than ~ 400 s. The non-linearity becomes increasingly pronounced upon approaching the final drying time and dh/dr eventually changes the sign, which is an indication of inflation at the centre of the drop.

The main limitation of simple interferometric measurements is a small number of data

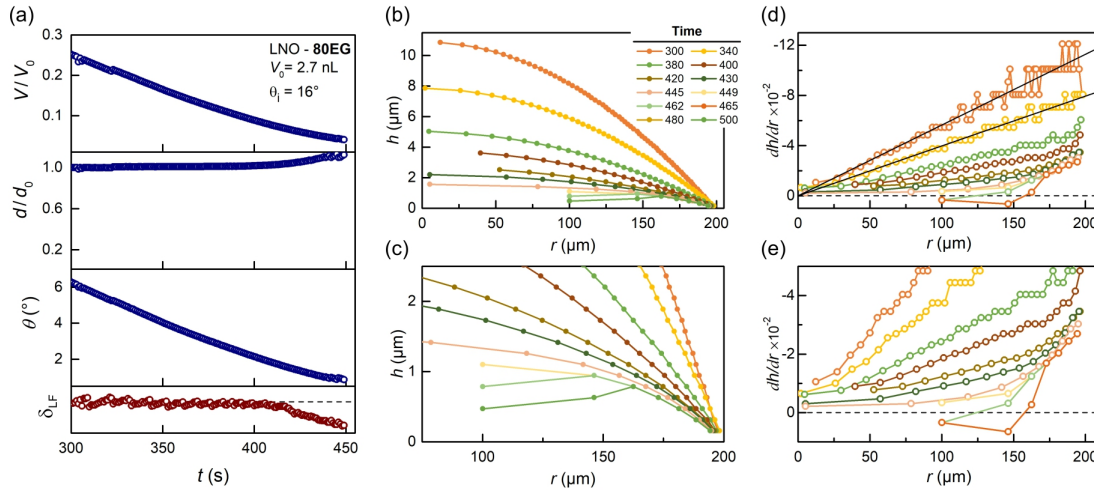


Figure 5.13: The interferometric study of the LNO-80EG ink drying on a nanotextured PMMA/PS surface at 16° initial contact angle. (a) The time evolution of volume, diameter and contact angle evaluated by a circular fit to $h - r$. (b) The height profiles at different times and (c) a magnified plot. (d) The local slope of the height profiles (a derivative of $h - r$). The drops were dried at 40°C .

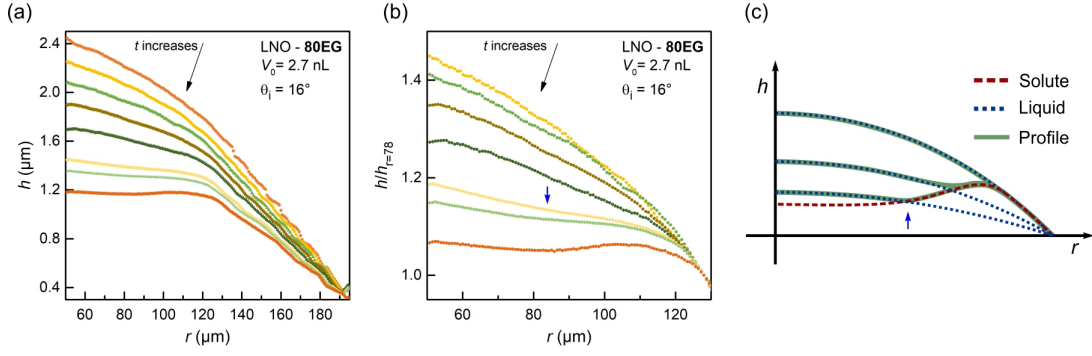


Figure 5.14: Detailed height profiles of the LNO-80EG ink drop at the very end of drying. The initial contact angle of the drop was 16° . (a) The height profiles of a drop obtained by measuring a laterally-resolved spectral reflectance and fitting the Fresnel equations to the data. (b) The height profiles normalized to the height of the drop at $r = 78 \mu\text{m}$. (c) Schematic drawing of the proposed mechanism of profile evolution at the very end of drying. Blue arrows in (b) and (c) indicate a local inflation point.

points when the thickness and its gradient become very small. Better data density can be obtained by measuring a local spectral reflectance across the drop and fitting the spectral data using the Fresnel equations. A rigorous examination of the detailed height profiles (Figure 5.14a,b) reveals that the CL is always pinned for the LNO-80EG ink (at $\theta_i = 16^\circ$) and the drops dry in accordance to the simulations performed by Park et al [170]. This begs a fundamental question: does drying involve a formation of a new CL once the gelled region forms, or does the drop behave like a liquid all the time (despite a large solute concentration, surface tension gradient and viscosity gradient)? The experiments support the second scenario as there is no clear evidence of a new CL formation. The drop height profile gradually transits from a spherical cap to the ring as suggested in Figure 5.14c.

The interferometric study on the LNO-80EA ink reveals a completely different behaviour (Figure 5.15). While the EG-based ink clearly dries in the CDR mode, the EA-based ink exhibits a dynamical behaviour of the CL. For the first 40 s of drying, the CL is pinned and the drop dries in the CDR mode (Figure 5.15a). The δ_{LF} changes sign in this regime. This is due to a transition of the drop shape from a weakly sub-linear to super-linear (see 0, 20 and 35 s in Figure 5.15d). After about 48 s, the CL begins to recede and the diameter decreases. The receding motion of the CL is clearly seen by looking at the height profiles (Figure 5.15b,c). The local slope of drop profiles (Figure 5.15d,e) acquired at 48 s (and later) exhibits a non-monotonic behaviour, with a local maximum at certain r values. Such non-monotonic behaviour is specific for the s -curved wedge, which occurs due to the deposition of the solute at the CL (curved wedge is not observed in the case of a solvent mixture without a solute). The position of the local maxima moves toward the drop center upon drying and marks the current position of the CL. The magnitude of dh/dr at the maxima corresponds to the receding contact angle, $\theta = \arctan |dh/dr|$. This reveals that the CL begins to recede at $\theta = 0.9^\circ$; however, θ_R is not constant, but decreases further with the drying time (Figure 5.15e).

The LNO-80EA drop discussed above exhibits a much smaller initial contact angle when compared to the LNO-80EG ink on the same surface, i.e. 1.7° vs. 16° . As θ_i can significantly impact the drying process as well as the morphology of the dried deposit, additional experiments were performed on textured PMMA/PS surfaces subjected to post-baking at 150°C for 10 s after the UV/O₃ treatment. This effectively increased the θ_i of

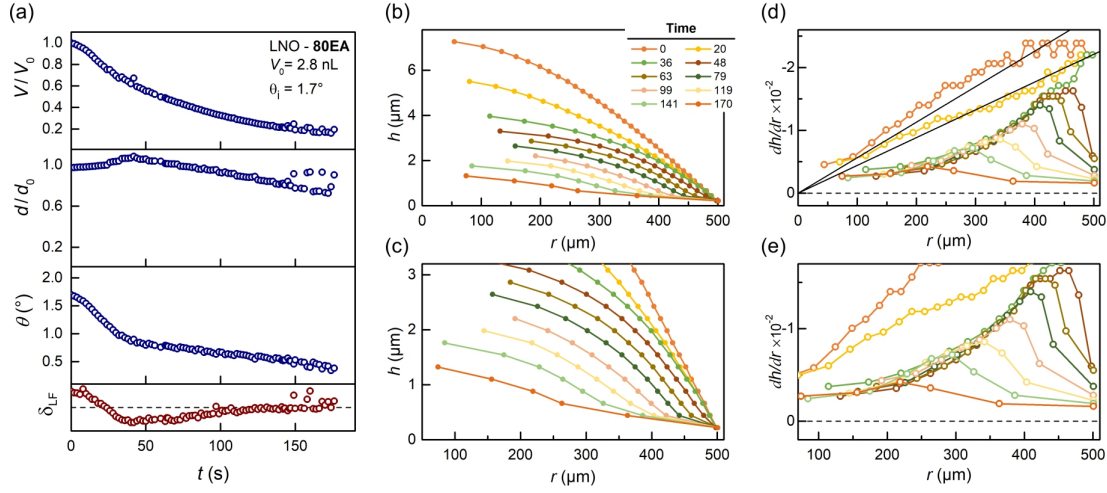


Figure 5.15: The interferometric study of the LNO-80EA ink drying on a nanotextured PMMA/PS surface at 1.7° initial contact angle. (a) The time evolution of volume, diameter and contact angle evaluated by a circular fit to $h - r$. (b) The height profiles at different times and (c) a magnified plot. (d) The local slope of the height profiles (a derivative of $h - r$). The drops were dried at 40°C .

the LNO-80EA ink to 16° . Figure 5.16a shows the evolution of the volume, diameter and contact angle at the end of drying. Again, the δ_{LF} reveals a deviation from the circular fit due to the distortion of a drop shape. This is confirmed by the height profiles acquired at different times (Figure 5.16b,c). The dh/dr plots reveal that the shape deviations are similar as for drops at $\theta_i = 1.7^\circ$. Due to the late appearance of a complete interference image required for a reconstruction of the height profile, the onset of the CL depinning

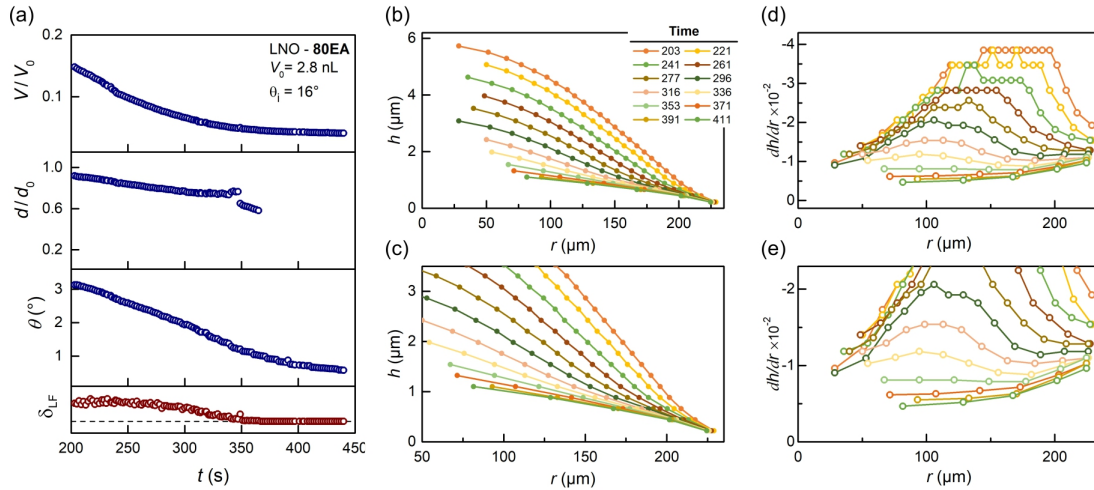


Figure 5.16: The interferometric study of the LNO-80EA ink drying on a nanotextured PMMA/PS surface at 16° initial contact angle. (a) The time evolution of volume, diameter and contact angle evaluated by a circular fit to $h - r$. (b) The height profiles at different times and (c) a magnified plot. (d) The local slope of the height profiles (a derivative of $h - r$). The drops were dried at 40°C .

is absent in Figure 5.16. It is estimated that $\theta_R > 3^\circ$. Similar to the previous case, the local maximum position and its magnitude decrease with the drying time until the local maximum disappears at $t \geq 353$ s. This indicates the disappearance of the CL and the formation a dome-shaped deposit (Figure 5.18b).

The last experiment examines the drying of LNO-80EG drops at a small initial contact angle ($\theta_i = 5^\circ$), which was achieved by prolonging the UV/O₃ exposure time. For the first 220 s the drop dries in the CDR mode, showing little deviation from the ideal circular shape (Figure 5.17). Surprisingly, the CL depins at about 240 s and exhibits a dynamical behaviour until the end of drying. The contact angle at the onset of CL depinning is 1.2° . After about 300 s, this angle reaches 0.6° and remains at that value until the end of drying. The drop profile evolution with the time is very similar to the one of LNO-80EA ink drying at $\theta_i = 1.8^\circ$; yet, the dried drop exhibits a weakly ring-shaped deposit morphology (Figure 5.18a).

By knowing a complete drying history of both inks at different initial contact angles, it is possible to discuss the final deposit morphology in the frame of CL dynamics (results are

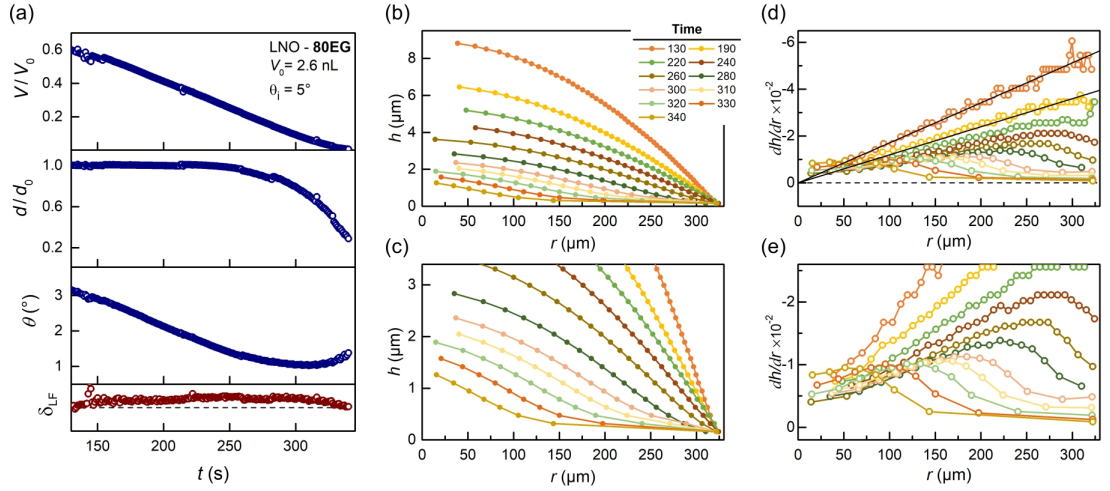


Figure 5.17: The interferometric study of the LNO-80EG ink drying on a nanotextured PMMA/PS surface at 5° initial contact angle. (a) The time evolution of volume, diameter and contact angle evaluated by a circular fit to $h - r$. (b) The height profiles at different times and (c) a magnified plot. (d) The local slope of the height profiles (a derivative of $h - r$). The drops were dried at 40°C .

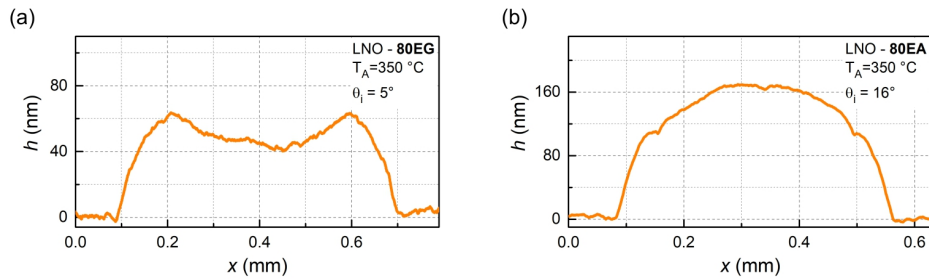


Figure 5.18: The thickness profile of dried drops for (a) LNO-80EG at $\theta_i = 5^\circ$ and (b) LNO-80EA at $\theta_i = 16^\circ$.

Table 5.3: A summary of the drying experiments on nanotextured PMMA/PS surface performed at different initial contact angles (θ_i).

Ink	θ_i	CL behaviour	Deposit morphology
LNO-80EG	16°	Pinned	Ring-shaped
	5°	Dynamic	Weakly ring-shaped
LNO-80EA	16°	Dynamic	Dome-shaped
	1.7°	Dynamic	Dome-shaped

gathered in Table 5.3). The LNO-80EG ink at $\theta_i = 16^\circ$ exhibits a pinned CL throughout the drying process and forms a typical ring-like deposit. The same ink exhibits a dynamical CL behaviour when $\theta_i = 5^\circ$ and the uniformity of the deposit somewhat improves (Figure 5.18a). On the other hand, LNO-80EA ink exhibits dynamical CL behaviour regardless of the initial contact angle—all drops exhibit essentially the same dome-shaped deposit.

It is presently unclear which mechanism is responsible for the CL depinning of LNO-80EG at small θ_i . Thermodynamically, a small θ_i should favour the zero receding contact angle and thus stabilize the CL pinning. In addition, no wetting transition is predicted for the 2EE–EG solvent mixture on highly polar surfaces at all solvent fractions (see the glass substrate in Figure 5.5). On the other hand, it is not clear if the solvent in the bulk of the drop can indeed efficiently replenish all the evaporated solvent at the periphery throughout the drying. It is possible that a critical contact angle exists for a certain group of control parameters (e.g., volatility, viscosity). The volatility strongly increases with temperature and it would be expected that a higher drying temperature would improve the deposit shape. In a drying experiment of LNO-80EG ink performed at room temperature the deposit uniformity improved, which is opposite to the expected behaviour. Another factor is the surface-to-volume ratio which becomes larger as the contact angle decreases. This makes the drop more sensitive to the exposure to ambient air. The absorption of humidity can potentially destabilize the CL due to the large surface tension of water. The relative humidity was not controlled in the drying experiments and the exact value of θ_i required to initiate the depinning of CL varied over several days of experiments. Additional experiments under controlled environment are required to relate the relative humidity to the CL dynamics.

In contrast to the EG-based ink, the inks containing EA exhibit a dynamic CL on virtually all investigated surfaces (glass, Si/SiO₂ wafers and polymeric layers) at all θ_i . The CL recedes even at extremely low θ_i —although it is possible that at small θ_i this effect occurs due to humidity absorption. From the perspective of solvent surface tensions, EG and EA have similar total surface tensions, but EA has a stronger dispersive character. The experiments with solvents of similar dispersive character (e.g., diethylene glycol) indicate that the CL depinning can occur also for these. However, such strong depinning tendency has been presently observed only for EA. It is possible that the depinning tendency of EA is caused by additional factors, such as a surface modification due to the adsorption of EA to the surface (N–H group can form hydrogen bond with O–H groups on the substrate).

