Design of UV-crosslinked polymeric thin layers for encapsulation of piezoelectric ZnO nanowires for pressure-based fingerprint sensors†


The demand for biometric identification, and more particularly fingerprint recognition, has significantly increased in recent years in domains such as national security, controlled access to health care, banking and leisure. Typical resolution of current fingerprint sensors constitutes 500 dpi, which conforms to the FBI standard for the detection of level 1 (pattern) and level 2 (minutiae) features. However, at least 1000 dpi is required to extract the tiniest level 3 features such as shape of pores and ridge edges. To address an increasing need for the highest reliability in fingerprint identification, this work presents the elaboration of a specific encapsulation polymeric layer for a new design of a pressure sensor which is expected to provide higher resolution and minimal volume occupation compared to already existing setups. The sensor comprises a periodic array of individually contacted piezoelectric ZnO nanowires (NWs), which generate piezopotentials when deformed (each electrically addressable NW constitutes a pressure-sensitive pixel). Fragile NWs cannot undergo direct contact with the finger, therefore a polymeric encapsulation layer is required to simultaneously provide physical protection and to transfer the force from the finger to the NWs. To ensure sensor robustness, the polymeric layer must also exhibit appropriate chemical inertness, and water- and oil-repellency. To achieve this aim, novel formulations of UV-crosslinkable polymeric materials were developed, prepared and deposited as thin layers on the NWs using spin-coating by following the recommendations derived from numerical simulations. An ideal balance between polymer formulation processability and final thin layer’s characteristics (Young’s modulus, thickness) was identified. The resulting encapsulation layer was proved to properly protect the piezoelectric ZnO nanowires from breaking under pressure forces and from being contaminated with external impurities while enabling successful collection of electrical signals in a bottom–bottom contacted NW configuration.

Introduction

A fingerprint sensor is one of the most powerful tools for biometric identifications since fingerprints are unique to individuals and are unchangeable over time.1,2 A large number of technologies have been developed to capture a 2D image of a fingerprint pattern using optical, capacitive, ultrasonic and thermal sensors.3,4 Because fingerprint authentication is planned to boom in the near future with a market expected to exceed 1.7 billion dollars in 2020,5 important efforts were dedicated in the last decade to increase the reliability of the fingerprint reading by reaching a resolution of over 1000 dpi.6 Even though some of these emerging fingerprint technologies attained this level of detection, 3D recognition of the fingerprint pattern could not be achieved simultaneously. A new architecture of the pressure-based fingerprint sensor is being...
implemented to achieve at the same time ultra-high resolution (over 5000 dpi) and reconstruction of a 3D profile of the fingerprint, with a minimal volume occupation for integration into built-in systems. This study focuses on the design of a suitable encapsulation polymeric material that is required for this new sensor configuration.

