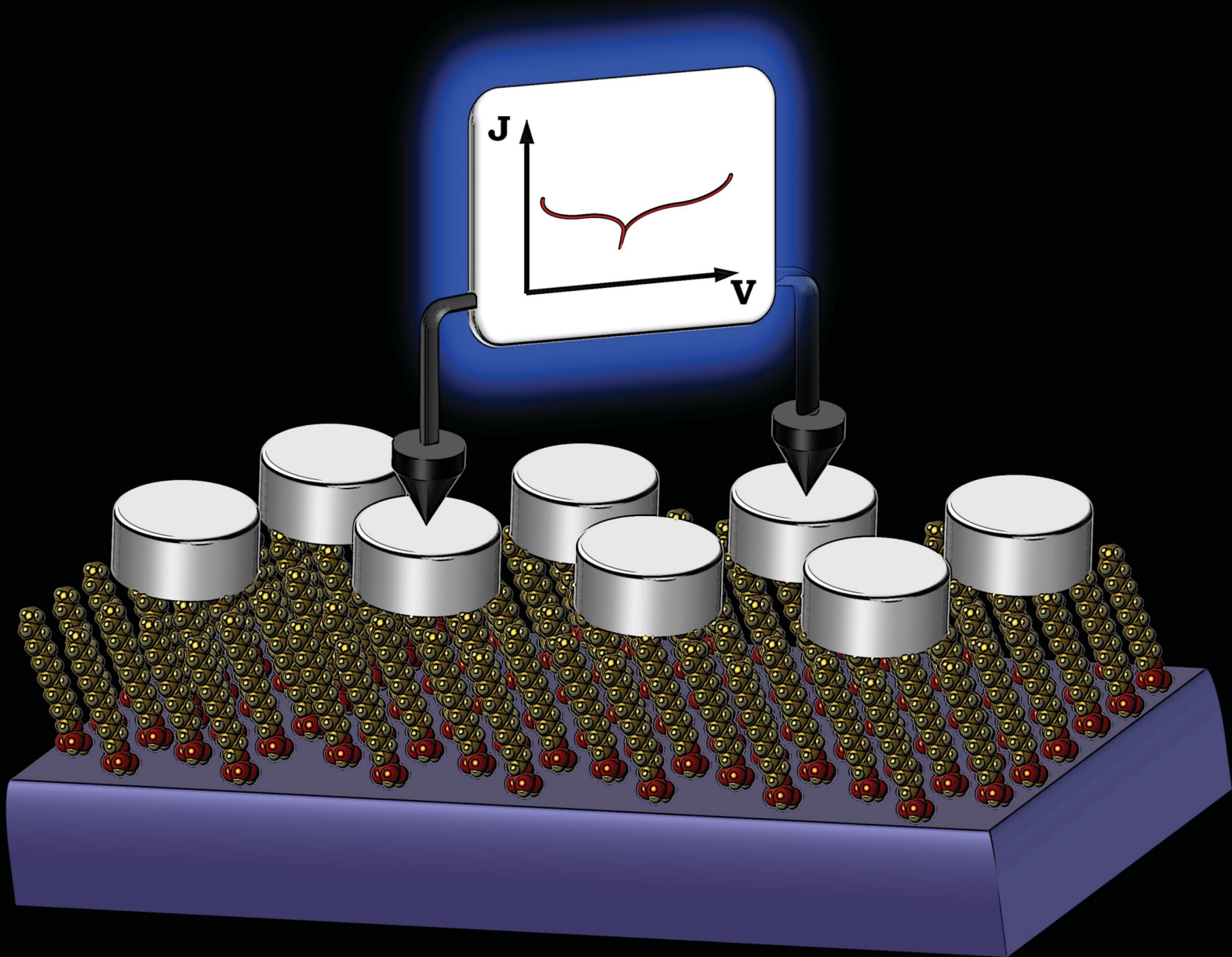


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Dielectric behavior of self-assembled monolayers on conducting metal oxides