For drops that undergo the CL depinning upon drying, the final deposit morphology will essentially depend on the V/V_0 ratio at which the depinning occurs and the receding contact angle, θ_R . At the beginning of the depinning event, the solute is already accumulated at the CL and its concentration depends on the amount of evaporated solvent (V/V_0 ratio). A gelled region is possibly formed at the onset of receding motion. The solute is continuously

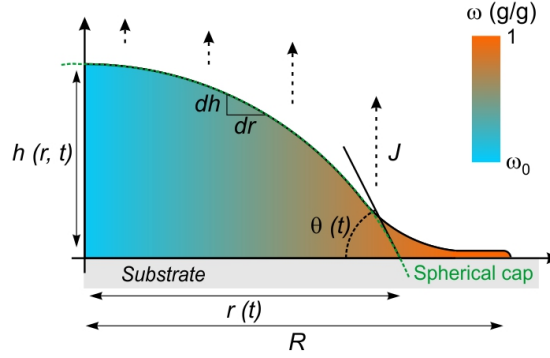


Figure 5.19: Cross-sectional illustration of a drying drop containing a solute with a dynamical CL at a small receding contact angle.

supplied to the CL by the capillary flow and the gelled region forms concurrently with the receding motion of the CL (Figure 5.19). The amount of the deposited solute will essentially depend on the balance between the evaporation rate and the CL velocity, which is indirectly determined by the θ_R . If θ_R is too large, then virtually no deposition occurs at the CL and all the deposit becomes concentrated at the center of the dried drop.

The dependence of the deposit morphology on the depinning V/V_0 ratio and θ_R has unique consequences. So far, only the drying of drops which have the same initial contact angle and the advancing contact angle was discussed [14]. This is, however, not necessarily true for printed 2-D patterns, where the volume of the ink per area is determined by the number of deposited drops per area. Thus, the drop spacing (pitch, p) can be used to control the V/V_0 ratio at the depinning event.

Let us first examine the morphology of dried squares printed from the LNO-80EG ink at conditions that should result in the CDR mode of drying. The advancing contact angle of the ink is estimated to be around 16° . Figure 5.20a shows a typical deposit morphology of a square dried under the CDR constraint. In addition to a pronounced ring deposit, it is also visible that the corners of the square are thicker than the sides. This occurs as more solute is transported to the regions of the highest curvature (lowest contact angle) due to the enhanced capillary flow. For features drying in the CDR mode increasing the drop spacing should result in a more pronounced ring deposit, which is demonstrated in Figure 5.20b. On the contrary, increasing the drop spacing in systems with a dynamic CL promotes the dome-shaped deposit formation (Figure 5.20e). Additionally, these dried squares exhibit slightly rounded edges due to the lower thickness at the corners (Figure 5.20d).

As demonstrated in Figure 5.17 it is possible that the LNO-80EG ink undergoes the CL depinning at a small θ_i . This can be simulated by printing the features at larger drop spacings. Indeed the squares printed at drop spacing of $\geq 25 \mu\text{m}$ exhibit characteristics of a dynamical CL. This is identified in Figure 5.20c by the change in the deposit morphology at the greater side length of a square pattern. For patterns printed at the drop spacing of 15 and 20 μm (CDR mode), the center-to-edge height ratio ($h_{\text{center}}/h_{\text{edge}}$) becomes smaller at larger squares dimensions. In contrast, for patterns printed at larger drop spacings the $h_{\text{center}}/h_{\text{edge}}$ ratio increases at larger dimensions.

The following observations are characteristic for systems that undergo CL depinning upon drying:

- Shift from a ring-like to a dome-like morphology with:
 - Increasing the drop spacing,

- Increasing the size of the printed feature.
- Rounded edges of the dried features and a lower thickness at the corners.

These indicators can be readily examined by printing a pattern of squares of different side-lengths at varying drop spacings. Some inks, such as LNO-80EG, can show a characteristic behaviour of a pinned system at small drop spacings and transit to the characteristics of an unpinned system at large drop spacings. It has been found that among all tested ink–substrate systems, the ones that could produce flat deposits always exhibited characteristics of a depinned CL. This suggests that the CL dynamics is a fundamental control parameter of the deposit morphology of solution-based inks.

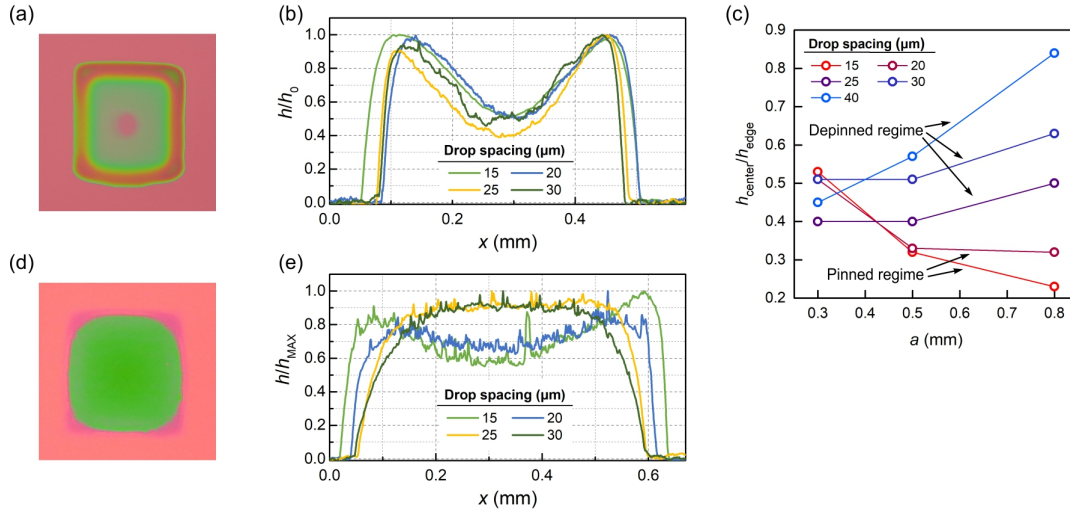


Figure 5.20: The deposit morphology of printed square patterns. (a) The image of a square pattern dried in CDR regime. (b) The normalized height profiles of $0.3 \times 0.3 \mu\text{m}$ squares printed at different drop spacings characteristic for the CDR regime. (c) Center-to-edge height ratio of squares of different sizes printed at different drop spacings showing a transition from the pinned to the unpinned regime at the drop spacing of $25 \mu\text{m}$ and larger. (d) The image of a square pattern dried in the depinned regime. (e) The normalized height profiles of $0.5 \times 0.5 \mu\text{m}$ squares printed at different drop spacings characteristic for the unpinned regime. The ink in (a–c) is LNO-80EG and the ink in (d,e) is LNO-64EA (precise solvent composition is given in Table 6.2).

Chapter 6

Inkjet-Printing of Functional-Oxide Thin-Film Multilayer Capacitors

Printed electronics is one of the key technologies toward economical and environmentally friendly production of electronic devices, such as sensors, displays and solar cells. To reach the full potential of the printing technology it is essential to have the capabilities of the layer-on-layer processing, which persists as a challenging issue.

A multilayer deposition of functional oxide layers is described in this chapter. The textured polymeric layer described in Section 4.5 was employed as the surface modification layer prior to each deposition and proved essential for layer-on-layer processing. The developed process is highly efficient and enables conformal stacking of functional-oxide layers according to the user-defined geometry, sequence arrangement and layer thickness. As a proof-of-concept, the all-printed ferroelectric oxide multilayer capacitors/transducers are demonstrated.

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6.1 Lanthanum Nickelate (LNO) Electrodes

To fabricate a thin-film capacitor, essentially two materials are required: an electrode and a dielectric. Conductive metal oxides have been identified as possible electrode materials for ferroelectric thin-film capacitors [171], [172]. Beside their cost- and processing-related benefits over noble metal electrodes, their use in ferroelectric thin-film capacitors often results in improved electrical response and stability during the electric field cycling [173], [174]. Conducting metal oxides with a perovskite structure include SrRuO_3 , $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and LaNiO_3 (or LNO). The latter is particularly interesting as both lanthanum and nickel are abundant elements, thin films can be easily processed from solutions, and it can be simultaneously used as a bottom electrode and a seed layer for growth of lead zirconate titanate (PZT) films [175]. In this section, the inkjet printing of LNO onto spin-coated PZT thin films is described and the functional properties of capacitors with printed electrodes are compared to the ones with sputtered Au and Cr/Au electrodes.

The first consideration in the ink synthesis is the chemical stability of the precursor solution and the co-solvents used. The outcome of the stability trials of the LNO precursor solution with some of common solvents is shown in Table 6.1. The LNO precursor solution was fully compatible only with ethylene glycol and ethanolamine. The addition of ethanolamine additionally stabilizes the solution via the complex formation with nickel acetate, which was evident from the colour change from green to dark blue. The inks with

Table 6.1: Stability tests of LNO precursor solution with the selected organic solvents.

Solvent	Stable?	Remarks
Ethylene glycol (EG)	Yes	Stable for months
1,2-propanediol (1,2PD)	Partially	Precipitates in a few weeks
1,3-propanediol	No	Precipitates in a few days
Glycerol	No	Precipitates in a few hours
2,4-pentanedione	No	Precipitates in a few hours
Ethanolamine (EA)	Yes	Stable for months

added 1,2-propanediol were stable for a few weeks, while the addition of 1,3-propanediol, glycerol and 2,4-pentadione induced precipitation of the solution after a few hours or days. In regard to stability tests, the inks based on solvent mixtures of ethanolamine–ethylene glycol (EA–EG) and 1,2-propanediol–ethylene glycol (1,2PD–EG) were tested for printing performance and morphological properties of the dried structures. Note that all inks contain about 20 vol% of 2-ethoxyethanol, which is used in the synthesis of the LNO precursor solution.

The detailed solvent composition of the investigated inks is given in Table 6.2. The compositions include two binary-solvent inks with either 80 vol% of EG or EA and five ternary-solvent compositions in EA–EG or 1,2PD–EG solvent systems. All inks could be printed and showed a stable jetting performance. To assess their drying performance, a square pattern of the LNO ink was printed onto the PZT thin film on a platinised silicon substrate.¹ Large variations in the shape of dried features were observed for different inks (Figure 6.1). As discussed in Chapter 5 the deposit shape predominantly depends on the contact line (CL) dynamics during the drying process. The EA-based inks exhibit a strong

Table 6.2: Investigated inks designations and their solvent compositions. LNO precursor solution contains 2-ethoxyethanol as the main solvent.

Ink	ϕ_{LNO} vol%	ϕ_{EG} vol%	ϕ_{EA} vol%	$\phi_{1,2\text{PD}}$ vol%
80-EG	20	0	80	0
80-EA	20	80	0	0
16-EA	20	64	16	0
64-EA	20	16	64	0
64-1,2PD	20	64	0	16
40-1,2PD	20	40	0	40
16-1,2PD	20	16	0	64

¹ The surface was coated by an 8 nm thick PMMA layer and treated with UV/O₃ for 150 s to adjust the wetting.

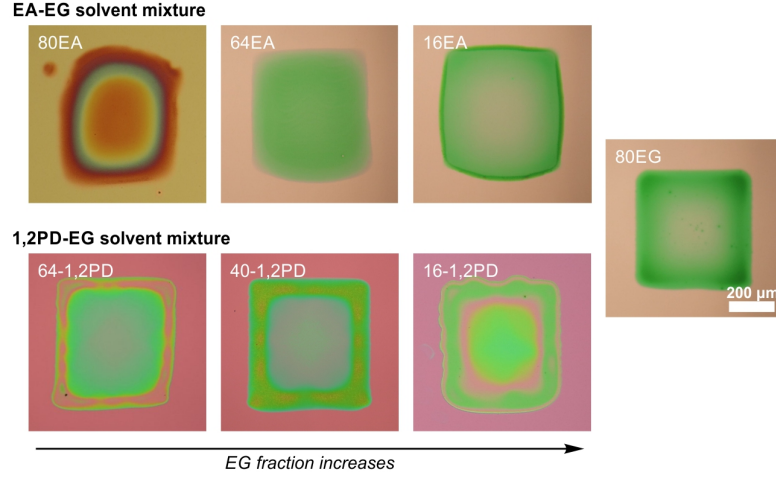


Figure 6.1: Optical images of LNO structures printed from different inks on PZT-coated Pt/Si substrates.

tendency toward CL depinning and the binary-solvent 80EA ink produced deposits with a dome-like morphology. The CL depinning dynamics can be tuned by addition of EG, which has a higher boiling point than EA and stabilizes the CL toward depinning. The deposit morphology thus shifts from dome-like to ring-like with the increasing EG fraction. Flat structures can be printed at the EA/EG solvent ratio of 64/16. Note that EA and EG have similar surface tensions (see Table 1.1) and a solvent-induced Marangoni flow is not expected to develop due to the compositional gradient of the solvents. The idea of CL dynamics impact on drying is further supported by observing the deposit morphologies of inks based on 1,2PD–EG solvent mixtures. 1,2PD has a lower surface tension and better wetting characteristics than EG, which further stabilizes the CL pinning. Accordingly, an enhanced ring deposit occurs for all compositions (bottom row of Figure 6.1).

The LNO structures printed from the 64EA ink exhibited the best thickness uniformity and were further studied in terms of structural and chemical analysis. The thickness of the annealed layers was about 50 nm. The analysis of the topography by an atomic force microscopy (AFM) and scanning electron microscopy (secondary electron imaging, SEI-SEM) revealed smooth and dense microstructures (Figure 6.2a,b). The cross-sectional SEM image shows easily resolved individual layers (the inset of Figure 6.2c). The LNO–PZT interface appears to be well-defined, which is supported by the depth profiling of the chemical composition by secondary ion mass spectrometry (SIMS) as shown in Figure 6.2c. The relative intensities of Pb, Zr and Ti species in the LNO layer decrease under 5 % about 15 nm away from the interface. Similarly, La and Ni species are detected up to about 10 nm into the PZT film. This relatively abrupt change in the chemical composition at the interface suggests only limited inter-diffusion between LNO and PZT. The different trend of Ti and Zr behaviour in the PZT layer—Zr intensity slightly increases when approaching the interface and simultaneously Ti intensity decreases—is related to the PZT film processing and occurs due to easier nucleation and crystallization of Ti-rich PZT compositions [176].

The polarization–electric field ($P - E$) hysteresis loops of capacitors with different top electrodes are presented in Figure 6.3a. The capacitors with the printed LNO top electrode (henceforth denoted as LNO capacitors) exhibit a symmetrical $P - E$ loop without any evident shift of the coercive field ($E_c = 25 \text{ kV cm}^{-1}$). It is known that metal-oxide electrodes can impede the leakage current characteristics [177]; however, our capacitors

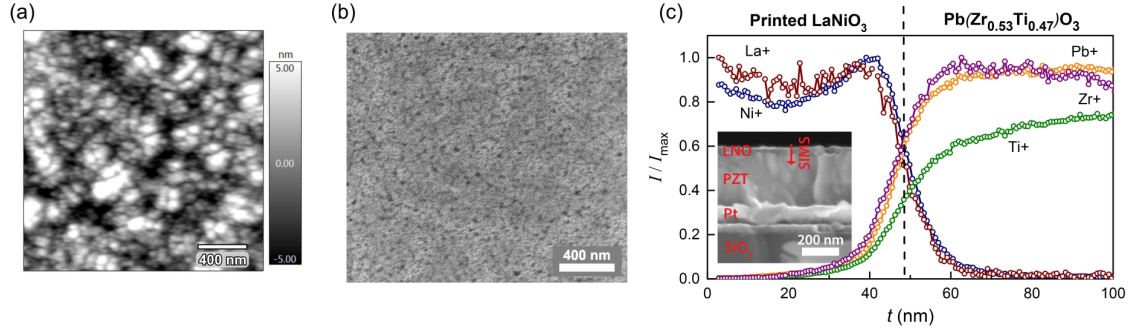


Figure 6.2: (a) AFM and (b) SEI-SEM topography image of the printed LNO top electrode using 64MEA ink. (c) SIMS analysis of the top 100 nm region of the LNO/PZT/Pt capacitor. The inset shows a cross-sectional SEI-SEM image of the structure. Reproduced from [159].

exhibited a stable response without breakdown and a low leakage current for electric fields up to 800 kV cm^{-1} . The $P - E$ hysteresis loop of capacitors with sputtered Au top electrodes (henceforth denoted as Au capacitors) are pinched and shifted toward negative electric fields. This indicates a presence of an internal bias field [178]—probably due to the presence of charged defects introduced by the sputtering process. A negative shift shows up also in the dielectric response under different DC bias fields (Figure 6.3b). Post-annealing the samples at 400°C improved the switching characteristics; however, pinching reappeared after a week of ageing. Capacitors employing a thin adhesion layer of Cr between the PZT and Au layers exhibit a highly asymmetric $P - E$ loop, which indicates a different switching behaviour at negative and positive electric fields. Again, the asymmetry reflects in the ϵ' behaviour at different bias fields (Figure 6.3b).

The LNO capacitors show a much larger dielectric permittivity when compared to Au capacitors, and even more to Cr/Au capacitors (Figures 6.3 and 6.4a). Note that the resistivity of printed LNO is approximately $5 \times 10^{-3} \Omega \text{ cm}^{-1}$, which impedes the use of electrodes at high frequencies [16]. The dielectric properties measured at 100 Hz

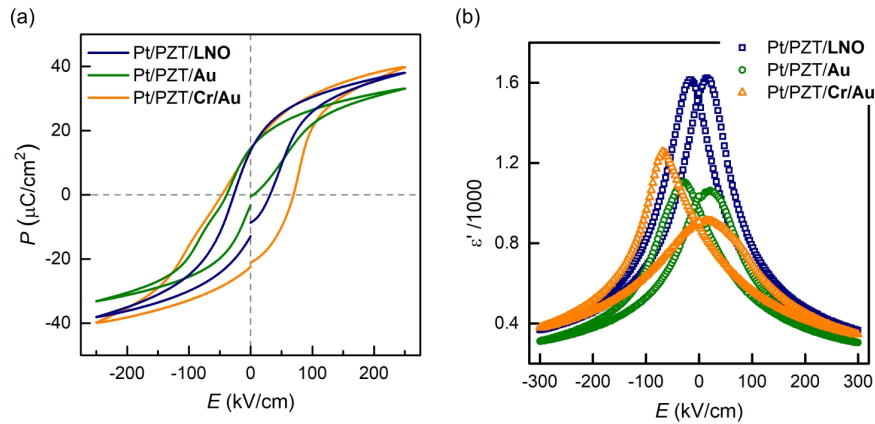


Figure 6.3: (a) $P - E$ hysteresis loops measured for capacitors with LNO, Au or Cr/Au top electrodes. (b) The DC bias field dependence of the dielectric permittivity (ϵ') for all three capacitor structures. Reproduced from [159].