For decades, polymeric materials have been applied for the protection of integrated circuits or the encapsulation of optoelectronic devices. Indeed, the miniaturization of devices, the exponential increase of components per chip as well as the need for low-cost materials promoted the use of polymers to protect the chip from external damage and contaminations.7,8 Such polymeric materials have also been used to prevent penetration of moisture and oxygen since optoelectronic devices are very sensitive to ambient water vapor and oxygen gases, which induce corrosion effects, film delamination and may ultimately lead to premature failure of the whole optoelectronic device.9–13 Apart from the physical protection function and depending on the targeted application, the encapsulation layer must also possess adequate dielectric and mechanical properties.14 High thermal stability, and chemical and solvent resistance are frequently essential as well. The polymers that are traditionally employed for the encapsulation of electronic devices are silicones, epoxy resins or polyimides.8,15 However, even though these common polymeric materials exhibit some of the required properties, they were not suitable for the encapsulation of this new architecture of a multi-NW pressure based fingerprint sensor. Indeed, in addition to acting as a protection layer for the sensor chip components, the polymeric encapsulation layer must also possess an appropriate set of properties which determine how pressure forces are transferred from a finger to the piezoelectric NWs. The considered pressure sensor is composed of a periodic array of individually contacted piezoelectric ZnO NWs, which were synthesized by wet chemical growth through nucleation windows on a ZnO seed layer prepared by pulsed laser deposition.16,17 When subjected to growth through nucleation windows on a ZnO seed layer electric ZnO NWs, which were synthesized by wet chemical finger to the piezoelectric NWs. The considered pressure sensor which determine how pressure forces are transferred from a fingerprint sensor. Indeed, in addition to acting as a protection layer for the sensor chip components, the polymeric encapsulation layer also had to be suitable for industrial microelectronic processes. Liquid deposition by spin-coating was then selected since it enables the production of uniform films with an accurate control of their thicknesses and ensure the polymer to be well-spread over the electronic components.19,20 Photopolymerizable formulation was targeted as well because of the numerous advantages that present UV-curing in terms of production speeds and energy savings.21 To fulfill these prerequisites, a solvent-free UV-crosslinkable formulation was developed.22 The ratio of two bis-functional (macro)monomers, 1,6-hexanediol diacrylate (HdA) and poly(propylene glycol) diacrylate (PPGdA) was adjusted in order to attain the targeted mechanical properties, which were predicted via FE simulations to be the most effective for the application. A calibration of the spin-coating process was also achieved in order to accurately control the thickness of the encapsulation layer according to the specificity of the ZnO NWs. Static electromechanical tests successfully demonstrated that NWs embedded in the encapsulation layer enable the generation of well-defined and reproducible electrical signals upon bending the set-up and therefore validate the proof of concept of this layer as a suitable interface between the finger user and the sensor. Subsequent process developments were pursued in order to impart certain surface properties to the proposed polymeric material including water- and oil-repellency. Such properties were implemented by introducing a new fluorinated additive into the formulations and conferred higher hydrophobicity and oleophobicity than that of the perfluorinated acrylate used in previous work. Such modification of the formulation was intended to improve the resistance of the sensor to external contaminants and thereby, prolong its life-time.

### Experimental

#### Materials

1,6-Hexanedioldiacrylate (HdA) (80%), poly(propylene glycol)-diacrylate (PPGdA), 2-hydroxy-2-methylpropiophenone (Darocure 1173) (97%), acryloyl chloride (97%), triethylamine (≥ 99%), dichloromethane (≥ 99.8%), anhydrous sodium sulfate, and n-hexadecane (≥ 99%), were purchased from Sigma Aldrich and used as received without any further purification. Fluorolink AD 1700 was provided by Solvay and used as it is.

#### Formulations of UV-curable thin layers

Four formulations were prepared by mixing HdA and PPGdA in various weight ratios from 80/20 to 20/80 HdA/PPGdA. Each formulation was prepared according to the following protocol. HdA and PPGdA were first introduced in a glass vial with 3 wt% of the photoinitiator (Darocur 1173) on top of the formulation. The solution was stirred by means of a vortex mixer for 30 seconds at room temperature. The solutions were then deposited by spin-coating for 30 seconds at room temperature with variable rotation speeds (from 2000 rpm to 8000 rpm). Different substrates were used during this study such as structured chips with and without NWs and glass for water/oil contact angle measurements. The samples were then exposed to UV light...
for 120 seconds using a LC6E benchtop conveyor equipped with a F300S UV lamp system from Fusion UV.

Characterizations

$^1$H NMR spectra were obtained using a Bruker Advance 300 (300 MHz) spectrometer equipped with a QNP probe at room temperature. For $^1$H NMR, chemical shifts were referenced to the peak of residual non-deuterated solvents at 7.26 ppm for CDCl$_3$. Thermal analyses were carried out by dynamic mechanical analysis (DMA) on rectangular samples by means of DMA 1 from Mettler Toledo. Uniaxial stretching of samples was performed while heating at a rate of 3 °C min$^{-1}$ from −60 °C to 130 °C, maintaining the frequency at 1 Hz. In order to perform measurements in the linear viscoelastic region, deformation was respectively retained at 0.05%, 0.06%, 0.2% and 0.2% for the materials with the following Hda/PPGdA proportions: 80/20, 60/40, 40/60 and 20/80. Viscosity measurements were performed on a RDDV-I-PRIME Brookfield viscometer with an SC4-21 spindle at 19 °C with a rotational speed of 10 rpm.