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Dielectric behavior of self-assembled monolayers on conducting metal oxides†

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Pt top contacts have been deposited by pulsed laser deposition (PLD) onto bare and tetradecylphosphate (TDP) self-assembled monolayer (SAM)-modified Nb-doped SrTiO₃ (Nb-STO) substrates. For the SAM-modified substrates, electrochemical Cu deposition occurred only at the places where electrical shorts existed between the top contact and the substrate. A nearly perfect yield of top contacts without shorts was obtained, which shows the dense packing and robustness of the SAM. The SAM decreased the leakage current about 500 times compared to the bare substrate. Alkylphosphate SAMs on conducting metal oxide substrates can therefore be used as dielectric thin films for device fabrication.

Introduction

Self-assembled monolayers (SAMs) are being used increasingly in the fields of molecular electronics and nanotechnology.^{1–10} The electronic properties of SAMs have been assessed,^{2,7,8} as well as their use in, for example, organic thin film transistors (OTFTs) and organic field-effect transistors (OFETs).^{11–15} Since SAMs are easily prepared with low cost and have only a few nanometre thickness, which can be tuned by systematic organic synthesis of the constituent adsorbates, they have proven to be excellent candidates for gate dielectrics in organic thin-film transistors.^{2,11,16,17} They can change the electronic properties of the underlying semiconductor substrates and can strongly reduce leakage currents.^{17–19}

The capacity of SAMs to function as dielectric layers has been studied before. However, in most of these studies hybrid dielectric layers composed of a SAM and Al₂O₃ or SiO₂ were used on Al or Si doped bottom electrodes, respectively.^{2,7,8,11,12,15,17,18,20,21} This makes the interpretation of the contribution of the SAM layer difficult.²¹ Here, we use a conducting metal oxide with a SAM as the dielectric layer without using any additional inorganic dielectric layer. SrTiO₃ is an insulator perovskite which becomes an n-type semiconductor or metallic conductor by doping with niobium (Nb).²² In order to use SAMs on such

oxides in electronic or spintronic devices, the dielectric properties of such SAMs need to be studied.

To study the electronic or dielectric properties of SAMs, top contacts need to be prepared. Conventional metal contact deposition methods fail, however, because they damage the thin organic layer and cause electrical short circuits.^{3,14,23,24} Several methods have been developed to avoid shorts such as the use of a Hg droplet as a top contact,^{24,25} the insertion of a conducting polymer layer between SAM and top contact,^{3,23} or the gentle approach of the substrate by a conducting AFM tip.²⁶

Pulsed laser deposition (PLD) has been used as a metal top contact deposition method as well because of its exquisite control of the impact energy by which materials can be deposited. PLD has been applied before for creating metal top contacts on SAMs of alkanethiols on gold, which resulted in a 15% yield of non-shorted top electrodes for an octadecanethiol SAM.¹⁴

Here, we apply the low kinetic energy deposition of metals to create Pt top contacts on alkylphosphate SAMs by PLD. We aim to study the stability of the SAMs in this top contact fabrication method as well as to show the usability of this architecture to assess the dielectric properties of the SAMs. The extent of shorts is assessed by electrodeposition of Cu while the alkylphosphate SAMs on the conducting Nb-STO substrates are characterized by *J–V* measurements using the deposited metal islands as contacts.

Results and discussion

In order to test the dielectric properties of SAM-covered Nb-STO, a SAM of tetradecylphosphoric acid (TDP) (Fig. S1, ESI†) was used as a dielectric barrier layer. As controls, a bare Nb-STO substrate and a substrate covered with a thin inorganic Al₂O₃ dielectric layer deposited by PLD were used (Fig. 1). Pt top contacts were deposited on the samples by PLD through a sieve

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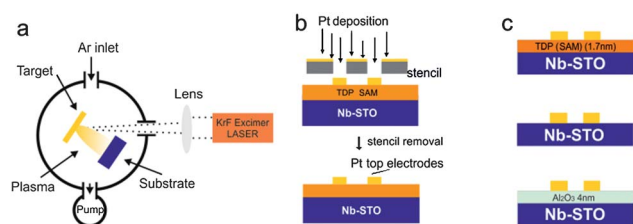


Fig. 1 (a) Schematic picture of the PLD system used. (b) Schematic representation of stencil deposition of Pt top contacts on a TDP SAM-modified Nb-STO substrate. (c) Sample architectures used here: bare, Al_2O_3 -covered and TDP SAM-covered Nb-STO, all with PLD-deposited Pt top contacts.