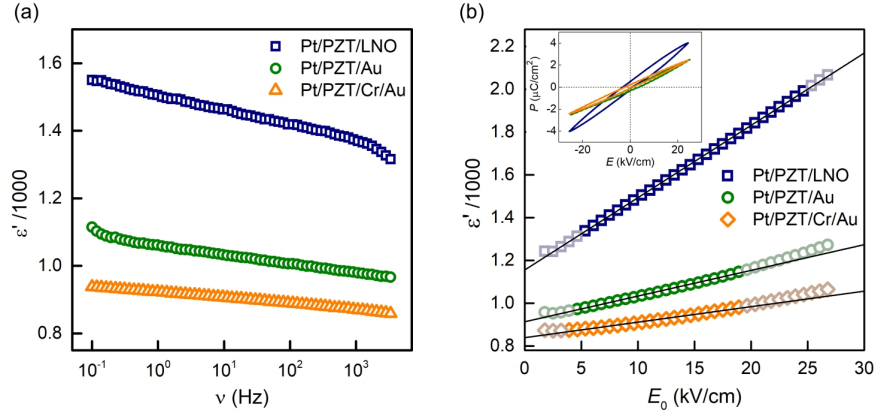


Figure 6.4: (a) The frequency dependent dielectric response of capacitors with different top electrodes. (b) The dielectric permittivity probed with different AC electric fields and fit of the unshaded data to the Rayleigh law. The inset shows the $P-E$ plots at sub-coercive fields for all three capacitor structures. Reproduced from [159].

are shown in Table 6.3. There are several possible reasons for the enhanced dielectric response of capacitors with LNO electrodes. Lanthanum is a well-known donor dopant for PZT, which enhances the dielectric response [179], [180]. However, since the diffusion of lanthanum into the PZT layers is limited to within 10 nm from the interface (as shown in Figure 6.2c), it is reasonable to assume that the properties of the "bulk" PZT are independent of the top electrode. It is known that the ferroelectric-electrode interface strongly affects the electrical properties of thin-film devices. The so-called scaling effects are especially pronounced in capacitors with metal electrodes, whereas for metal-oxide electrodes they are less pronounced [181]. Several mechanisms have been proposed to explain the observed phenomenon: presence of a thin low-permittivity layer (often referred to as the "dead layer"), finite screening length of the electrode, inhomogeneous distribution of charged defects at the interface [182], and formation of the Schottky barrier between the ferroelectric and the electrode [183]. While in epitaxial films or single crystals the nature of bonds formed at the ferroelectric-electrode interface affects the macroscopic properties [184], in polycrystalline thin films the detected macroscopic properties depend on additional parameters, including the film microstructure, domain structure, and mechanical boundary conditions.

We analysed the dielectric response of capacitors in terms of Rayleigh law (see Appendix C for details). Figure 6.4b shows the dependence of the dielectric permittivity on the probing AC electric field. The data are fitted using a linear function to extract the ϵ_{init} and α_ϵ (Table 6.3). The range of fitted data is selected for each sample where the linear behaviour of permittivity is observed (unshaded data points in Figure 6.4b). The irreversible Rayleigh coefficients α_ϵ of Au and Cr/Au capacitors are comparable to the reported values for the PZT films of similar composition [139]. It is acknowledged that α_ϵ may contain also contributions from irreversible displacement of phase boundaries, given the fact that PZT has a composition near MPB. For the LNO capacitors the reversible and irreversible contributions are significantly higher, which is also reflected in the $P-E$ plot at sub-coercive fields (the inset of Figure 6.4). The α_ϵ value, which is about 2.5 times higher for LNO capacitors than that of the Au capacitors, shows that the mobility of ferroelectric domain walls is strongly enhanced in capacitors with the printed LNO electrodes. The enhanced domain wall motion could be due to effective compensation of oxygen va-

Table 6.3: Dielectric permittivity, dielectric losses and Rayleigh constants at 100 Hz for capacitors with different top electrodes.

Top electrode	ε'	$\tan\delta$ %	$\varepsilon_{\text{init}}$	α_ε cm kV ⁻¹	$\alpha_\varepsilon/\varepsilon_{\text{init}}$ cm kV ⁻¹
LNO	1410	2.8	1160	33.8	0.029
Au	1000	1.7	910	12.0	0.013
Cr/Au	890	1.4	840	7.2	0.0086

cancies by the oxide electrode, thinner depletion regions at the LNO–PZT interface (due to a higher potential barrier at the PZT-metal interface) [185], and a lower concentration of charged defects introduced by processing.

The superior performance of the capacitors with printed LNO top electrodes is reflected also in the stability of the ferroelectric response with electric field cycling (Figure 6.5a). The $P - E$ characteristics of LNO capacitors remain mostly unaffected even after 10^7 bipolar switching cycles (Figure 6.5b). On the contrary, Au and Cr/Au capacitors exhibit severe ferroelectric fatigue. The fatigue in PZT capacitors with metallic electrodes is a well-known issue and is related to the accumulation of charged defects at the interface, which can lead to pinning of the domain walls [186]–[188]. These defects, however, can be efficiently compensated and screened by the oxide electrodes, leading to the improved fatigue properties.

The results show that inkjet-printed LNO electrodes are compatible with lead zirconate titanate ferroelectric layers. The ink solvent composition with EA to EG ratio of 64/16 produced flat and uniform LNO structures. At 0.1 mol L^{-1} ink concentration the printed structures were about 50 nm thick. The electrical characterization showed that the capacitors with LNO top electrodes have a significantly larger dielectric permittivity, lower coercive field, and better fatigue properties than the capacitors with metal electrodes.

6.2 Lead Zirconate Titanate (PZT) Ferroelectric Layers

The PZT ink was synthesised by using the same solvent composition as for the LNO electrodes, i.e. 64/16 volume ratio of EA and EG. The PZT ink was expected to behave somewhat differently due to different precursor chemicals used in the stock solution. LNO ink contains lanthanum nitrate and nickel acetate as metal precursors, which were shown to increase the surface tension (γ_L) of the ink with concentration (Section 5.1.2). On the other hand, PZT inks contain lead acetate (expected to increase γ_L) as well as zirconium n-butoxide and titanium n-butoxide (expected to decrease γ_L). In addition, the sensitivity to hydrolysis and condensation reactions is much higher for transition metal alkoxides.

First, the influence of the drying temperature on the morphology of dried structures was studied. Low drying temperature and long drying times (the first and the third figure in Figure 6.6a) resulted in severe cracking of the PZT layer (Figure 6.6a). It proved better to shorten the drying time to the minimum, i.e. to the time required to evaporate the majority of the solvents. The shortest drying time depends on the temperature and is about 240 s at 50 °C, 120 s at 60 °C, 60 s at 70 °C and 30 s at 80 °C. The morphology of the structures remains relatively constant up to the drying temperature of 80 °C, but changes at 150 °C. The drying temperature of 70 °C and time of 60 s were selected for further experiments.

Another important parameter in inkjet printing is the drop spacing (p), which determines the amount of ink delivered per area.² As demonstrated in Section 5.3, the drop spacing strongly impacts the thickness uniformity of the dried structures. The optical micrographs of the structures printed at the drop spacing ranging from 15 μm to 30 μm are shown in Figure 6.6b. The structure printed at 15 μm cracked due to a large thickness. The profilometry measurements show that the morphology of the structures changes from ring-like to dome-like with increasing drop spacing (right part of Figure 6.6b). A similar phenomenon occurs when the side length (a) of the square pattern increases (Figure 6.6c). The best result for $0.8 \times 0.8 \text{ mm}^2$ structures—the dimensions that will be later used for the fabrication of fully printed capacitors—is obtained at the drop spacing of 20 μm .

A very useful feature of inkjet printing is a known volume of the ink deposited per area. This allows an estimation of the layer thickness according to the material properties and printing parameters. For a rectangular structure the thickness is given by

$$t = \frac{V_d M_{\text{ox}}}{\rho_{\text{ox}}} \times \frac{1}{p^2}, \quad (6.1)$$

where V_d is the volume of a single drop, M_{ox} is the mass concentration of oxide material in the ink, ρ_{ox} is the density of the oxide layer and p is the drop spacing. V_d is readily measurable by research-line inkjet printers. M_{ox} is calculated for a given ink concentration by $M_{\text{ox}} = x \sum \gamma_i$, where x is the mass ratio of the metal oxides and their precursor

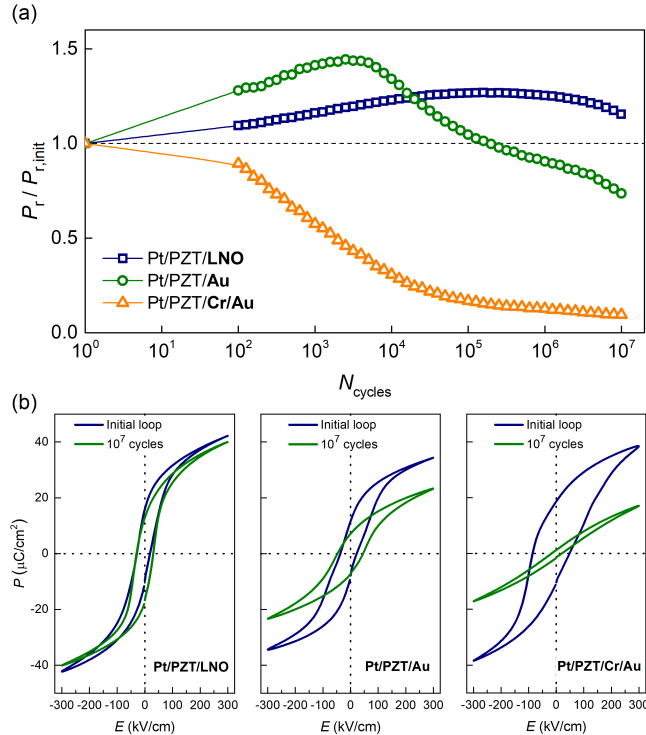


Figure 6.5: (a) The normalized remanent polarization with the electric field cycling for PZT capacitors with different top electrodes. (b) A comparison of the initial $P - E$ loop and a loop after 10^7 electric field cycles for capacitors with (a) LNO, (b) Au, (c) Cr/Au top electrode. Reproduced from [159].

² In the inkjet printing community, a common parameter is dots-per-inch (dpi), which is related to drop spacing by $\text{dpi} = 25400/p$, for p in μm .

chemicals, and $\sum \gamma_i$ is the total mass concentration of the precursors. ρ_{ox} is a material property which can be usually found in handbooks (although the exact density value can depend on the preparation method and conditions).

For the printed PZT structures, its thickness can be estimated by using the following values: $V_d = 10 \text{ pL}$, $M_{\text{ox}} = 32.6 \text{ g L}^{-1}$ (at $c = 0.1 \text{ mol L}^{-1}$, $x = 0.452$), $\rho_{\text{ox}} = 7.9 \text{ g cm}^{-3}$ [189]. In Equation 6.1 the dried structure is assumed to be a perfect rectangular object. In practice, the shape of printed structures differs from ideal due to the non-uniform thickness (e.g., a small sidewall angle, coffee stain effect). To compensate for the non-uniformities, the average thickness is extracted through the integration of the height profile (see inset of Figure 6.7a). Equation 6.1 shows a relatively good fit to the experimental data (Figure 6.7a), especially at $p \geq 20 \text{ }\mu\text{m}$.

Figure 6.7b shows the thickness of PZT layers printed at drop spacing of $20 \text{ }\mu\text{m}$ at different ink concentrations. Equation 6.1 can also be used to estimate the thickness of the printed structures, with the M_{ox} parameter being linearly dependent on the ink concentration. The calculated thickness is presented by the dotted lines. Compared to the experimental data, Equation 6.1 slightly overestimates the layer thickness. A possible source of deviation is an error in estimation of V_d and ρ_{ox} . Another error can be due to a larger actual area of the printed structures, which is due to the finite size of the wetting drops. An actual width of a printed feature when compared to the digitally specified side-length will be larger for a diameter of the wetting drop.³ Consequently, the actual area will deviate from the calculated, especially for small patterns with dimensions comparable to the wetting drop diameter. The overspilling due to exceeding the advancing contact angle can additionally enlarge the area of a printed feature. To take into account the errors in

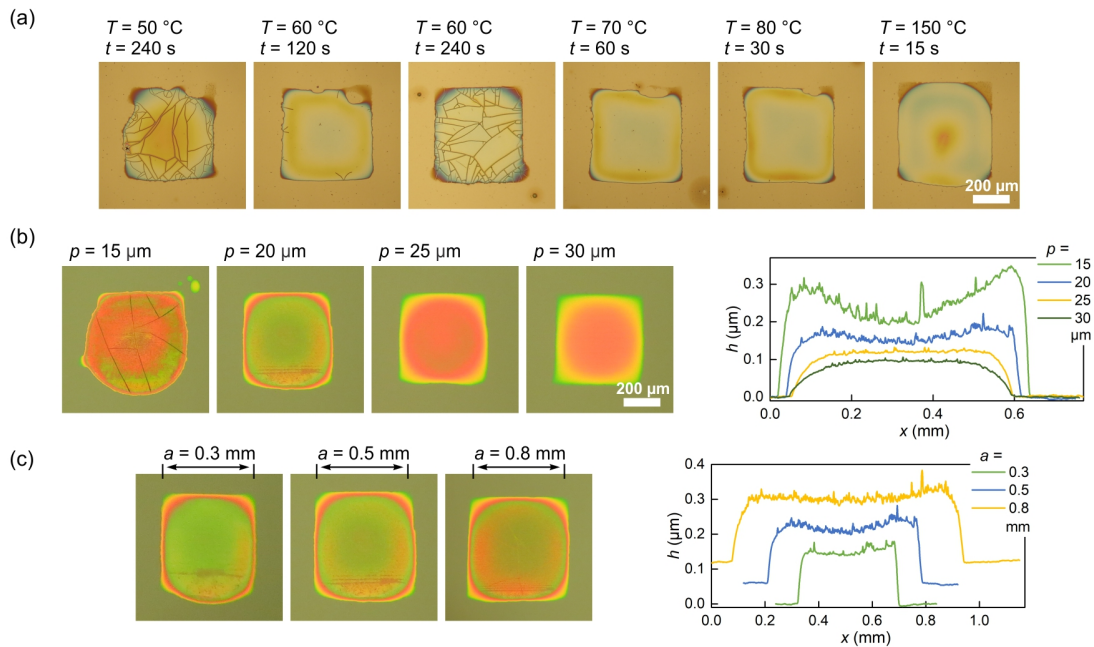


Figure 6.6: The morphology of the printed square pattern as a function of (a) drying temperature, (b) drop spacing and (c) a pattern size. The plots in the right part of (b) and (c) show the height profiles measured across the structure.

³ In a raster scan, one half of the first printed drop spills out of the digitally specified location. The same occurs for the last printed drop at the opposite side of the square pattern.

the feature area, the thickness can be multiplied by a correction factor

$$t_{corr} = t \times \frac{A}{A_m}, \quad (6.2)$$

where A is the calculated area and A_m is the measured area. The result of Equation 6.2 is presented by the solid lines in Figure 6.7b and exhibits a better agreement with the experimental data.

The single-layer thickness of PZT structures printed onto LNO/SiO₂/Si wafers at drop spacing of 20 μm increases from 50 nm for 0.05 mol L⁻¹ ink to 180 nm for 0.2 mol L⁻¹ ink. In addition, the ink concentration influences also the microstructure of the printed layers (Figure 6.8). All layers exhibit a dense microstructure without any traces of surface

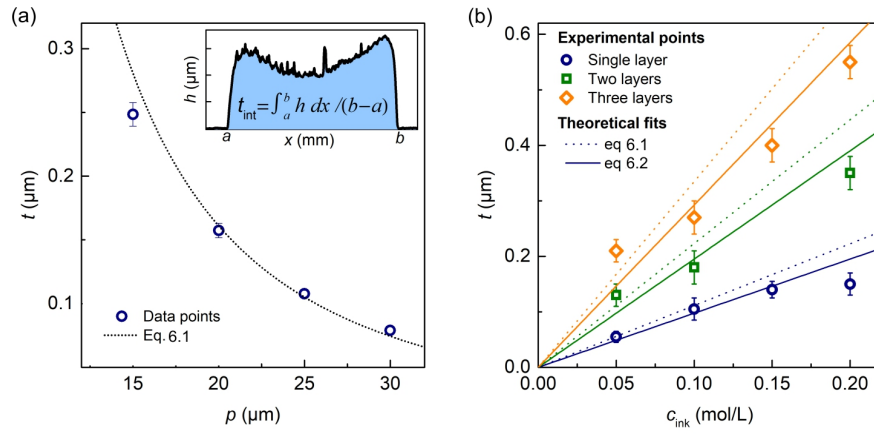


Figure 6.7: The thickness of printed PZT structures as a function of (a) drop spacing (at $c = 0.15 \text{ mol L}^{-1}$) and (b) ink concentration (at $p = 20 \mu\text{m}$).

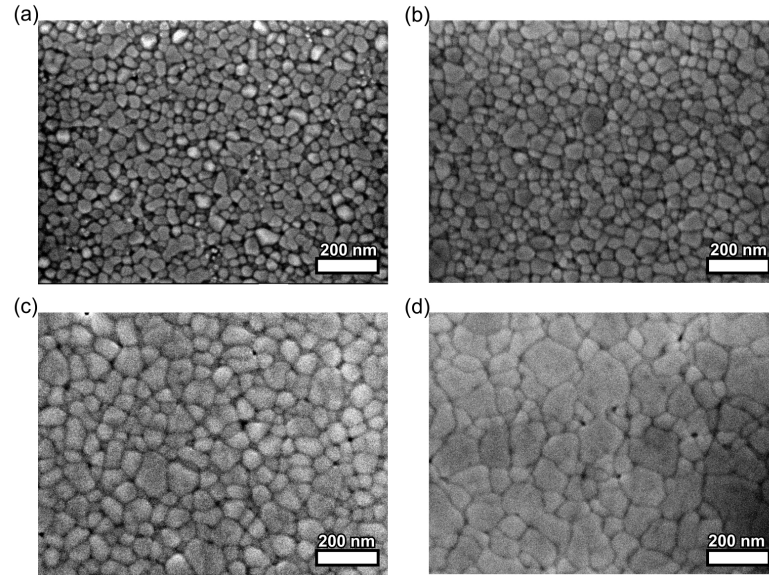


Figure 6.8: Microstructure of single-layer PZT structures printed from (a) 0.05 mol L⁻¹, (b) 0.1 mol L⁻¹, (c) 0.15 mol L⁻¹, (d) 0.2 mol L⁻¹ inks.