Polymer thicknesses were measured by ellipsometry in the spectral range from 0.7 to 3.2 eV. The probed sample area was about 5 × 7 mm$^2$. Confocal spatially resolved micro-reflectance was performed using a custom-made setup in a spectral range from 1.8 to 3.1 eV by using a Xenon lamp as the light source, which was focused onto the sample surface by using an objective. The spot in the micro-reflectance setup had a diameter of about 2–5 μm and thus the patterning of the sample by the metal layer could be neglected here. In both experiments, the thickness of the polymer layer was deduced from a line shape analysis by using the transfer-matrix technique taking into account a layer stack model describing the structure of the sample.

Regarding the electromechanical measurements, nanowire bending tests were achieved using a Smart SPM 1010 (AIST-NT) scanning probe microscope. The lateral force ($F_l$) signal of the applied multimode AFM tip (Multi75E-G, BudgetSensors) was calibrated by another, more compliant contact type reference probe ($k_{ref} = 0.435$ N m$^{-1}$) which was vertically mounted on the AFM stage, i.e. the free end of the cantilever was directed upwards. During the calibration process, the tip of the multimode AFM probe was pressed against the contact mode reference cantilever from its backside, while the AFM stage with the calibrator was moved back and forth along the x-axis in a typical range of $\Delta x = 15$ μm. From the displacement of the reference cantilever the lateral force was calculated ($F_l = k_{ref} \Delta x_{stage}$). Thus, the slope of the recorded $L_d$ vs. $F_l$ curve provides the necessary conversion constant (C) for NW bending measurements. C is characteristic of the combination of the used AFM probe and the instrument. The chip to be tested was glued on a small size chip holder printed circuit board (PCB). 8 selected NW circuits out of 64 were wire-bonded at once and tested using a source measure unit. After mounting the PCB on the AFM and connecting source–drain contacts into the conductive unit of the instrument, NWs were localized by tapping mode. It was followed by a slow descending with a continuous line scan of the tip in contact mode without any feedback. As soon as a lateral force signal was detected, the tip approach was stopped. The selected NW was then bended in a very gentle way from the side of the NW by changing the lateral x position of the sample. By monitoring the $L_d$ signal, the actual bending load ($F_l = C^{-1} L_d$) can be determined. Current–voltage curves were recorded in the range of [−1; +1] V at a current compliance of 100 nA.

Results and discussion

Design and operation of the NW-based pressure sensing array

The architecture of the chip consists of an 8 × 8 matrix of interconnected ZnO NWs, which are grown on the ZnO seed islands separated by 5 μm from each other (Fig. 1). Each NW can be addressed electrically by connecting it individually to the external circuit using a pair of bottom-contacted side electrodes together with the associated signal lines and pads. ZnO nucleation seed islands in the 8 × 8 array are etched and contacted by a pair of Ti/Au metal lines individually using nanolithography. Subsequently, ZnO NWs are grown from the nucleation sites, and finally encapsulated in the polymer (see ESI† Section S1). The fabrication procedure and the detailed analysis are described elsewhere.

It is anticipated that during the actual sensor usage, when a finger with its irregular surface will come in contact with the encapsulated NW array, the resulting pressure load will include not only the vertical force component (dominant), but also the horizontal one. As a consequence, the deformation will propagate in different directions throughout the polymeric layer and, therefore, the NWs will undertake a complex deformation state due to simultaneously acting compression and bending forces. In the case of pure bending, the maximal piezopotential gradient is located near the root of the NW, which is expected to provide an enhanced piezoelectric signal through a pair of metal electrodes.

Fig. 1 Schematic of main successive steps required for the implementation of a NW-based pressure sensing array (a representative portion with only 4 NWs is depicted). (a) Fabrication of the individual conductive circuit elements (yellow) and NW growth islands in a ZnO seed layer deposited on a silicon wafer (pink), (b) wet chemical growth of ZnO NWs (purple), (c) polymer (blue) encapsulation of the chip.
Finite element analysis of the encapsulated ZnO NW array

Performance of the fingerprint capture sensor depends on the ability of piezoelectric NWs, functioning as pressure-sensitive pixels, to produce detectable strain-dependent electrical signals when deformed by an external force. Therefore, mechanical and geometrical properties of the encapsulation layer, serving as an interface between the user finger and the NWs, have a major impact on the characteristics of the force transfer and the consequent charge generation processes, which predetermine the intrinsic sensitivity of the sensor.

Software COMSOL Multiphysics was used to develop a 2-D FE model of the polymer-encapsulated array of ZnO NWs connected to external capacitors (piezo-pixels). The array is composed of 5 vertically aligned piezoelectric transducers of a rectangular cross-section (width: 0.5 μm, length: 2.5–15 μm), which are positioned on ZnO seed islands and are embedded within the dielectric polymer layer (Fig. 2a). The modeled NWs have bottom–bottom electrode configuration, which enables the collection of electrical signals via side electrodes located at the NW root. The encapsulation layer is treated as isotropic and its top boundary is imposed with downward ramp-type load, which imitates the gradual pressing action exerted by a finger. The modeled load scenario represents the case where the array is pressed by a fingertip region corresponding to a ridge edge, i.e. the force is applied above NW1, NW2 and NW3, while the remaining NW4 and NW5 are not directly pressed. Parametric time-dependent simulations were conducted in order to predict the most rational (near-optimal) values of the Young’s modulus $E^*$ and cap height $h_{\text{pol}}$ (thickness of the polymer layer above the NWs), which allow maximizing the average generated voltage $V_a = (V_{\text{NW1}} + V_{\text{NW2}} + V_{\text{NW3}})/3$.

Numerical results in Fig. 2b and c reveal strong dependence of average generated voltage on load orientation, exhibiting a more complex variation of $V_a$ with changing $E^*$ and $h_{\text{pol}}$ when horizontal load component is introduced (Fig. 2c). Opposite $V_a$ variation trends are observed when the NW array is deformed by the purely vertical force and the oblique one. In the latter load case (Fig. 2c), the average voltage output strongly diminishes with the thickening of the polymer cap (at lower $E^*$ values) and for $E^*$ exceeding 0.2 GPa. Meanwhile, in the former case (Fig. 2b) $V_a$ increases slightly with larger $h_{\text{pol}}$ and for $E^* > 0.2$ GPa (the outputs are essentially insensitive to polymer hardening above 0.4 GPa). The presented results suggest that it is difficult to unambiguously determine the near-optimal values of $E^*$ and $h_{\text{pol}}$ since the orientation of applied load during actual sensor usage will vary from user to user. However, it may be realistically assumed that compression force will highly predominate, though it is reasonable to expect at least some contribution of the horizontal load component when the fingerprint sensor will be pressed. Therefore, the safe recommendation for the targeted near-optimal values of polymer Young’s modulus and cap height are within the range of 0.1–0.4 GPa and 2–4 μm, respectively. Consequently, these simulation-based guidelines entail that the implementation of the polymer formulation and the spin-coating process should ensure that both the polymer Young’s modulus and thickness of
the encapsulation layer can be adjusted with sufficiently high accuracy in order to attain the targeted values within the recommended ranges.

In summary, it can be noted that the results of these FE simulations indicate that the relationships between the magnitude of piezoelectric outputs and the input dimensional, material and loading properties are noticeably more complex in the case of an encapsulated array of ZnO NWs with bottom–bottom electrode configuration when compared to the conventional top-bottom NW contacting option.