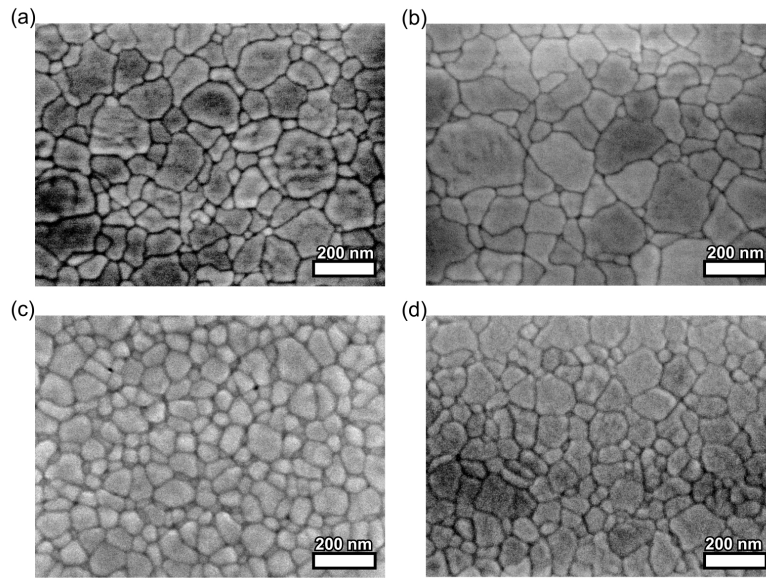


Figure 6.9: Microstructure of three-layer PZT structures printed from (a) 0.05 mol L^{-1} , (b) 0.1 mol L^{-1} , (c) 0.15 mol L^{-1} , (d) 0.2 mol L^{-1} inks.

pyrochlore phase. The average grain size of the layers deposited from 0.05 and 0.1 mol L^{-1} inks is about 40 nm and increases to about 100 nm for the layers deposited from 0.2 mol L^{-1} ink. The microstructure changes significantly upon repeating the printing/thermal treatment three-times (Figure 6.9). The average grain size increases to about 150 nm for three-layered structures printed from 0.05 mol L^{-1} and 0.1 mol L^{-1} inks, but remains relatively constant for 0.15 mol L^{-1} and 0.2 mol L^{-1} inks.

To assess the electrical properties of the printed structures, a LNO top electrode was printed onto PZT to fabricate the LNO/PZT/LNO capacitor structure. It was found that higher ink concentrations and more printing repetitions give better results in terms

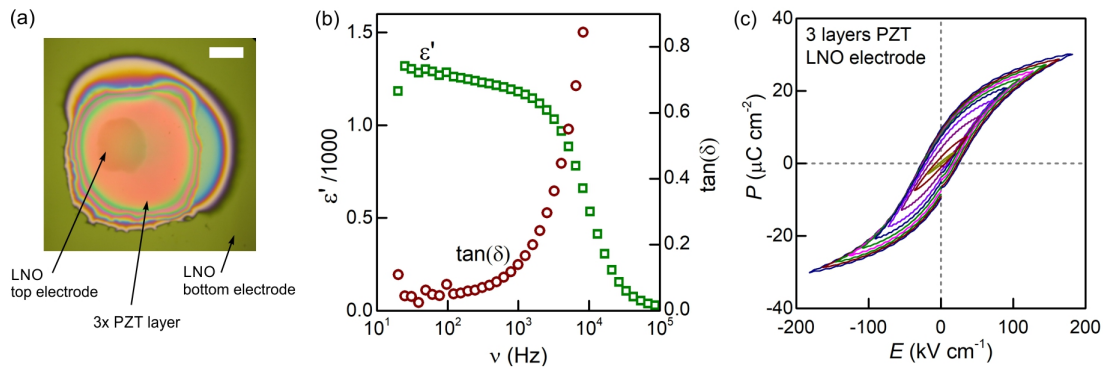


Figure 6.10: (a) Optical micrograph of the $0.8 \times 0.8 \text{ mm}^2$ PZT structure printed from the 0.2 mol L^{-1} ink. The printing/annealing process was repeated three times to yield an about 550 nm thick PZT layer. The scale bar is $250 \text{ }\mu\text{m}$. (b) Dielectric properties of the printed PZT structure with LNO bottom and top electrodes. (c) The polarization–electric field hysteresis loops obtained at different maximum electric fields.

of performance reliability and polarization switching characteristics. Single PZT layers typically exhibited a large leakage current, probably due to several pinhole defects, which can form conductive paths through the layer by the infiltration of the LNO ink. Electrical properties of a 550 nm thick PZT structure composed of three layers printed from the 0.2 mol L⁻¹ ink are presented in Figure 6.10. The optical micrograph shows the PZT structure with the printed LNO top electrode (Figure 6.10a). The pattern definition of the PZT structure is slightly distorted due to some misalignment of the sequentially deposited layers. The capacitance measurements show that the dielectric permittivity of printed PZT is about 1300 at 100 Hz. The dielectric response is stable at low frequency, but gets deteriorated at frequencies higher than 3 kHz due to the finite resistivity of LNO electrodes. The polarization–electric ($P-E$) field hysteresis loops show a typical ferroelectric switching behaviour, with the coercive field of 26 kV cm⁻¹ and the remanent polarization of about 10 $\mu\text{C cm}^{-2}$.

6.3 Fully-Printed Capacitors/Transducers

6.3.1 Single-layer devices

A thin-film ferroelectric capacitor consists of a ferroelectric layer sandwiched between two electrodes. The fabrication of such a structure by inkjet printing proceeds by a sequential deposition of LNO bottom electrode, PZT ferroelectric layer and LNO top electrode. The deposition of each layer follows the methodology presented in Figure 6.11a. First, the substrate's surface properties are adjusted to ensure optimal wetting of the ink. Secondly, the printer dispenses the ink onto digitally-defined locations on the substrate, which eventually produces a desired pattern. In the third step, the printed pattern is dried and thermally-treated to yield a functional oxide. The device architecture is then realized by repeating these three steps.

The digital definition of a pattern offers freedom over the device design (regardless of the resolution limit of inkjet process). The capacitors reported here follow a design with 90° rotation–translation of bottom and top LNO electrodes (Figure 6.11b). The printing/annealing process of LNO was repeated twice for the bottom electrode and once for the top electrode to produce 120 nm and 60 nm thick layers, respectively. Larger thickness of the bottom electrode is required to ensure adequate conductivity—it has been noted that the deposition of PZT layer over LNO electrode degrades its conductivity, especially for thin LNO layers ($t < 50$ nm). On top of the LNO bottom electrode, PZT layer was printed three-times to increase its thickness to about 400 nm and improve the yield of working devices. The concentration of LNO and PZT inks was 0.2 mol L⁻¹ and 0.15 mol L⁻¹, respectively.

The deposition methodology presented above (Figure 6.11a) was used to fabricate capacitors on Si/SiO₂ wafers, thin alumina plates and nickel foils (Figure 6.11c). The silicon wafers were passivated by 35 nm thick Al₂O₃ film to prevent reaction between SiO₂ and PbO [147] and nickel foils were passivated by 100 nm of HfO₂ to prevent/minimize the oxidation of nickel. The SEI-SEM images (bottom part of Figure 6.11c) show a dense and uniform microstructure of the PZT surface without any evident secondary phases. The images were acquired in the region where PZT is on top of LNO bottom electrode. It is known that LNO can act as a seed layer for the crystallization of PZT [175]. Therefore, microstructure is expected to be different in regions where PZT is in contact with Al₂O₃ or LNO. A detailed SEM analysis performed in different regions of the capacitor structure is presented in Figure 6.12. Indeed, the microstructure somewhat differs in the area where PZT is deposited directly onto a Al₂O₃ layer (Figure 6.12c). Yet, this difference is not considered critical for the electrical properties, as the active part of the device is only in the

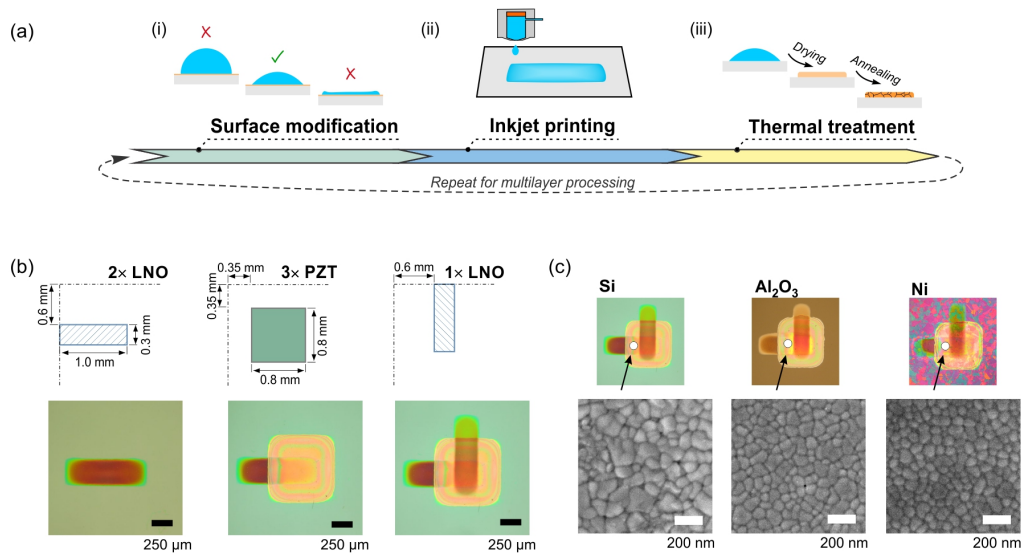


Figure 6.11: (a) A flowchart showing three main phases in inkjet printing of an individual layer. (b) The geometrical design of thin-film capacitors and optical micrographs corresponding to each step in device fabrication. (c) Optical images of printed capacitors on Al₂O₃-passivated Si/SiO₂ wafers, alumina substrate and nickel foil. The bottom part shows the SEI-SEM images of the PZT surface, recorded at the regions marked with the arrows.

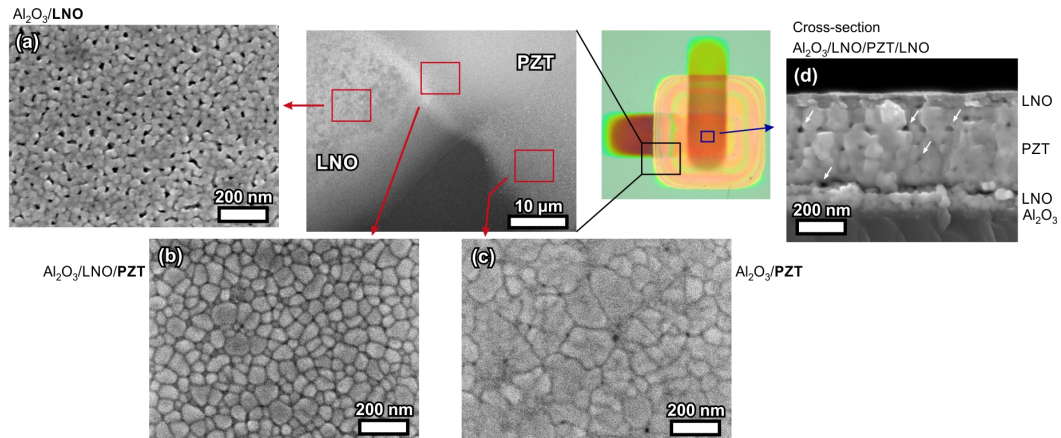


Figure 6.12: SEI-SEM images of different regions of printed capacitors. The region of interest is marked in the optical micrograph. (a) The microstructure of the bottom LNO electrode. The microstructure of PZT on top of (b) the LNO bottom electrode and (c) the Al₂O₃ passivation layer. (d) Cross-sectional SEI-SEM image of the printed capacitor in the active area of the device.

region where PZT is on top of the LNO bottom electrode. The cross-section of the printed capacitor is presented in Figure 6.12d. The individual layers of the Al₂O₃/LNO/PZT/LNO structure are easily resolved. The white arrows indicate some residual pores which predominantly occur at the interfaces between printed layers. The microstructure and structural properties of the printed capacitors will be considered in detail in the following section.

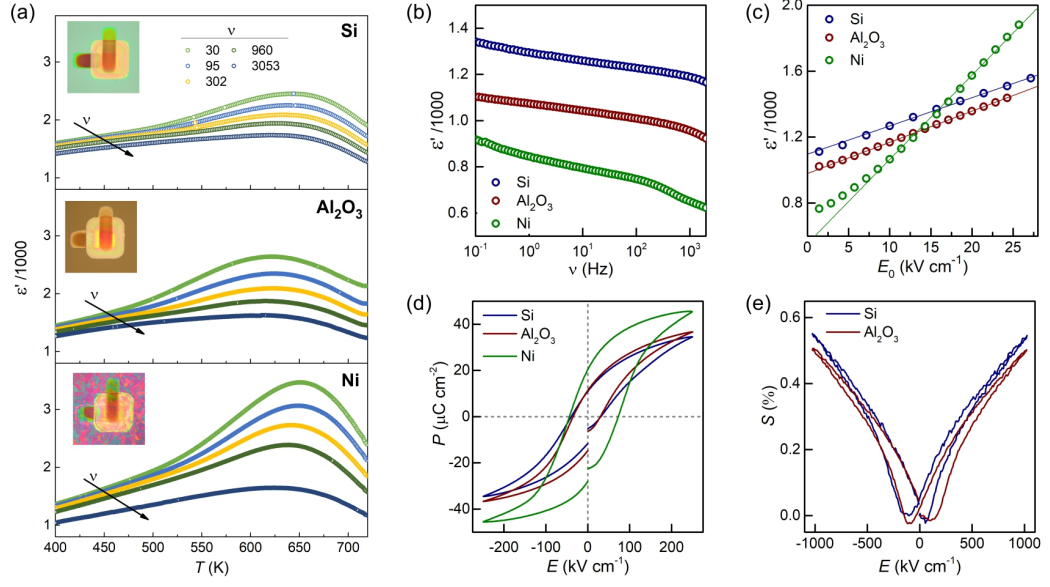


Figure 6.13: (a) Temperature dependence of the dielectric permittivity of capacitors on Si wafer, Al_2O_3 substrate and Ni-foil. (b) Dielectric permittivity as a function of frequency. (c) Dielectric permittivity of the unpoled samples as a function of the AC field amplitude. (d) Polarization–electric field (P – E) hysteresis loops of the capacitors. (e) Strain–electric field (S – E) loops of the capacitors.

The dielectric response of the printed capacitors over a 400–750 K temperature range is shown in Figure 6.13a. A broad peak in dielectric permittivity (ϵ') occurs at ~ 640 K and is associated with a ferroelectric–paraelectric phase transition. The same dielectric anomaly occurs at 660 K for bulk PZT (53/47) ceramics and is much more pronounced and sharper [179]. The suppression and broadening of the peak in dielectric properties at the phase transition is due to a small grain size of the PZT layer, its low thickness and the clamping imposed by the substrate [181]. The peak is slightly larger and sharper for capacitors on nickel foils, probably as a result of reduced substrate clamping effects due to the low thickness of the foil (25 μm) and larger ductility of metals when compared to ceramics or silicon. The frequency scan of the dielectric properties at room temperature reveals significantly larger ϵ' of capacitors on silicon when compared to the ones on alumina and nickel (Figure 6.13b). This has been previously attributed to the domain reconfiguration due to residual thermal stresses in the PZT layer, which occur due to a mismatch of the thermal expansion coefficient (TEC) of PZT and the substrate [190]. In comparison, the average TEC of silicon ($\text{TEC} = 3.5 \times 10^{-6} \text{ K}^{-1}$, Ref. [191]) is smaller than that of PZT ($\text{TEC} = 5.5 \times 10^{-6} \text{ K}^{-1}$, Ref. [191]), rendering the PZT layer under tensile stress. On the contrary, TEC of nickel ($\text{TEC} = 17.7 \times 10^{-6} \text{ K}^{-1}$, Ref. [190]) is larger than that of PZT, which will put the PZT layer under compressive stress after thermal processing. It has been shown that a tensile stress favours a higher fraction of a -domains which have larger ϵ' than c -domains [190]. The compressive stress in PZT films favours the higher fraction of c -domains, which accounts for the lower ϵ' of capacitors on a nickel foil. The capacitors on the alumina substrate ($\text{TEC} = 8 \times 10^{-6} \text{ K}^{-1}$, Ref. [192]) are expected to be under tensile stress, which is—due to a smaller difference in TEC—much smaller when compared to samples on silicon wafer. Thus, ϵ' of capacitors on alumina is between the values obtained for silicon and nickel substrates.

Table 6.4: Dielectric permittivity, dielectric losses and Rayleigh coefficients at 10 Hz of printed capacitors on silicon wafer, alumina substrate and nickel foil. The longitudinal piezoelectric coefficient was measured at 1 kHz under DC bias of 200 kV cm⁻¹.

	Si-wafer	Al ₂ O ₃	Ni-foil
ϵ'	1250	1050	800
$\tan\delta$ (%)	3.5	2.3	5.1
ϵ_{init}	1090	980	550
α_ϵ (cm kV ⁻¹)	17.1	19.3	51.1
$\alpha_\epsilon/\epsilon_{\text{init}}$ (cm kV ⁻¹)	0.016	0.019	0.093
d_{33} (pm V ⁻¹)	70	68	—

The domain wall contributions to the response of capacitors on different substrates were probed in the frame of the Rayleigh law (Appendix C). The dielectric non-linearity, which is associated with the enhanced irreversible domain wall contributions, is clearly larger for capacitors on nickel foil (Figure 6.13 and Table 6.4). This supports the postulate of weaker substrate clamping of these capacitors, although it is also possible that a higher non-linearity originates from the difference in domain configurations. The α_ϵ coefficient of capacitor on alumina substrate is larger than of the capacitor on silicon; the latter exhibits the lowest non-linearity. When compared to the spin-coated PZT films with LNO top electrodes (Section 6.1), the irreversible parameter $\alpha_\epsilon/\epsilon_{\text{init}}$ is smaller for printed capacitors on silicon substrate (cf. 0.029 cm kV⁻¹ and 0.016 cm kV⁻¹), which might be due to residual porosity present in the printed capacitors.

The polarization–electric field ($P - E$) hysteresis loops are presented in Figure 6.13d. The capacitor exhibits the hysteresis loops typical of domain switching in ferroelectrics. The hysteresis loops of capacitors on silicon and alumina substrates are symmetric and comparable, with slightly larger maximum polarization of the latter. The coercive field is about 50 kV cm⁻¹ and corresponds to the applied voltage of 2 V. The capacitor on nickel foil exhibits a less slanted $P - E$ loop and larger polarization values. The coercive field at the positive electric field is slightly larger than the negative coercive field, suggesting a presence of a weak bias field in the PZT layer. The larger remanent polarization of the capacitor on Ni-foil indicates more efficient domain wall switching in this sample.