Tuning the mechanical properties of the UV-crosslinkable formulation

For the reasons mentioned above, the performance of the fingerprint sensor is determined by the mechanical properties of the polymeric encapsulation layer. The formulation of the encapsulation layer corresponds to a mixture of hexanediol diacrylate (HdA) and polypropyleneglycol diacrylate (PPGdA) in the presence of a photoinitiator. The influence of different HdA/PPGdA ratios on the formulation viscosity and on the Young’s modulus of the UV-crosslinked materials was thus evaluated (Fig. 3a). To achieve this aim, various formulations of the two monomers were prepared and UV-cured in parallelepiped silicon molds. Viscosity of each formulation was measured using a Brookfield viscometer. The values of the Young’s modulus ($E^*$, at 25°C) of the corresponding UV-cured materials were determined by means of dynamic mechanical analysis (DMA). Since a solvent-free process was required, it was not possible to reduce the viscosity by adding some solvent into the formulation. Results presented in Fig. 3a clearly demonstrate that the increase of PPGdA content in the formulation is accompanied by a non-linear increase of the viscosity from 10 cP to 105 cP. Since the viscosity varies as a function of PPGdA content, it implies that the layer thicknesses obtained by spin-coating will be different depending on the Hda/PPGdA ratios of the acrylate formulations.

Furthermore, it was proven that the thickness-rotation speed’s profiles obtained using these liquid formulations were consistent with the theory of Emslie et al. (see the ESI† S2.1). For a given spin-coating rotation speed, the formulations with low PPGdA content will conduct to relatively thin layers whereas thicker layers will be obtained by deposition of formulations with higher PPGdA content and therefore higher viscosity (Fig. 3b). For example, the formulation containing 20 wt% of PPGdA with a viscosity of 15 cP provides layer thicknesses within the range of 0.7–2.4 μm depending on the rotation speed, whereas the formulation containing 60 wt% of PPGdA (40 cP) leads to layer thicknesses within the range of 1.2–3 μm. It is important to note here that it was impossible to uniformly spread formulations with PPGdA content higher than 80 wt% on the chips by spin-coating and thus the resulting film thicknesses could not be investigated for these concentrations. Indeed, the formulations were overly viscous to be dripped easily on the substrate and the resulting films were therefore inhomogeneous. As the formulation with 80 wt% of PPGdA was not suitable for the purpose, it was finally decided to use PPGdA content between 20 wt% and 60 wt%. Even though the corresponding formulations were processable by spin-coating, the maximal polymer thickness obtained using these formulations was not sufficient to reach the targeted $h_{pol}$ for NWs higher than 1 μm. Since the NWs grown on the developed chips have a length of about 3.5 μm, a layer-by-layer process was implemented to increase the polymer thickness in order to attain targeted $h_{pol}$.

PPGdA content also has a significant influence on the Young’s modulus of the UV-cured materials. As shown in Fig. 3a, it was clearly observed that an increase of the PPGdA content (from 20 wt% to 80 wt%) results in a decrease of the Young’s modulus ($E^*$ from 0.5 GPa to 0.02 GPa). As expected, increasing the relative amount of high molecular weight macromonomers imparts more flexibility of the polymeric chains to the material, which leads to lower Young’s modulus. Taking into consideration the results provided by FE simulations, the formulations containing 60 wt% and 80 wt% of PPGdA resulted in an overly soft material ($E^* < 0.1$ GPa) whereas the
formulation with 20 wt% of PPGdA led to an excessively rigid material ($E^* = 0.48 \text{ GPa}$). These formulations could not be, for these reasons, used as the encapsulation layer. Finally, UV-cured materials containing 40 wt% of PPGdA exhibited a Young’s modulus of 0.12 GPa, thereby yielding mechanical properties that were in conformance with the near-optimal values predicted by the FE model.

According to these results, the formulation containing 40 wt% of PPGdA was adopted as the most favorable compromise between the targeted mechanical properties ($E^* = 0.12 \text{ GPa}$) and formulation viscosity (25 cP). This formulation was then used for all the subsequent investigations presented in this work.

**Development of the spin-coating deposition process**

As demonstrated by the FE analysis, the polymer cap height ($h_{\text{pol}}$) is one of the key sensor design parameters that strongly influences the magnitude of generated piezoelectric signals. In this case, the recommended $h_{\text{pol}}$ values fall in the range of 2–4 μm which implies that with the length of the NWs being equal to 3.5 μm, the targeted total thickness of the encapsulation layer is in between 5.5 μm and 7.5 μm.

The first objective in the development of the encapsulation layer deposition method consisted of accurately adjusting the spin-coating process to enable fine-tuning of the polymer cap height within the targeted range. Various samples were encapsulated using the selected formulation (containing 40 wt% of PPGdA) and spin-coated at rotation speeds varying from 2000 rpm to 8000 rpm. Then, the encapsulated chips were subjected to different characterizations using micro-reflectance spectroscopy, ellipsometry and scanning electron microscopy (SEM) techniques in order to determine the encapsulation layer thickness (Fig. 4a). The nondestructive nature of the employed optical methods and high spatial resolution of the micro-reflectance analysis were highly advantageous during the measurements of polymer layer thickness. These methods are described in detail in the ESI† Section S2.2.1. It has to be noted that the calibration of the deposited polymer thickness as a function of the rotation speed was performed on structured chips without NWs by using all three measurements techniques. It was expected that the presence of NWs should not modify the distribution of the encapsulation layer thickness as they were grown at the center of the chip in a very small area with respect to the total area subjected to deposition.

As observed previously, experimental results clearly demonstrate that the increase in the rotation speed leads to the reduction of the encapsulation layer thickness. Furthermore, results in Fig. 4a reveal that there is reasonable agreement between the thickness values obtained by means of ellipsometry, micro-reflectance and those determined by SEM. In the case of the SEM-derived thickness values (Fig. 4a), the decrease of thickness due to polymer shrinking during the SEM process had to be taken into account (see the ESI† Section S2.2.2).

The results, presented in Fig. 4a, also show that it was possible to control the polymer layer thickness between 0.2 and 2.5 μm by applying the proper spin-coating conditions. For a NW length of about 3.5 μm, a minimal total polymer thickness of 5.5 μm was required based on the recommendations derived from the simulations. Therefore, further experiments were carried out by employing a layer-by-layer stacking approach in order to achieve the proper thickness of the encapsulation layer.

Encapsulation of chips without NWs was performed via multiple stacking with 1, 4, and 6 layers deposited at 2000 rpm, followed by a UV-curing step in between each layer deposition. In Fig. 4b, the thickness of the multiple layers measured by micro-reflectation at different spatial positions on the chip are presented as a function of the number of polymer layers stacked. The results are similar for the two positions, indicating that the encapsulation layer is uniformly distributed in the central area of the chips where the NWs are located after the growth. It can also be observed that the encapsulation layer thickness increases linearly with the number of polymer layers and total polymer thicknesses up to 17 μm can be obtained. Consequently, this method was demonstrated to be appropriate for attaining the targeted range of polymer cap heights. The second objective of the development of the spin-coating process was to evaluate its ability to achieve proper encapsulation of the NWs. Since the implementation of the fingerprint sensor involves heterogeneous integration, it was important to examine that the encapsulation layer provides adequate physico-chemical compatibility with the different chip components and properly adheres to the inorganic surface. Besides, it had to be verified that after spin-coating, the NWs retained their structural integrity. To achieve this objective, chips with NWs (lengths of 3–3.5 μm) were encapsulated using the
selected formulation so that the NWs were left completely submerged within the polymer (two layers deposited at 2500 rpm were here required). SEM cross-sectional images of the encapsulated chip (see Fig. 4c) reveal that both the selected polymer formulation and the spin-coating process are suitable for the encapsulation of the NWs. Indeed, it is clearly visible that the polymeric material completely covers the surface of the wafer and fully surrounds the NWs. Besides, there are no indications that the encapsulation process degraded the structural integrity of the NWs since their configurations (geometry, orientation and location) were retained after spin-coating. Furthermore, it could be noted that the layer-by-layer stacking process did not cause any interfacial issues since the individual layers are entirely coalesced and the boundary between them is not visible in the image.