The piezoelectric properties of printed capacitors were assessed by measuring the electric field-induced displacements by double-beam laser interferometry. Due to curling of the nickel foil, only the capacitors on silicon and alumina were characterized. Under a large electric field both samples show a characteristic butterfly shape of strain–electric field loops ($S - E$). The maximum strain measured at 1 MV cm⁻¹ is 0.55 % and 0.51 % for capacitors on silicon and alumina, respectively. The piezoelectric coefficients measured on poled samples at 1 kHz are around 70 pm V⁻¹ and are comparable for both samples (see Table 6.4).

6.3.2 Multilayer devices

Multilayer capacitors (MLCs) consist of several basic LNO/PZT/LNO units stacked together. Due to a high capacitance density, MLCs have enormous use in electronics [193],

and there have been efforts to realize the MLCs with insulator thickness below $0.5\ \mu\text{m}$ by thin-film processing technology, including RF magnetron sputtering [194] and chemical solution and vapour deposition [195], [196].

The printed MLCs follow the same principal design as single-layer capacitors (SLCs) reported in Section 6.3.1, except that the rotation/translation of the LNO electrode proceeds until four individual electrodes are formed. This gives a MLC with three active PZT layers, while each of these can be individually addressed (Figure 6.14). It takes a total of 16 depositions to fabricate a complete MLC structure.⁴ The substrates used herein are Al_2O_3 -passivated Si/ SiO_2 wafers, although other substrates may also be used.

The printed structures have a good lateral definition and are conformally deposited

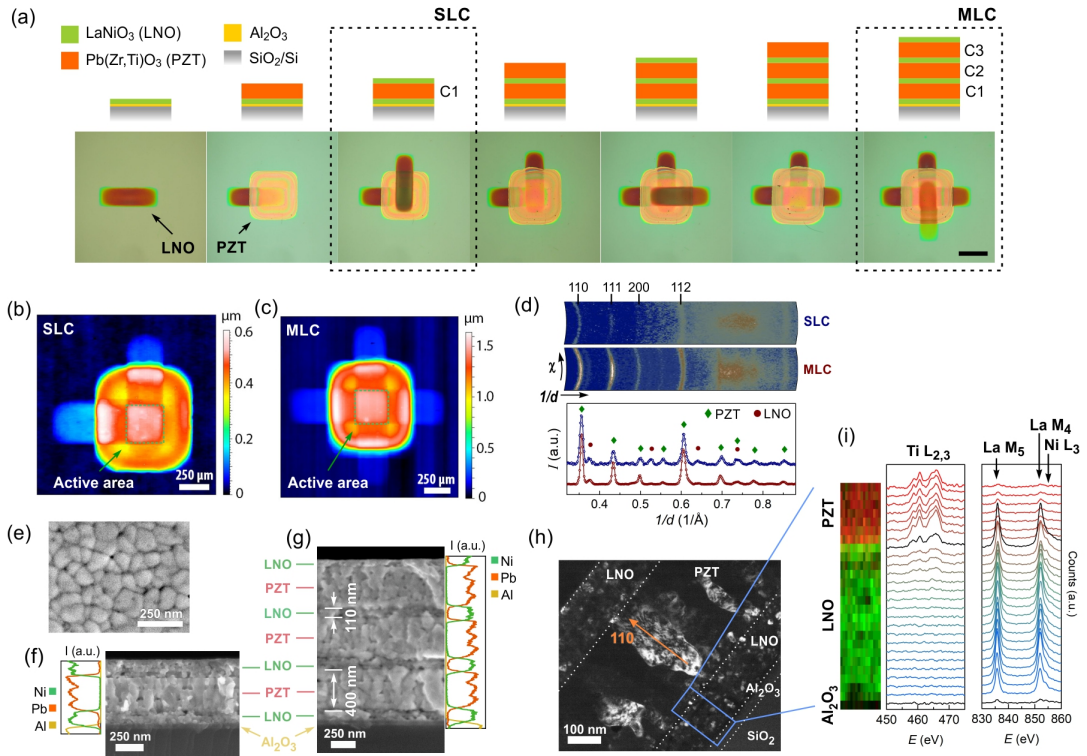


Figure 6.14: (a) Optical images of sequentially printed LNO and PZT structures and a schematic of a corresponding cross-section. Alternating stacking of these layers is used to fabricate a single-layer capacitor (SLC) and a multi-layer capacitor (MLC) with three active layers. (b,c), The contact profilometry 2-D scans of the printed SLC and MLC. (d) 2-D X-ray diffraction patterns recorded in an active area of SLC and MLC. The 1-D plots obtained by integration of 2-D data show only the peaks corresponding to LNO and PZT perovskite phase. (e) SEI-SEM images showing the surface of the PZT layer and (f) the cross sections of SLC (g) and MLC. The plots at each side of cross-sectional images are secondary ion mass spectrometry (SIMS) depth profiles. (h) Dark-field transmission electron microscopy image (DF-TEM) of the SLC cross section. (i) Electron energy loss spectroscopy (EELS) map of a $100 \times 170\ \text{nm}^2$ region across the Al_2O_3 /LNO/PZT interface. A sharp compositional transition is visible by a rapid change in Ti and La signal intensities. The analysis pixel size is $6.4\ \text{nm}$. Reproduced from [197].

⁴ Each PZT layer was printed three times and each LNO layer two times (except for the topmost which was printed once).

over the pre-existing layers (Figure 6.14b,c). The line edge roughness of printed structures is $\sim 7 \mu\text{m}$ and the sidewall angle of the LNO bottom electrode is about 0.3° . One of the crucial parameters for a reliable operation of electrical devices in the metal–insulator–metal (MIM) configuration is the thickness uniformity of the insulating layer. The edge-to-center thickness across the whole printed PZT layer varies as much as 15 %; however, in the electrically active area of the device (the $0.3 \times 0.3 \text{ mm}^2$ overlapping area of the top and bottom LNO electrodes) the thickness uniformity is better than 5 %. SEI-SEM image of the PZT surface (Figure 6.14e) shows a dense microstructure with 100–200 nm grains, without any traces of surface pyrochlore. The cross-sectional analysis (Figure 6.14f,h) shows that some PZT grains extend throughout the layer thickness, while some extend only through 2/3 or 1/3 of the whole thickness (note that each PZT layer consists of three separately crystallized sub-layers). The LNO layers consist of much finer equiaxed grains about 10–20 nm in size. The X-ray diffraction (XRD) analysis of the active area of capacitors (Fig 6.14d) reveals diffraction peaks associated with LNO and PZT perovskite phase and silicon wafer. The peaks of LNO phase are weak and broad, consistent with very fine grains and low layer thickness. The detailed analysis of PZT peaks reveals that the 111 peak intensity decreases significantly as a function of angle to the normal direction, *i.e.* the azimuthal angle, χ . While some drop in intensity is expected as a result of the diffraction geometry, the angular dependence of the 111 peak intensity is much stronger than is measured in a randomly oriented specimen. Thus, both SLC and MLC can be said to have a 111-type preferred orientation in the out-of-plane direction of the film. The LNO/PZT interface is well defined as indicated by the chemical composition mapping by electron energy-loss spectroscopy (EELS, Figure 6.14i). The intensity of the titanium $L_{2,3}$ edge decreases abruptly from the interface into the LNO layer and simultaneously the intensity of lanthanum $M_{4,5}$ edge increases. In addition to local EELS analysis we performed depth profiling of chemical composition by secondary ion mass spectroscopy (SIMS). The Ni, Pb and Al ions intensity plots reveal good chemical homogeneity in SLCs (left part of Figure 6.14f). A faint zigzag behaviour of the Pb intensity could be due to the matrix effect (note that small changes in chemical environment cause large deviation in the signal) or some residual porosity at the bottom of each deposited PZT layer. Good chemical homogeneity is retained also in the MLCs composed of three alternating LNO/PZT stacks (right part of Figure 6.14g).

The access to all four LNO electrodes in a MLC structure enables the electrical characterization of each PZT layer (top part of Figure 6.15). The dielectric measurements reveal a clear difference in the response of individual PZT layers, depending on their position in the MLC structure. The middle capacitor (Cap. 2) exhibits about 25 % larger dielectric permittivity (ϵ') than the topmost (Cap. 3) and the bottommost (Cap. 1). Similarly, the $P - E$ hysteresis loop of Cap. 2 exhibits the largest maximum and remanent polarization values (Figure 6.15b). The coercive field of all three PZT layers is identical. In contrast to polarization values, the electromechanical response is comparable for all three capacitors as indicated in the $S - E$ plots (Figure 6.15c). The piezoelectric coefficient of capacitors measured at 1 kHz under DC bias of 200 kV cm^{-1} is $70\text{--}75 \text{ pm V}^{-1}$.

To investigate the discrepancy in the dielectric response of individual capacitors comprising the multilayer structure, reference samples with the same geometry were prepared using lithography. The samples consisted of spin-coated PZT active layers and sputtered platinum electrodes. The functional response of these MLCs was studied in two different wiring configurations. In the first configuration, the measured capacitor was connected to LCR meter, while the inactive electrodes were kept floating (top part of Figure 6.16a)—same as for all-printed MLCs (Figure 6.15). In this configuration, the measured capacitance for the middle capacitor (Cap. 2) was again significantly larger than the capacitance of

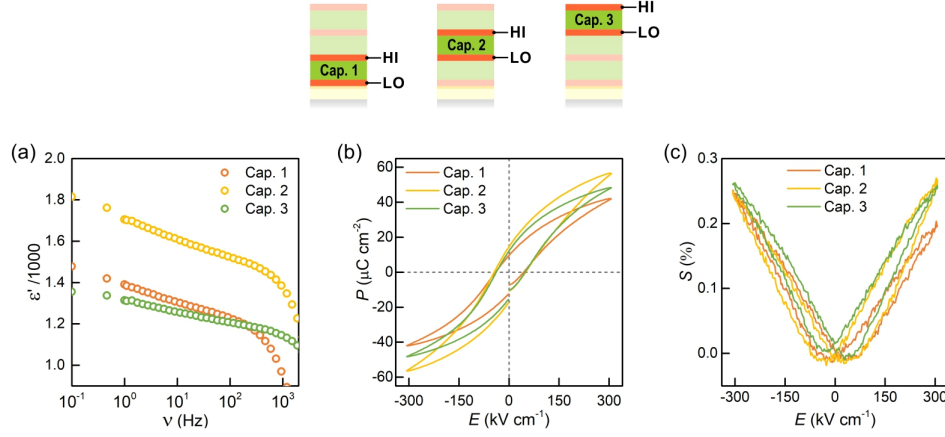


Figure 6.15: (a) Frequency dispersion of the dielectric permittivity. (b) Polarization–electric field and (c) strain–electric field hysteresis loops measured with a bipolar electric signal of 100 Hz. The thickness of individual PZT layer was 400 nm.

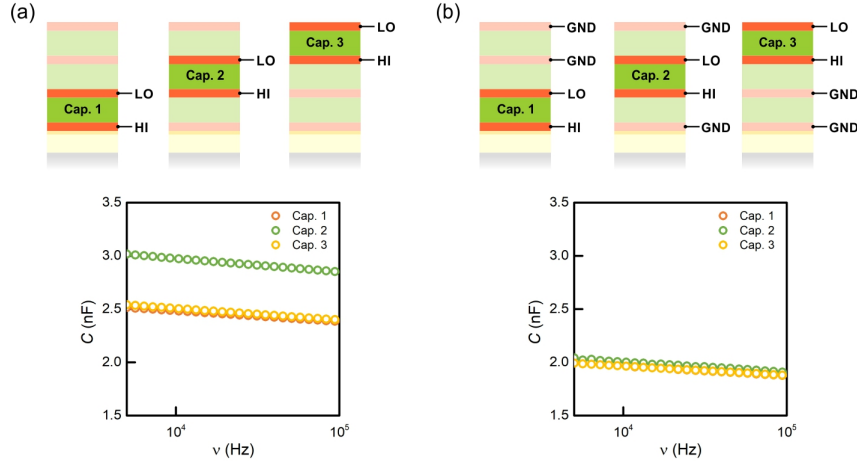


Figure 6.16: The measured capacitance of individual capacitors in a three-layer MLC. The bottom and top electrode of measured capacitor are connected to LCR meter, while (a) remaining inactive two electrodes are floating (b) the inactive electrodes are grounded. This particular MLC structure consists of 530 nm thick spin-coated PZT active layers and sputtered Pt electrodes.

the bottom and top capacitor (Cap. 1 and 3, see bottom part of Figure 6.16a). In the second configuration, the inactive electrodes were grounded (top part of Figure 6.16b). A relatively high frequency (> 5 kHz) had to be used to obtain a stable reading of capacitance. Grounding of inactive electrodes resulted in overall smaller capacitance values, which were almost identical for all three capacitors (bottom part of Figure 6.16b). The capacitance of Cap. 1 and 3 in grounded configuration was 20 % smaller than in the floating configuration. The most drastic difference occurred for Cap. 2, which exhibited 33 % smaller capacitance when inactive electrodes were grounded. In contrast to Cap. 1 and Cap. 3, which both have one adjacent inactive electrode, Cap. 2 has two adjacent inactive electrodes, which contribute twice as much to the measured response. The difference between measured capacitance in both configuration was independent of the thickness of

active layers (270 nm, 530 nm and 800 nm were tested) and temperature (RT to 450 °C were tested). We assume that floating electrodes contribute to the measured response via electrostatic charging; however, the exact underlying mechanism is presently unclear.

The functional properties of individual capacitors in multilayer structure are gathered in Table 6.5. The dielectric permittivity was estimated by multiplying the measured capacitance with a correction factor, which was extracted from the measurements of reference samples discussed above (Figure 6.16). For Cap. 1 and 3 the correction factor was 0.8, while for Cap. 2 it was 0.67. The direct measurement of the dielectric properties in grounded configuration of printed samples was impossible due to their low characteristic frequency (< 1 kHz), while higher frequency would be required to obtain stable capacitance reading.

One of the key features of multilayer capacitors is the additivity of total capacitance (C_{tot}) when the individual capacitors are connected in parallel

$$C_{tot} = \sum_{i=1}^N C_i. \quad (6.3)$$

C_i is the capacitance of each capacitor and N is the number of connected capacitors. As some of the electrodes are shared in a MLC structure, the equivalent circuit becomes more complicated if the electrodes have a finite resistivity. The equivalent circuit of a MLC with three active layers and resistive electrodes is shown in Figure 6.17b. The equivalent circuit simplifies to an ordinary circuit with capacitors connected in parallel if the resistivity of electrodes is neglected. The capacitive response of the equivalent circuit (Figure 6.17b) is presented in Figure 6.17c. It can be seen that additivity of capacitance (Equation 6.3) holds. The characteristic frequency of the capacitance drop due to the electrode resistance shifts toward lower frequency values with the increasing number of active layers (right part of Figure 6.17c, and asymptotically approaches about 1/2 of the characteristic frequency of a single-layer capacitor.

Figure 6.17d shows the measured capacitance as a function of frequency of the individual capacitors in a MLC structure and the capacitors wired in parallel. In the latter case, all electrodes are connected and there should be no stray contributions of floating electrodes. Hence, it is expected that the measured capacitance of a MLC with three active layers will be smaller than the summarized uncorrected capacitances of individual capacitors (which contain stray contributions from floating electrodes). This is indeed the case, as evidenced by black points in Figure 6.17d, which exhibit about 24 % larger capacitance values than the measured MLC capacitance. Better agreement is found if the capacitance

Table 6.5: Dielectric permittivity and dielectric losses of individual PZT layers in a MLC structure measured at 10 Hz. The dielectric permittivity was estimated by applying correction factors determined from Figure 6.16. The longitudinal piezoelectric coefficient was measured at 1 kHz under DC bias of 200 kV cm⁻¹. The thickness of individual PZT layer was 400 nm.

	Capacitor 1	Capacitor 2	Capacitor 3
ϵ'	1040	1070	1000
$\tan\delta$ (%)	3.4	3.3	3.4
d_{33} (pm V ⁻¹)	70	73	72

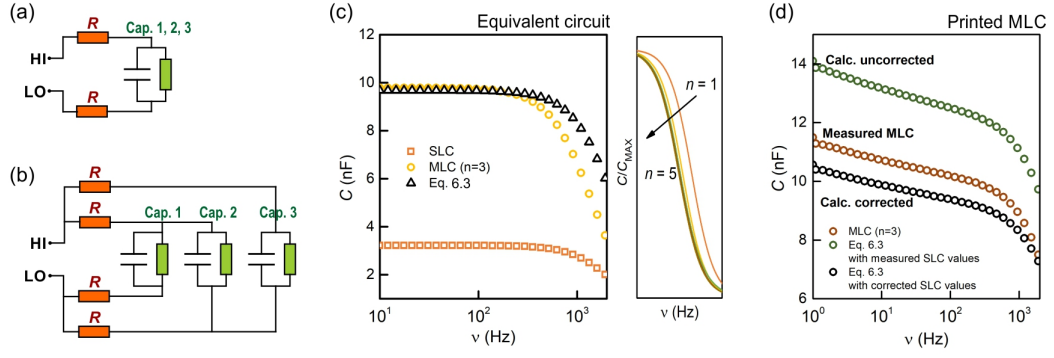


Figure 6.17: (a) The equivalent circuit of (a) a SLC and (b) a MLC with three active layers. (c) The capacitive response of equivalent circuits shown in (a,b). Right part shows the shift in characteristic frequency due to the finite resistivity of electrodes. (d) The measured capacitance of a MLC and the calculated MLC capacitance for uncorrected and corrected values of capacitance of individual capacitors. The thickness of PZT active layers was 400 nm.

values of individual capacitors are corrected before summation according to Equation 6.3; then the calculated capacitance is about 7 % smaller than measured MLC capacitance.