NW bending tests

The polymeric encapsulation layer must guarantee the deformation of the ZnO NWs under mechanical pressure so that they deliver a sensor signal. Fig. 5 shows the contacted polycrystalline ZnO NW array before and after polymer coating. In this experiment, a very thin layer of polymer was selected to enable the localization and direct bending of the NW by a probe of atomic force microscopy (AFM).

Static electromechanical tests of the contacted and polymer-coated NWs were carried out in an AFM-based measurement setup by means of the simultaneous monitoring of the lateral force signal and source–drain current as depicted in Fig. 6a. Prior to the actual measurement, the lateral force signal of the AFM probe/instrument system was calibrated by a vertically mounted tip operating in contact mode. The details of the calibration, sample preparation, NW localization, and height adjustment are described in the Experimental section. It was found that the as-grown NWs without polymer protection fracture easily during the test (see the ESI† Section S3). On the other hand, with polymer coating (Fig. 5b) the NWs withstood several bending cycles with a maximum lateral force of about 2 μN without any fracture event, which demonstrates the ability of the polymer to consolidate the NWs at their roots. Moreover, as shown in Fig. 6b, a significant and fairly reproducible change of the non-linear current–voltage characteristic was recorded under the influence of the lateral load ($F_l = 1.1 \text{ μN}$), which validates the force sensing capability of the polymer-coated ZnO NW. Extensive analysis of the different aspects of the NW sensor such as time-domain current monitoring upon application of different lateral force loading cases and bias voltages as well as the underlying physical origin of the signals, are detailed in another paper.17 It was demonstrated that current modulations reproduced the shape of the lateral force modulation, which boded well for grey scale fingerprint sensing. Indeed, instead of binary information corresponding to the relaxed or bent configuration, collected electrical data were proportional to the magnitude of the lateral bending force. Even though mapping of the NW array was not achieved at this stage and the resistance of the NWs at their roots still needed to be improved, these results demonstrated that the polymeric layer developed here was successfully designed to meet the specified goals and validated the proof of concept of a new technology for developing a very high-resolution fingerprint sensor.

Chemical inertness and surface properties

Since the encapsulation layer corresponds to the part of the sensor that is in direct contact with the environment, it must also exhibit other specific properties such as hydrophobicity, oleophobicity and chemical inertness. Indeed, the whole sensor must be resistant to external contaminants, for instance to water, skin grease or cleaning solvents. Because crosslinking reactions are irreversible reactions that lead to thermosetting materials exhibiting a three-dimensional structure, chemical resistance was expected for the developed encapsulation layer. Robustness toward acetone was indeed demonstrated as the polymer did not show any sign of degradation after immersion in acetone for 1 h (see the ESI† Section S4).28

In order to impart oleophobicity and hydrophobicity to a material, fluorinated building-blocks are usually employed because of the distinctive characteristics associated with the C–F bonding chemistry.29,30 Different strategies are described in the literature for introducing these desired properties to the material’s surface, such as surface treatment by chemical grafting,31,32 or self-stratification which is based on the ability of fluoro-compounds to migrate towards the air-interface during film formation.33,34 However, in the latter case, the fluorinated molecules are not chemically linked to the material and are easily removed by accidental scratches or rubbing.

Fig. 6 (a) Schematic of the AFM-based NW bending setup (b) current–voltage curves recorded at subsequent loading cycles. The unloaded and loaded curves indicated an acceptable degree of reproducibility.