The capacitance-per-area (or capacitance density) is about 30 nF mm^{-2} for an SLC with a 400 nm thick PZT layer (Figure 6.18a), while it greatly increases for MLCs. A MLC with the same thickness of PZT exhibits a capacitance density of 80 nF mm^{-2} (red symbols in Fig 6.18a). Another strategy on enhancing the capacitance density is via a reduction of the active layer thickness. Accordingly, the printed MLCs with 200 nm thick PZT layers have about twice larger capacitance density as MLCs with 400 nm thick active layers (green symbols in Figure 6.18a). A similar enhancement of the response is observed also in electromechanical properties. Figure 6.18b shows the electromechanical displacement of poled capacitors under unipolar electric excitation. The slope, which corresponds to the voltage sensitivity, increases from 80 pm V^{-1} for SLC to 200 pm V^{-1} for an MLC with 3

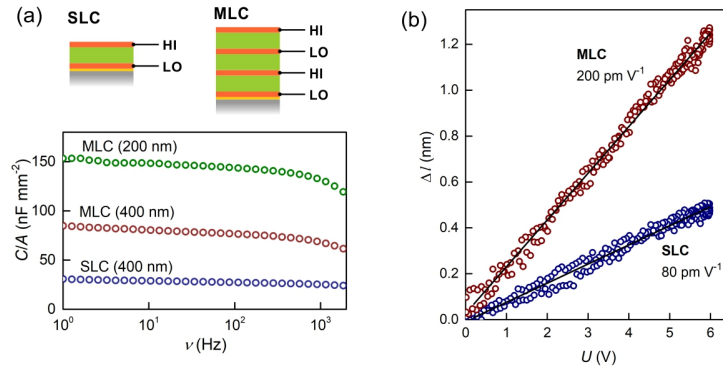


Figure 6.18: (a) Frequency dispersion of the capacitance density of an SLC and an MLC with 400 nm thick PZT layers and an MLC with 200 nm thick PZT layers. (b) Electromechanical displacement of SLC (400 nm thick PZT) and MLC (3 active layers, 400 nm thick PZT) under unipolar electric signal. Reproduced from [197].

active layers. Interestingly, the electromechanical response of an MLC is also smaller than the predicted value obtained by the summation of the response of individual capacitors.

Chapter 7

Nanostructured Ferroelectric Films with Greatly Enhanced Piezoelectric Response

The coupling of the electric and elastic fields in ferroelectrics makes them indispensable in electromechanical applications such as transducers, sensors and energy harvesters. When a ferroelectric material is in the form of a thin film, its piezoelectric properties are often strongly reduced. For one of the technically most important materials, $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PZT), the d_{33} coefficient measured in thin films is typically only about one third of that of bulk ceramics. Several mechanisms have been proposed to explain lower piezoelectric properties. The rigid mechanical coupling of the piezoelectric film with the inactive substrate in combination with the transverse piezoelectric effect accounts for about 30 % lower d_{33} values [198]. The suppression of extrinsic contributions in terms of domain-wall (DW) motion by the substrate constraints may account for additional 50–80 % reduction of the overall response [199].

It has been demonstrated that the electromechanical response increases when a continuous ferroelectric thin film is patterned into discrete nanosized features, mainly because of the dramatically reduced substrate-induced constraints and also due to changes in the domain structure occurring as a result of downsizing [200], [201]. Finite-element modelling and synchrotron X-ray diffraction experiments reveal that the largest increase in the response occurs when the lateral dimensions of the feature becomes comparable to its thickness [202]. Keech et al. showed that for structures with the width to thickness aspect ratio larger than 3:1 the piezoelectric response across the structure becomes non-uniform, with smaller response in the center of the structure than on its edges [203]. The fabrication of such nanosized features relies mainly on the use of focused-ion-beam milling, which can introduce detrimental ions into the functional layer and has limited scalability for high-throughput production [204].

In the following section, a soft-chemistry technique based on the self-assembly of organometallic precursors in a polymer matrix is devised for the deposition of nanostructured oxide thin films. The implemented macro-porosity leads to local elastic relaxations and greatly enhances the macroscopic electromechanical response. Exceptionally large measured piezoelectric coefficients—reaching the level of bulk ceramics—are associated with the increased elastic compliance of the nanostructured films and the highly mobile ferroelastic domain walls.

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7.1 Self-Assembly and Device Fabrication

In recent years, the self-assembly of thin films has been reported as an important breakthrough in materials science [205]. The self-assembly of surfactants, solid polymeric particles or a polymer-assisted phase separation have been used to prepare materials with micro-, meso- or macro-porosity and various morphological features [206]. To enhance the piezoelectric response, nanostructuring should produce a film with grains that are weakly bound in the in-plane direction. A surfactant—or particle-assisted self-assembly—typically produces films with a continuous metal-oxide structure having a spherical, closed porosity. A more suitable microstructure for an enhanced electromechanical response should have a macroporous bicontinuous morphology, which develops when polycondensation reactions lead to a controlled phase separation in a modified sol-gel system [207].

To synthesize $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ films with the desired microstructural features we used chemical solution deposition with the coating solution modified using a phase-separating polymer. The method is shown in Figure 7.1. The coating solution contains highly reactive organometallic precursors and polyvinylpyrrolidone (PVP) dissolved in an organic solvent (Figure 7.1a). The phase separation and self-assembly occur during the spin coating as a result of hydrolysis and the polycondensation of organometallic precursors. In the course of the polycondensation reactions—and the associated particle growth—the solvent gradually evaporates and the particles become encapsulated in the PVP matrix (Figure 7.1b and Figure 7.2b). The double-bonded oxygen atoms in the PVP interact with the hydroxy groups of the hydrolysed particles through the hydrogen bonding—evidenced by an Fourier-transform infrared spectroscopy as a shift in $\text{C}=\text{O}$ stretch—and thus the PVP actively interacts with the polycondensation reactions. The phase separation, particle growth and self-assembly are all dynamic processes; thus the parameters that influence the hydrolysis and condensation rates also influence the final morphology of the film. For example, the addition of chemical modifiers, such as acetic acid or ethanolamine, effectively changes the film morphology (see Figure 7.2a,c for details).

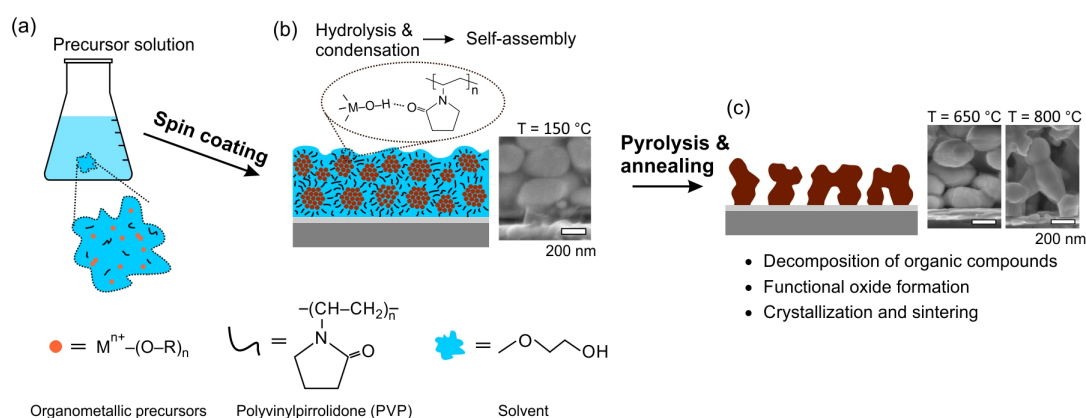


Figure 7.1: Scheme of the nanostructured film synthesis approach. (a) Polyvinylpyrrolidone (PVP) is added to the sol-gel precursor solution, composed of organometallic precursors and solvent, to yield a stable and viscous coating solution. (b) Exposure to humidity in the air during spin coating initiates the hydrolysis and condensation reactions of the sol-gel precursors and leads to phase separation mediated by PVP molecules. (c) A subsequent high-temperature treatment causes the organic phase to decompose and induces the crystallization and sintering of the nearby particles. Figure adapted after [208].

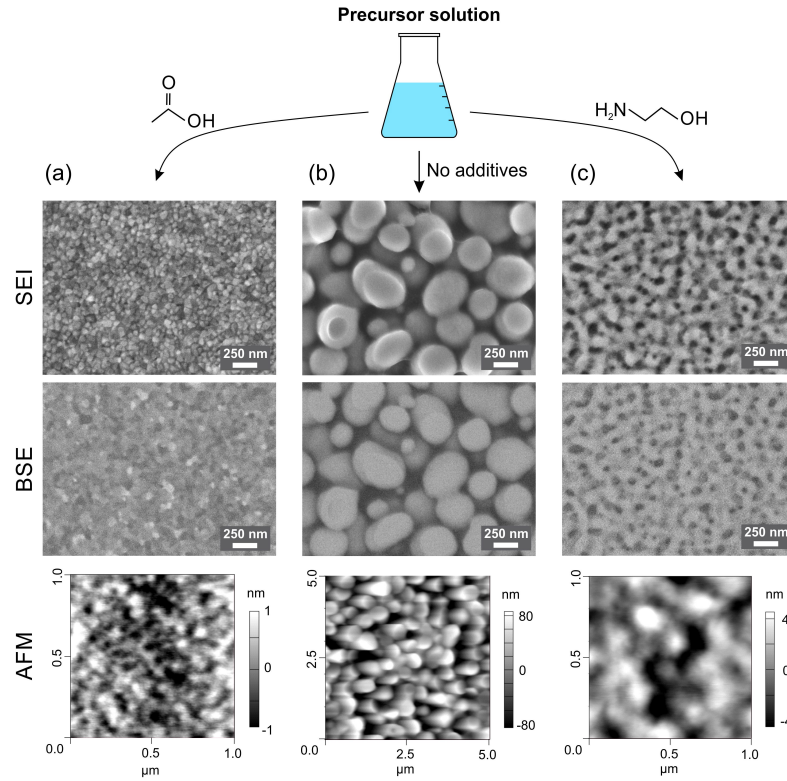


Figure 7.2: Microstructure evolution of films deposited from PVP-modified sol-gel solution and heated at 150 °C on a hotplate. SEI and BSE correspond to secondary electron and backscatter electron-imaging modes in electron microscopy and AFM corresponds to atomic force microscopy. (a) Addition of acetic acid leads to homogeneous and smooth films without any observable phase separation. (b) Unmodified solution produces fragmented structure with large condensed particles (seen as the bright spots in BSE images) encapsulated in PVP polymer (dark spots in the same images). (c) Addition of MEA produced films with fine bi-continuous structure. The ratio between chemical modifier and (Zr+Ti) was 3 to 1. Figure adapted after [208].

The nanostructured film prepared from PVP-modified solutions shows a fragmented morphology after the drying step, meaning that the hydrolysed particles are not interconnected, but are uniformly dispersed in the PVP polymer (Figure 7.1b and Figure 7.2b). The as-prepared, self-assembled PZT particles require high-temperature annealing to convert the hydrolysed species into functional oxide, induce the crystallization and remove the organic phase. The onset of PVP decomposition/oxidation occurs at ~ 300 °C and it fully decomposes at temperatures higher than 430 °C. The thermal activation as well as the large surface curvature (associated with the nanoscale particle size) are sufficient to promote the surface diffusion and sintering (Figure 7.1c). A highly porous metal-oxide framework remains preserved even after the high-temperature anneal (Figure 7.1c, $T = 650$ °C), while at even higher annealing temperatures the necks between the particles grow and the connectivity increases (Figure 7.1c, $T = 800$ °C). After the annealing step, the nanostructured PZT films crystallize into the pure perovskite phase with a slight 100 preferential orientation.

The piezoelectric thin film devices that operate in thickness mode (d_{33} -mode) are typically in parallel plate capacitor configuration. Such capacitors thus consist of a piezoelectric

layer sandwiched between bottom and top electrodes. For films with open paths through the thickness of the film (our case, Figure 7.3a), the top electrode cannot be deposited directly, but requires special processing. To avoid any penetration of the metal into pores and to retain its integrity during sputter-deposition, we temporally filled the voids with an epoxy-based resin (Figure 7.3b). After the deposition of Au electrodes (Figure 7.3c), the epoxy was burned-out by heating the samples to 450 °C in air (Figure 7.3d). At this temperature the epoxy steadily decomposes and about 5 min of heating fully removed the filler. As shown in Figure 7.3d the integrity of the top electrode was completely preserved, even after the burnout of the epoxy filler. Due to a large fraction of open porosity, the humidity in environment tends to absorb along the pore walls, which deteriorates the electrical properties of the capacitors. The absorption typically occurs within a few days of exposure; however, the absorption/desorption process is fully reversible by heating the samples at elevated temperature for a few minutes. For long term stability, the epoxy filler could be retained in the pores with only the topmost layer removed.

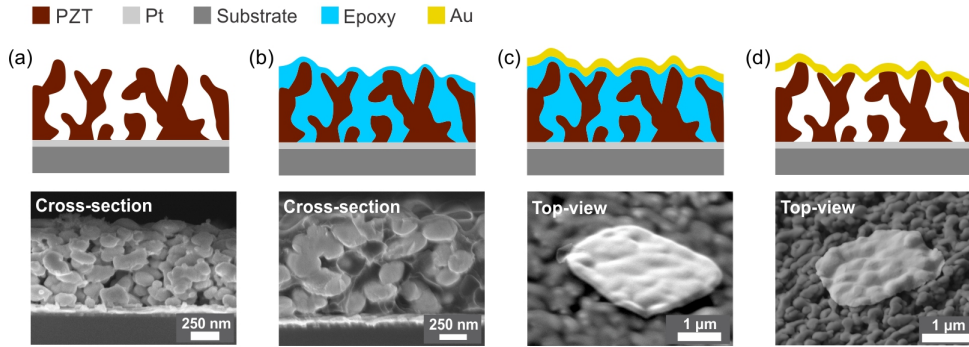


Figure 7.3: The SEI-SEM images and schematic representation of the main steps in the thin-capacitor fabrication process: (a) deposition of nanostructured film, (b) filling the metal-oxide framework with the epoxy resin, (c) sputtering of the gold top electrode, (d) thermal burnout of the resin. Figure adapted after [208].

7.2 Electromechanical Response

The polarization switching behaviour of thin-film capacitors with top electrodes of different diameters and their electromechanical response are presented in Figure 7.4. For comparison, approx. 1.5- μm -thick dense film was prepared by spin coating the PZT precursor solution without any PVP.

The dense film exhibits a response typical of a PZT thin film with a near-MPB composition, while the porous film shows a 20 % lower remanent polarization and a 35 % higher coercive field. This can be explained by the composite approach: the porous film consists of a high-permittivity PZT phase and a low-permittivity air phase (pores), which yield lower dielectric permittivity and polarization values than the pure PZT. The increase in the coercive field is probably related to a lower average electric field due to the inhomogeneous field distribution in porous materials [209]. Despite the inhomogeneous electric field in the porous film the polarization switching is similar to that of the dense film and polarization saturates fully at electric fields exceeding the coercive field (Figure 7.4a).

A striking difference between the dense and the porous films appears in the electromechanical response. The field-induced strain (Figure 7.4e) and d_{33} - E_{BIAS} hysteresis (Fig-

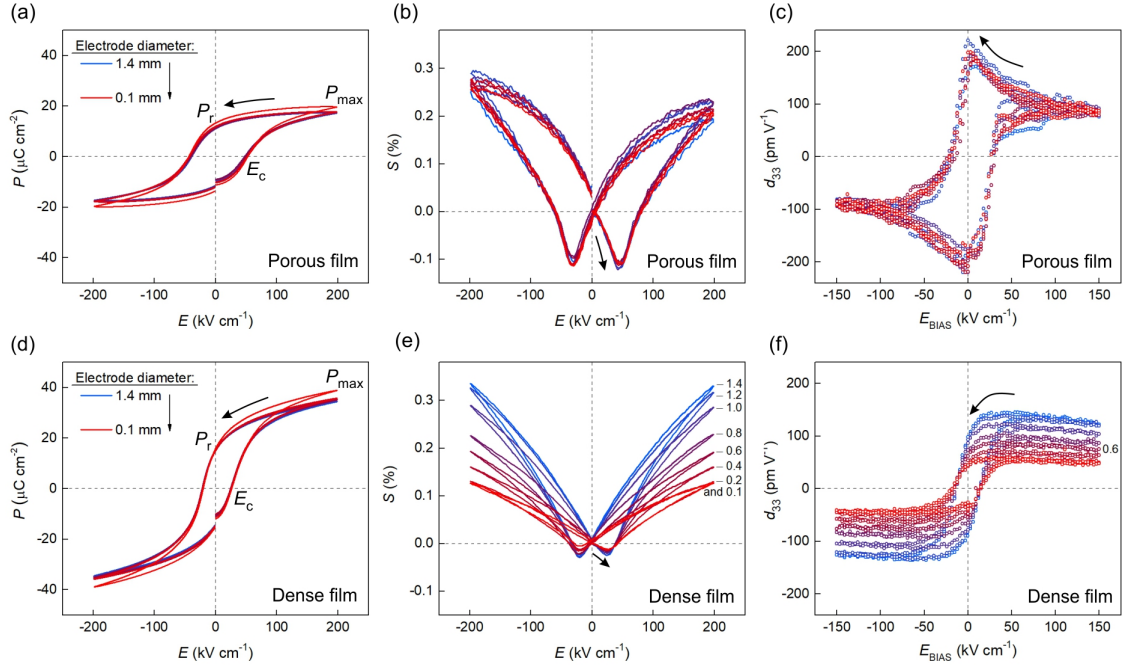


Figure 7.4: The electric-field dependence of (a, d) the electrical polarization and (b, e) the strain. (c, f) Small-signal piezoelectric coefficient d_{33} at different DC bias fields. a–c correspond to the porous film and d–f show identical quantities for the dense PZT film. The measurements were performed on electrodes with a diameter ranging from 0.1 mm to 1.4 mm. Reproduced from [208].

ure 7.4f) of the dense film are strongly dependent on the diameter of the top electrode. This is due to the substrate-clamping effects and the associated development of the in-plane and out-of-plane stress inside the substrate when the electric field is applied. For large electrode sizes, a strong in-plane compressive stress develops in the substrate due to substantial bending of the sample, while the out-of-plane stresses are negligible—this results in positive net contribution to the measured electromechanical response. In contrast, for small electrodes the sample bending is minimal and piezoelectric film pushes down the substrate at the interface, resulting in strong out-of-plane compressive stress—this produces a negative net contribution to the measured electromechanical response. For a PZT film on a silicon substrate, the true piezoelectric properties are measured when the electrode diameter is approximately equal to the thickness of the substrate [210]—in our case that is for an electrode diameter of 0.6 mm. In contrast, the porous film shows an electromechanical response that is independent of the electrode size and much larger strain and d_{33} values (Figure 7.4b,c). There is also a clear difference in the qualitative behaviour of the electromechanical response. As evident in the S – E plot (Figure 7.4b), the porous film shows a large negative strain just before the switching event and a very hysteretic strain loop. In comparison, the negative strain and hysteresis are much smaller for the dense film (Figure 7.4e). In small-signal measurements of d_{33} at different DC bias fields, the most prominent difference appears when the bias field approaches zero from its maximum (decreasing branch of the hysteresis; see arrow in Figure 7.4c,f). For the porous film, the d_{33} reaches a maximum value near zero bias, while the dense film reaches its maximum d_{33} value at $\sim 40 \text{ kV cm}^{-1}$ bias and d_{33} decreases by 35 % at a zero bias field. Such a decrease of the piezoelectric properties is associated with the domain back-switching [140]

and is also reflected in the polarization loops (arrow in Figure 7.4d), where the maximum polarization (P_{max}) is $2.5\times$ larger than P_r . In the porous film, the domain structure at a low bias field is stable and P_{max} is only $1.5\times$ larger than P_r .