![Fig. 5 SEM images of the individually contacted ZnO NWs before (a) and after (b) polymer coating.](image-url)
In order to avoid the release of the additives from the coating, the fluorinated compound chosen in this study was functionalized with acrylate functions and thus, was chemically bound to the polymer network. 35

Several formulations with different ratios of the commercial perfluoropolyether bis-acrylate Fluorolink AD 1700 (FAD) (from 1 to 5 wt%) were prepared in order to evaluate the influence of FAD content on both hydrophobic and oleophobic properties (Fig. 7a). Thin layers were obtained by spin-coating. Contact angle measurements were carried out by means of a simplified experimental setup using drops of deionized water and n-hexadecane, to assess respectively the hydrophobicity and oleophobicity of the encapsulation layer. 36

First, Fig. 7a confirms that the introduction of fluorinated additives is required to provide hydrophobicity and oleophobicity to the encapsulation layer developed in this work. Indeed, the formulation without FAD molecules exhibits a contact angle of 50.6° for water and a flat puddle for hexadecane, characteristic of complete wetting. However, enlarging the content of FAD from 1 to 5 wt% within the formulation results in an increase of both water and hexadecane contact angles. In particular, thin layer containing 5 wt% of FAD exhibits a water contact angle of 106° and an oil contact angle of 65°. In addition, the results demonstrate that even at a low FAD concentration, a high water contact angle is achieved (103.8° at 1 wt% of FAD). However, high oleophobicity requires larger FAD content. The oil contact angle doubles when the FAD content is increased from 1 to 2.5 wt% (33° and 64° respectively).

Finally, the results of this study highlighted that it was possible to introduce high hydrophobicity and oleophobicity to the UV-crosslinked polymeric layers by incorporating small content of FAD into the formulation. Since only a small amount of this commercially available compound was required to yield the required properties, it was assumed that the properties of the encapsulation layer would not be impacted. Thus, this method was demonstrated to be promising for the improvement of the contamination resistance of the whole device.

Conclusions

In this study, a novel polymeric encapsulating material was designed, formulated and practically implemented in order to meet specific operational requirements that are posed for the multi-NW pressure-based fingerprint sensor under development. Based on the results of parametric simulations performed using the FE model of the encapsulated multi-NW array, the near-optimal values of Young's modulus and polymer layer thickness were established with the aim to maximize electrical signals generated by the piezoelectric NWs, which would facilitate the ultra-precise reconstruction of the smallest fingerprint features. The development of the polymeric formulation and its deposition process was undertaken in order to attain the recommended values of these two parameters. To accomplish this aim, UV-crosslinkable formulations with different ratios of HdA/PPGdA were prepared and characterized by means of DMA and viscosimetry. The formulation containing 40 wt% of PPGdA was identified to provide the most favourable combination of physical properties (Young’s modulus of 0.12 GPa and viscosity of 25 cP). The conducted experimental studies demonstrated that the selected formulation was amenable to thin-film deposition by spin-coating and that the proposed chemical composition confers on the polymer the required degree of compatibility both with the ZnO NWs and the associated chip components. It was experimentally verified that the adopted spin-coating process enabled accurate regulation of the encapsulation layer thickness within the targeted range of values. In addition, it was demonstrated that it was possible to achieve adequate hydro-oleophobic characteristics of the polymer surface by incorporating fluorinated acrylate into the formulation. The resulting polymer surface provides enhanced smudge resistance against external conditions such as wet, oily or dirty fingers, which in turn would help in prolonging the service life of the fingerprint sensor. AFM-assisted bending tests accompanied by the electromechanical measurements were performed on polymer-coated ZnO NWs and force-dependent piezoelectrically modulated electrical signals with a sufficient degree of reproducibility were successfully measured. Besides, it was demonstrated that the recollection of these electrical signals was made possible by the presence of the developed UV-crosslinked polymeric material, successfully maintaining the structural integrity of the NWs during multiple bending cycles. This experiment was the first experimental proof-of-concept of an encapsulated bottom–bottom contacted multi-NW pressure-based sensor which could be developed for ultra-high-resolution fingerprint recognition.
Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by EC funding for the FP7 ICT-2013.3.3 project PiezoMAT (611019).

Notes and references

5 M. Boustany, IHS Technology, 2014.