In bulk piezo-composites d_{33} typically decreases with the introduction of the inactive phase (or remains constant for some types of connectivity patterns) [211]. This is not the case for thin-film composites where the mechanical clamping of the substrate opposes the piezoelectric deformation of the film. The electrode size-independent response of the porous film (Figure 7.4b,c) indicates that the clamping is strongly reduced in such films, which should increase the piezoelectric properties. It has been further demonstrated that substrate clamping has a strong effect on the DW motion: in dense films it is impaired by clamping [212], while even small isolated pores can promote the ferroelastic DW motion, as shown by an x-ray diffraction study [213], [214]. However, neither a significant enhancement of d_{33} or a characteristic effect on the domain back-switching behaviour (described in the previous paragraph) have been observed for films with small isolated pores. In our nanostructured films the pores otherwise extend throughout the thickness, which effectively releases the substrate constraints and strongly affects the DW configuration and mobility.

7.3 Origins of the Enhanced Piezoelectric Response

To further elucidate the de-clamping effect of pores on DW displacements, weak-field dielectric and piezoelectric properties were analysed in the framework of Rayleigh's law (see Appendix C). The AC field dependencies of the dielectric permittivity and the longitudinal piezoelectric coefficient are presented in Figure 7.5a–d. The porous film exhibits about five times lower dielectric permittivity values than the dense film, and accordingly smaller ε_{init} and α_ε (Figure 7.5a). Yet, the field-dependence of the $\varepsilon'/\varepsilon_{init}$ ratio—which describes the irreversible DW displacement contribution relative to the reversible response—reveals that the nonlinearity is higher in the porous film (Figure 7.5b) and is associated with the enhanced irreversible DW displacements. We acknowledge that in materials with two or more coexisting ferroelectric phases (such as rhombohedral and tetragonal in MPB PZT) the interphase boundary motion might also contribute to the nonlinear response in addition to the DW motion. It is important to note that the hysteretic nature of the irreversible DW motion should result in an increase of the losses with the AC field. This indeed occurs for both the dielectric and piezoelectric losses (ε'' and d_{33}'') of the porous and dense films as predicted by Rayleigh's law (Figure 7.6).

In the first approximation, the dielectric response of unpoled films (Figure 7.5a) contains contributions of both 180° and non- 180° DW displacements. Differently, the main contribution to the piezoelectric response of the poled films represents the non- 180° DW displacements (although it was shown using a dynamic poling model [215] that 180° DW displacements might also contribute somewhat to the piezoelectric second-harmonic response). As evident in Figure 7.5c, the porous film exhibits nearly six times larger piezoelectric coefficients than the dense film, and also larger $d_{33,init}$ and $\alpha_{d_{33}}$. The field-dependence of $d_{33}'/d_{33,init}$ reveals that the piezoelectric nonlinearity is higher for the porous film (Figure 7.5d)—similar as in the case of the dielectric permittivity. In addition, for the porous film, good agreement is found between the measured strain loops at sub-switching electric fields and the calculated loops (Figure 7.5e) according to the Rayleigh relation. The stronger contribution of the irreversible DW motion—and the associated greater loss—is clearly evident for the porous film from the higher strain values and the larger hysteresis (Figure 7.5e).

The enhancement of the non- 180° ferroelectric DW motion in the porous film is additionally supported by unipolar strong-field strain measurements of the unpoled samples

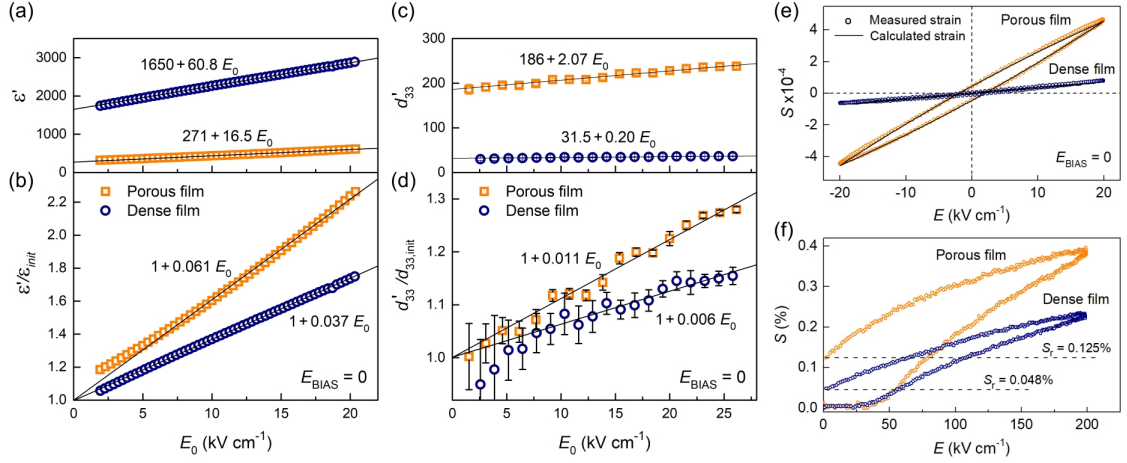


Figure 7.5: Evaluation of the reversible and irreversible contributions to the dielectric and piezoelectric responses of the porous and dense PZT films. (a) Dielectric permittivity (ϵ') and (b) normalized dielectric permittivity ($\epsilon'/\epsilon_{init}$) of the unpoled films as a function of the AC field amplitude. (c) and (d) show the same dependency for the longitudinal piezoelectric coefficient of the poled films. The higher slope of the linear fit in the normalized plots (b,d) indicates larger, irreversible DW contributions relative to the response extrapolated to zero field (ϵ_{init} , $d_{33,init}$). (e) Measured and calculated sub-switching strain-field hysteresis loops of the poled films. The porous film exhibits higher strain values as well as a larger hysteresis, which is in agreement with the stronger irreversible contribution to the piezoelectric response. (f) First-cycle unipolar strain loops of virgin films revealing the difference in the remanent strain for the porous and dense films. Reproduced from [208].

(Figure 7.5f). Initially, the unpoled film exhibits zero macroscopic polarization; thus the strain is nearly zero for the electric fields below the coercive field and non-zero for higher fields, when the film becomes poled. The maximum strain of the porous film is nearly twice as high as in the dense film. The remanent strain—i.e., the strain at zero field upon its removal—is in a simplified scenario zero in the case of solely 180° DW switching and non-zero in the case of non-180° DW switching. In the dense film the remanent strain is 0.048 %, which indicates some irreversible non-180° DW switching. On the other hand, the porous film exhibits a much higher remanent strain of about 0.125 %, which indicates a strong irreversible non-180° DW switching. This behaviour is consistent with the higher contribution of the irreversible DW displacement in weak fields (Figure 7.5d,e).

It is clear that the release of the elastic constraints in the porous film leads to a strong enhancement of the non-180° DW motion; however, the same stress relaxation should in addition impact on the electromechanical response for exclusively mechanical reasons. To assess this impact in the porous and dense films, their field-induced electromechanical response was simulated using the finite-element method (FEM). The model includes the geometrical, electrical and mechanical aspects of the materials, but excludes the nonlinearity due to DW motion. As shown by the spatial strain map (Figure 7.7a), the distribution of local piezoelectric displacements is inhomogeneous in the porous film. Large strain is observed in areas where the PZT extends nearly vertically across the thickness of the film, which is in accordance with the theoretical predictions for composites with a 2-2 or 1-3 configuration [211]. The thickness-averaged strain (shown in the upper plot of Figure 7.7a) varies by as much as 10 % over different locations in the x-direction. The FEM simulations reveal that the in-plane stress in the porous film is localized at the piezoelectric-substrate

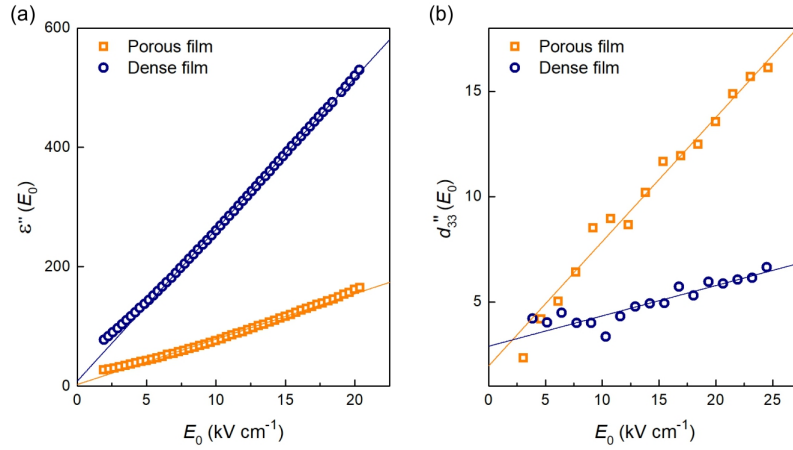


Figure 7.6: (a) The imaginary part of the complex dielectric permittivity ($\epsilon^* = \epsilon' - i\epsilon''$) and (b) the imaginary part of complex piezoelectric coefficient ($d_{33}^* = d_{33}' - id_{33}''$) as a function of applied AC field amplitude. A linear increase of ϵ'' and d_{33}'' is consistent with Rayleigh relation (see Appendix C for details).

interface, but diminishes just a few hundred nanometers away from the contact. In the contact, the idealized dense film is under a strong tensile stress over the whole film thickness, and the substrate is under a strong compressive stress in the region adjacent to the piezoelectric–substrate interface. This occurs due to the transverse piezoelectric effect combined with the rigid mechanical coupling of the piezoelectric PZT film with the inactive silicon substrate. The average strain in the porous film is thus almost double that in the dense film (compare upper parts of Figure 7.7a and c), despite the lower average electric field. The main mechanical aspects responsible for the larger electromechanical response in the porous film are reduced substrate clamping of the film and the macroscopic increase of the elastic compliance of the film.

The piezoelectric response of the porous film and its DC bias field's dependence (Figure 7.7e) compare very well with bulk PZT ceramics of the same composition: it achieves the d_{33} values of the bulk ceramics and exhibits bulk-like piezoelectric behaviour, although the grain size in the porous film is nearly two decades lower (in PZT ceramics the piezoelectric properties are significantly reduced for grain sizes below $1\ \mu\text{m}$) [216]. The much larger coercive field of both thin films, as compared to the bulk ceramics, implies the presence of the scaling effects in combination with the existence of a depletion layer at the electrode–ferroelectric interface [159]. Recently, Denis et al. demonstrated strong dependence of dielectric Rayleigh coefficients on the thickness of $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$ films doped with 2 % of niobium [217]. The dielectric nonlinearity increased significantly when the clamped films were partially released from the substrate, but still exhibited non-monotonic thickness dependence. Another study on pulsed-laser-deposited PZT thin films with laterally separated columnar grains shows that for 1–4- μm -thick films the d_{33} at zero bias field is a strong function of the film thickness and the d_{33} under a DC bias field of $200\ \text{kV cm}^{-1}$ is thickness independent [218]. This suggests that even in elastically relaxed films the extent of the ferroelastic DW motion strongly depends on the thickness of the ferroelectric layer—a feature that is usually observed for dense films and was related to the reduced substrate clamping in thicker films. Additionally, in bulk ceramics the strain fields can extend several microns away from the DWs [219] and can be present across several grains. These long-range strain fields cannot exist in a nanostructured film due to the absence of

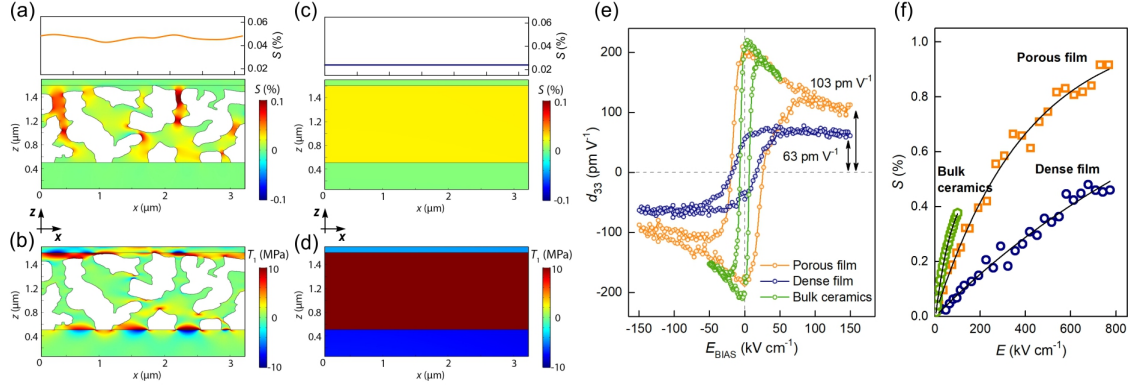


Figure 7.7: FEM simulation and experimental determination of the electric-field-induced elastic deformations and stress development in thin films. The spatial map of the simulated (a) out-of-plane strain and (b) in-plane stress for the porous film. (c,d) shows the same plots for an idealized dense film. In the porous film the local strains are inhomogeneous, yet, the thickness-averaged strain (shown in the plots above the strain maps) is much larger than in the dense film. The electric-field-induced stress in the porous film (b) is much smaller and present at the ferroelectric-substrate contact, whereas the dense film (d) is under high tensile stress and the underlying substrate is under a strong compressive stress. (e) The measured piezoelectric coefficient as a function of the applied DC electric field. The porous film and bulk ceramics show comparable qualitative and quantitative behaviour, while the dense film shows much lower d_{33} values. (f) The maximum unipolar strain as a function of the applied electric field amplitude. Bulk ceramics exhibit the steepest increase in strain, but also the lowest breakdown field. On the other hand, the porous film shows a nearly ten times larger breakdown field and much larger maximum strain values. Reproduced from [208].

grain-to-grain elastic coupling. It is currently unclear if the scaling effects are driven by the electrode–ferroelectric interface or are related to grain-size effects.

The large-signal measurement of maximum strain (Figure 7.7f, determined from unipolar S – E plots) reveals a more distinct difference in the response of bulk ceramics, porous and dense films. At 100 kV cm^{-1} the bulk ceramic exhibits the highest strain value of 0.37 %, while the strain in the porous film is about 0.26 % and only 0.08 % in the dense film. This electric field, however, is close to a typical breakdown field for most ferroelectric ceramics, while the breakdown field of thin films is a magnitude higher. The largest attainable strain is thus 2.5-times higher in the porous film when compared to the bulk ceramics and the dense film.

Chapter 8

Conclusions and Outlook

The thesis presents a comprehensive study of the fundamentals of wetting regulation and drying phenomena with the aim to develop a universal deposition process for printed oxide electronics. The last chapter is devoted to the tailoring of the material's nanostructure through self-assembly techniques for the enhancement of the piezoelectric response of ferroelectric thin films.

The wetting of different substrates was efficiently controlled by the deposition of thin polymeric layers. The layers of poly(vinyl alcohol) and poly(vinyl pyrrolidone) on glass exhibit hydrophilic surface properties, while the poly(methyl methacrylate) and poly(styrene) layers render the surfaces hydrophobic. Theoretical predictions based on wetting diagrams correlate well with the inkjet printing of two inks with different polarities. The printing of structures with more complex geometries requires a rigorous adjustment of the surface properties. This was achieved by the thermal decomposition of the poly(methyl methacrylate) layer, which results in a smooth transition from polymer-like towards substrate-like surface properties. The surface free energy analyses of the layers heated for different times at 350 °C suggest that this transition originates from the percolation of the underlying substrate surface through small, non-interacting spots in the polymer layer. The method is efficient on homogeneous substrates; however, it produces poor results on surfaces with pre-patterned structures due to the irregular decomposition of the polymeric layer. For inhomogeneous substrates, much better results are obtained when the polymeric layer is exposed to oxygen plasma or UV/ozone. The exposure introduces polar functional groups to the layer surface and increases the surface free energy and polarity. The wetting could be continuously tailored by setting the exposure time. The practical applicability of thin polymeric layers was exemplified by three ink–substrate systems, which originally exhibited a poor printing performance. Adjusting the ink–substrate interactions by implementing polymeric layers improved the wetting behaviour and made it possible to print structures with a well-defined geometry and morphology.

Another parameter for successful inkjet-based deposition is the ability to control the morphology of the dried deposits, thus the drying of solvent mixtures composed of two solvents with different volatility and surface tension was investigated in detail. The systems with a large fraction of a more volatile solvent tend to exhibit wetting instabilities upon drying as a result of compositional changes. A de-wetting transition can occur when the less-volatile solvent exhibits a larger contact angle on a selected surface, while a spreading transition can occur when the solvent exhibits a smaller contact angle. The solvent mixtures with 80 vol% of a less-volatile solvent were least prone to major wetting transitions and were further studied for the deposit morphology. Two investigated inks contained LaNiO_3 sol-gel precursors dissolved in a solvent mixture of 2-ethoxyethanol and (i) ethylene glycol (EG) or (ii) ethanolamine (EA). EG and EA have similar physical properties,

but yield completely different deposit morphologies after drying: a ring-like shape for the EG-based ink and a dome-like shape for the EA-based ink. The examination of the drop height profiles upon drying using an interferometric method revealed a distinct difference in the contact-line dynamics of both inks. At a large initial contact angle, the EG ink exhibits a static contact line (pinned throughout the drying process), while the EA-ink exhibits a dynamic contact-line behaviour (receding contact line). The contact line of the EA-based inks recedes at a small contact angle ($< 5^\circ$), which results in a simultaneous deposition of a solute at its location. The final deposit shape then depends on the local concentration of the solute at the contact line and the receding contact angle. The initial contact angle affects the contact-line dynamics only in the case of the EG ink. The transition from static to dynamic behaviour occurs at small contact angles, which is evidenced in the drying of single drops on surfaces of different wettability and in the drying of squares printed at different drop spacings. It is demonstrated that printing the square patterns of varying dimensions and drop spacings and the examination of their thickness profiles can be used to readily distinguish between the static and dynamic contact-line behaviour. The results indicate that the contact-line behaviour is a critical parameter for the morphology of the dried patterns.

Full control over the wetting and drying behaviour has enabled the deposition of high-quality functional layers. The printing process was first adapted for the deposition of lanthanum nickelate (LNO) top electrodes onto spin-coated lead zirconate titanate (PZT) films on the platinised silicon substrates. The ternary-solvent inks containing 20 vol% 2-ethoxyethanol, 64 vol% ethanolamine and 16 vol% ethylene glycol were used to prepare about 50-nm-thick, uniform and laterally well-defined structures. The electrical characterization revealed that the capacitors with LNO top electrodes have a significantly larger dielectric permittivity, a lower coercive field and better fatigue properties than the capacitors with sputtered Au or Cr/Au top electrodes. Afterwards, the inkjet printing of PZT structures onto spin-coated LNO films on silicon wafers was investigated using inks with the same solvent composition as the LNO ink. It was found that the drying of printed PZT structures at low temperature for a long time results in extensive cracking of the layers after annealing. The optimised thermal treatment produced crack-free layers with a uniform grain size distribution and no secondary phases. Crack-free PZT structures could be printed when the thickness of a single layer was less than about 180 nm. The overall thickness could be increased by repeating the printing/annealing process several times, which also improved the electrical reliability of the printed structures, most probably due to the reduced concentration of pinhole defects.

The all-printed thin-film capacitors were fabricated by the sequential deposition of LNO electrodes and the PZT ferroelectric structure. The printed stacks consisted of a 120-nm-thick LNO bottom electrode, a 400-nm-thick PZT layer and a 60-nm-thick LNO top electrode. The individual structures had good lateral definition and were conformally deposited over the pre-existing layers. The capacitors were demonstrated on silicon substrates, thin alumina plates and flexible nickel foil, and could, in principle, be printed on virtually any optical grade substrate. The dielectric permittivity of single-layer capacitors on silicon wafers was 1350, which is comparable to the capacitors with a spin-coated PZT layer. On the other hand, the capacitors on alumina and nickel exhibited a lower dielectric permittivity, but a higher remanent polarisation. This is probably related to different domain configurations in the PZT layers governed by the residual stresses that develop due to the different thermal expansion coefficients of the substrate and the printed structures. The longitudinal piezoelectric coefficient of devices on silicon and alumina was about 70 pm V^{-1} .

The developed processing methodology allowed a further extension from single-layer

capacitors (SLC) to multilayer capacitors (MLCs) with three active PZT layers. Extensive chemical and structural analyses showed that the chemical homogeneity is retained in multilayer devices and the crystal texture is similar for SLCs and MLCs. A special device architecture allowed the separate electromechanical characterisation of each active layer in a MLC. The measurements revealed differences in the dielectric properties of individual active layers, with the middle one exhibiting the highest dielectric permittivity and maximum polarization values. On the contrary, the piezoelectric response was constant and comparable to single-layer devices. When the active layers were wired in a parallel configuration, the measured capacitance values differed from that predicted by the theory. In particular, the measured values were about 18 % smaller than the summarized capacitances of individual active layers. Nevertheless, the capacitance density increases from 30 nF mm^{-2} for SLC to 80 nF mm^{-2} for MLC with three active layers. Upon reducing the thickness of the active PZT layer from 400 nm to 200 nm the capacitance density of the MLC increased to about 150 nF mm^{-2} . These results demonstrate that inkjet printing is capable of depositing high-quality oxide layers and is potentially viable as a next-generation technique for the additive manufacturing of thin-film multilayer devices.

The last part of the thesis focuses on the maximization of the piezoelectric response of ferroelectric thin films through morphological design, with a simple and robust method for the chemical solution deposition of self-assembled ferroelectric thin films with a porosity-mediated release of the substrate's mechanical constraints. The nanostructured PZT thin films exhibit a much larger piezoelectric response than the dense films, being comparable to a bulk PZT ceramic. The strain-relaxation in nanostructured films enhances the piezoelectric properties by (i) eliminating the clamping effects of the substrate and (ii) making the ferroelastic domain walls mobile. Consequently, these films are more efficiently poled, exhibit much larger strain and d_{33} values, and have an electromechanical response that is independent of the electrode size. The enhanced functional response and easy scalability of the deposition process to large surfaces and industrial applications makes this method interesting for the development of a new generation of electromechanical devices. The synthesis approach can be applied for the deposition of a wide selection of simple or complex metal oxides. Materials with strong coupling between the elastic field and electric and/or magnetic fields are particularly interesting. These materials—when prepared as dense thin films—usually show significantly reduced coupling coefficients due to the substrate constraints, which can be efficiently released by the nanostructuring described in this work. A large fraction of open porosity in the nanostructured films offers an additional opportunity to design and synthesize new types of strain-coupled thin-film composites with a 3-2 or 3-3 geometry.

Appendix A

Owens–Wendt–Rabel–Kaelble Surface Energy Model

The surface free energy (SFE) of a solid cannot be directly measured, but is estimated using models. The Owens–Wendt–Rabel–Kaelble (OWRK) model is a two-component model based on the Fowkes assumption that two types of interactions exist at the solid–liquid interface [220]. The SFE of a solid or a liquid is divided into its dispersive and polar components, which are related by geometrical mean values. The solid–liquid interfacial tension, γ_{SL} , is

$$\gamma_{SL} = \gamma_L + \gamma_S - 2 \left(\sqrt{\gamma_L^D \gamma_S^D} + \sqrt{\gamma_L^P \gamma_S^P} \right), \quad (\text{A.1})$$

where γ_L is the overall SFE of the liquid, γ_S is the overall SFE of the solid, and the D and P superscripts correspond to the dispersive and polar contributions to the SFE. Inserting the above relation into Young–Laplace equation, $\gamma_S = \gamma_{SL} + \gamma_L \cos \theta_{eq}$ (Equation 1.4), results in

$$\frac{\gamma_L (\cos \theta + 1)}{2\sqrt{\gamma_L^D}} = \sqrt{\gamma_S^P} \sqrt{\frac{\gamma_L^P}{\gamma_L^D}} + \gamma_S^D, \quad (\text{A.2})$$

which is actually a linear equation. In a polar-coordinate system, Equation A.2 becomes

$$r(\varphi) = \left(\frac{\sqrt{\gamma_S^D \cos \varphi} + \sqrt{\gamma_S^P \sin \varphi}}{\cos \varphi + \sin \varphi} \right)^2 \left(\frac{2}{1 + \cos \theta} \right)^2. \quad (\text{A.3})$$

The SFE parameters of a surface are calculated by measuring the contact angles of at least two probe liquids with known γ_L , γ_L^D and γ_L^P , and then performing a linear fit in the $\gamma_L (\cos \theta + 1)/2\sqrt{\gamma_L^D}$ vs $\sqrt{\gamma_L^P/\gamma_L^D}$ plot. The same set of probe liquids should be used when comparing the surface properties of different solids to improve the reliability of the method [221]. The probe liquids used for estimation of the SFE in Chapter 4, together with their surface-tension values, are collected in Table A.1.

The dispersive and polar components of surface tension of a liquid can be assessed by measuring its interfacial tension in air and in other liquid medium. The interfacial tension between two liquids is

$$\gamma_{1,2} = \left(\sqrt{\gamma_1^D} - \sqrt{\gamma_2^D} \right)^2 + \left(\sqrt{\gamma_1^P} - \sqrt{\gamma_2^P} \right)^2, \quad (\text{A.4})$$

Table A.1: Set of probe liquids with corresponding surface-tension values (from Ref. [221]).

Liquid	γ_L	γ_L^D	γ_L^P
	mN m ⁻¹		
Water	72.8	26.4	46.4
Glycerol	63.4	37.0	26.4
Benzyl alcohol	39.0	30.3	8.7
Toluene	28.4	26.1	2.3

where subscripts 1, 2 denote liquid 1 and 2. If a liquid with a zero polar contribution is selected as a liquid medium, the polar contribution to the surface tension of a test liquid can be readily calculated from Equation A.4. The common liquids with $\gamma_L^P = 0$ are alkanes, such as hexane, octane and cyclohexane.

OWRK model only roughly estimates the surface energy of a solid and the evaluation relies on certain mathematical assumptions. Furthermore, the estimation of solid SFE is also obstructed by the fact that the equilibrium contact angle cannot be directly measured—by contact angle measurements only the apparent contact angle is assessed [56]. The methods for the evaluation of Young contact angle are still under intensive debate and research [49], [222]. Yet, the simplicity and a relatively good agreement with experiments make the OWRK model the most widely used SFE model. For a substrate with given γ_S^D and γ_S^P , the OWRK model allows a convenient prediction of the wetting-ability for a random liquid with given γ_L^D and γ_L^P via the construction of wetting envelopes (Figure 1.8). It is important to note that—according to the OWRK model (and other multi-component models)—the wetting does not directly depend on the overall SFE, but is determined by the degree of polar–polar and dispersive–dispersive interaction between the solid and the wetting liquid.

Appendix B

Geometrical Relations in a Spherical Cap

Ideally, a small sessile drop assumes the shape of a spherical cap due to dominant surface tension forces. The spherical cap is axisymmetric and its height from the center to the edge is given by

$$h(r) = a + \sqrt{R^2 - r^2}, \quad (\text{B.1})$$

which is a section of a circle in the first quadrant in a Cartesian coordinate system. a is the offset of the drop radius on the z -axis and R is the radius of the circle. The physically meaningful is the segment above r -axis where $h \geq 0$, that is for r values between 0 and $d/2$, where $d/2 = \sqrt{R^2 - a^2}$.

The fit of the circular section (Equation B.1) to experimental height data can be used to extract the volume of the sessile drop from

$$V = \frac{1}{3}\pi h^2(3R - H) \quad (\text{B.2})$$

and the contact angle as

$$\theta = \arccos\left(1 - \frac{H}{R}\right), \quad (\text{B.3})$$

where H is the height of the circular segment at $r = 0$. The experimental height profiles may deviate from the ideal shape due to distortions caused by internal liquid flows or solute accumulation at the periphery of the drop. The deviations are better observable by looking at the derivative of the height profile

$$\frac{dh}{dr} = -\frac{r}{\sqrt{R^2 - r^2}}. \quad (\text{B.4})$$

For drops with the contact angle much smaller than 90° , $R \gg r$ and Equation B.4 becomes

$$\frac{dh}{dr} = -\frac{1}{R}r, \quad (\text{B.5})$$

which is a simple linear function with the slope of $1/R$ and the origin at $\{0,0\}$. The height profile and its derivative for an ideal drop are shown in Figure B.1b. Let us now take a look at two particular deviations from the ideal circular shape. In the first case the drop inflates in the central region of the drop (Figure B.1c) and the height derivative becomes non-linear. Such shape distortion would be an indication of solute accumulation at the pinned contact line. If the contact line depins and the solute is deposited at the receding

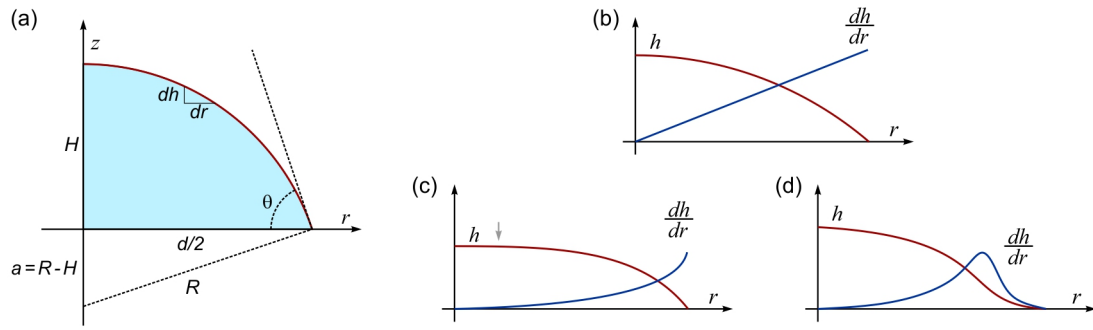


Figure B.1: (a) The circular segment. The height profile and its derivative for (b) ideal drop shape, (c) drop inflated in the central region, (d) drop with the s -shaped contact line.

contact line, the drop adapts the s -shape shown in Figure B.1d. The derivative of such a profile has a local maximum at the position of the contact line.

Appendix C

Rayleigh Law in Ferroelectric Materials

Upon cooling a ferroelectric through the paraelectric–ferroelectric phase transition a complex domain structure develops in a material due to energy minimization. The region that separates two adjacent domains is called a domain wall (DW). The type of a DW depends on the polarization vector of the domains it is separating. For example, the domains of opposite polarization are separated by 180° DWs, while the domains with a mutually perpendicular polarization are separated by 90° DWs [223]. The possible DW types that can be present in a material depend on the symmetry of nonferroelectric and ferroelectric phases [178].

DWs may be displaced by an external field and thus strongly contribute to the properties of many ferroelectric materials. The displacement of 180° DW results in a change in macroscopic polarization (Figure C.1a) and these DWs may contribute to the dielectric response. The displacement of non- 180° DWs is accompanied by a change in both polarisation and strain; thus non- 180° DWs may contribute to dielectric and piezoelectric properties. It should be noted that also 180° DW displacements can contribute somewhat to the piezoelectric second-harmonic response via dynamic poling model. [215] For DWs located in a medium with randomly distributed pinning sites, the Rayleigh law [224] predicts that the coefficient (m) is a linear function of the applied sub-switching AC field amplitude (E_0)

$$m(E_0) = m_{\text{init}} + \alpha_m E_0, \quad (\text{C.1})$$

as shown in Figure C.1c. m can be the dielectric permittivity ε' or the piezoelectric coefficient d_{33}' (i.e., real parts of complex quantities $\varepsilon^* = \varepsilon' - i\varepsilon''$ and $d_{33}^* = d_{33}' + i d_{33}''$). For clarity reasons the sign $'$ is omitted from the notation of Rayleigh coefficients α_m and m_{init} .

The reversible parameter m_{init} describes the intrinsic lattice response and the reversible DW motion (or other interfaces), while the irreversible parameter α_m is related to the irreversible displacement of the interfaces, including the DWs. The ratio α_m/m_{init} ratio describes the irreversible DW displacement contribution relative to the reversible response.

The general response of the material to the electric field can be expressed as

$$M(E) = (m_{\text{init}} + \alpha_m E_0)E \pm \frac{\alpha_m}{2}(E_0^2 + E^2), \quad (\text{C.2})$$

as shown in Figure C.1d. M can be macroscopic polarisation or strain and E is the driving field ($E = E_0 \sin(\omega t)$). The Rayleigh coefficients m_{init} and α_m are extracted from

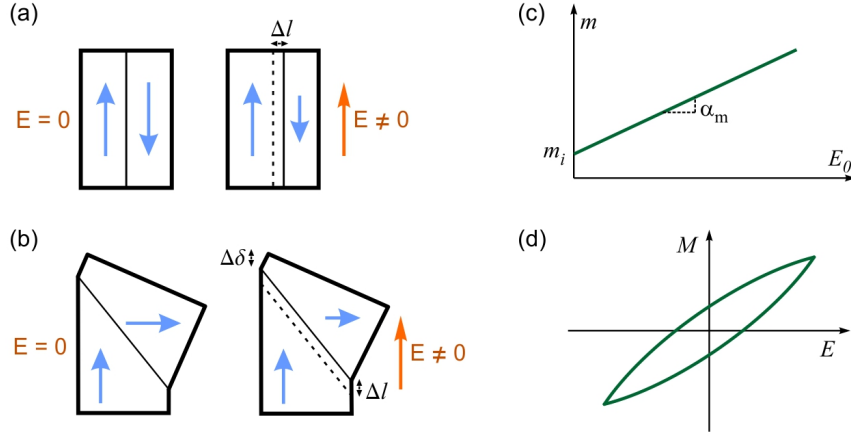


Figure C.1: The displacement of (a) 180° and (b) 90° domain walls by an external electric field. (c) The AC field dependence of the material coefficient m according to the Equation C.1. m can be dielectric permittivity or the piezoelectric coefficient. (d) A hysteresis loop of a generalized material response M according to Equation C.2. M can be polarization or strain.

AC measurements (Equation C.1). It is important to note that a higher nonlinearity—associated with a larger contribution of the irreversible DW displacements to the response—associates with the increased losses, which is understood in the frame of the hysteretic nature of irreversible DW motion. To formulate a relationship between nonlinearity and hysteresis, a Rayleigh model (Equation C.2) is expanded using Fourier series:

$$M(E) = (m_{\text{init}} + \alpha E_0)E_0 \sin(\omega t) - \frac{4\alpha E_0^2}{3\pi} \cos(\omega t) - \frac{4\alpha E_0^2}{15\pi} \cos(3\omega t) - \frac{4\alpha E_0^2}{105\pi} \cos(5\omega t) + \dots \quad (\text{C.3})$$

The expanded Rayleigh relation predicts a linear increase of m'' with the field amplitude according to:

$$m'' = \frac{4\alpha}{3\pi} E_0. \quad (\text{C.4})$$

The measurement of Rayleigh parameters is relatively simple and straightforward. However, the interpretation of the results requires certain precautions as the nonlinear response might be affected by several factors that are not related to the DW motion. In materials with two or more coexisting ferroelectric phases (such as rhombohedral and tetragonal in MPB PZT) the interphase boundary motion might also contribute to the nonlinear response. Additional contributions might arise if the material under test exhibits significant (nonlinear) conductivity.

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Publications Related to the Thesis

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Biography

Aleksander Matavž was born on 6 November 1991 in Slovenj Gradec, Slovenia. He obtained a Bachelor's degree in Chemistry from the University of Maribor in 2013 (thesis entitled: Sintering and stereological analysis of electrocaloric ceramics based on $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$). In 2015, he obtained a Master's degree in Nanosciences and Nanotechnologies from the Jožef Stefan International Postgraduate School (thesis entitled: Inkjet printing of transparent metal oxide-based nano-capacitors).

During studies he visited several institutions abroad and attended international conferences. In 2014, he participated in an Erasmus traineeship exchange programme at Université François Rabelais in Tours, France, where he worked on the dielectric and electromechanical characterization of piezoelectric thick films. In 2015, he visited the School of Electronic and Information Engineering at University of Xi'an, China, where he performed dielectric measurements on oxide thin films in the microwave frequency range. In 2017, he visited the Department of Materials Science and Engineering at Pennsylvania State University, USA, where he worked on piezoelectric characterization of ferroelectric thin films.

His current research interests include wetting and drying phenomena of inkjet-printed patterns, developing materials for novel nanotechnology devices based on solution-derived metal oxides by tailoring the functional performance via morphological and structural modification, and electromechanical characterization of piezoelectric thin films.

Awards:

- The award for the best presentation at the 9th Jožef Stefan International Postgraduate School Students' Conference, Ljubljana, 2017.
- The award for the best contribution at the 25th International Conference on Materials and Technology, Portorož, 2017.