(stencil). The extent of electrical shorts on these substrates was assessed by electrochemical Cu deposition and the dielectric properties of the layers were investigated by J - V measurements.

Sample preparation

In our previous work, we have shown the detailed characterization of TDP SAMs on alumina which resulted in the successful formation of a homogeneous TDP SAM with a high coverage.²⁷ The height of the TDP features was around 1.5 nm. This is somewhat lower than the extended adsorbate length (2 nm), which indicates a tilt in the SAM layer similar to various alkyl-phosph(on)ate SAMs on metal oxides.^{28–30}

The preparation of monolayer-modified Nb-STO substrates was performed according to literature procedures.^{27–33} Clean Nb-STO substrates were immersed into TDP solutions for two days at room temperature, rinsed afterwards with solvent and dried under a flow of N_2 to yield a SAM-functionalized substrate. By measuring the height of PLD-deposited Al_2O_3 patterns by AFM, deposition rates were determined and the deposition time was adjusted in order to have a 4 nm alumina layer on Nb-STO as one of the control samples.

Basic characterization of the TDP SAM on Nb-STO has been reported by us before.³³ In short, the water contact angle (CA) of oxygen plasma-cleaned Nb-STO was below 10° , which increased to 115° upon coverage with a TDP SAM. The high CA value for TDP indicates a quite hydrophobic surface which confirms the CH_3 termination. Atomic force microscopy (AFM; Fig. S2, ESI†) and scanning tunneling microscopy (STM) confirmed the smoothness of both the Nb-STO and the TDP-covered Nb-STO substrates. XPS measurements on TDP SAM-modified Nb-STO showed that all the expected elements were present on the surface in the expected ratios. Angle-dependent XPS indicated that binding to the surface occurred through the PO_4 headgroup, and indicated a layer thickness of 1.7 nm. In conclusion, the measurements indicate the successful formation of a TDP SAM on Nb-STO.

Pt top contact fabrication and assessment of short-circuits

Here, we used Si_3N_4 membranes embedded in a silicon chip as stencils for the patterned deposition of metals on SAMs by pulsed laser deposition (PLD) as described before.^{14,34} Fig. 1a shows the PLD procedure, in which the Nb-STO substrate is placed parallel to a Pt target.³⁵ The laser hits the target and

creates a plasma of the target material in the presence of Ar background gas with reduced pressure. At low background pressure, the mean free path (mfp) of the ablated species (Pt) is larger than the distance between the target and the substrate, which results in high-energy Pt atoms¹⁴ and thus potentially damages the SAM. When a higher Ar background pressure is used, the mfp of Pt is smaller than the target–substrate distance which results in thermalized and low-energy Pt atoms. This is of high importance in order not to damage the organic thin film.¹⁴ By clamping a stencil on a bare or modified substrate, Pt was deposited only through the stencil apertures, and a Pt top contact pattern was created (Fig. 1b). At low Ar pressure more directional deposition and thus a sharper pattern is expected while at higher background pressure a broadened pattern may be expected.²

Fig. 2a and b and 3a show a TDP SAM-modified Nb-STO surface after Pt deposition. Stencil deposition by PLD created clean, uniform and well-defined Pt patterns with a height of 17 nm. As expected, the edges are somewhat “fuzzy”, indicating gradually lower thicknesses from center to edge of the features, in line with the relatively high Ar background pressure used here to avoid damage to the SAM.

In order to assess the extent of shorts occurring between the substrate and the top contacts, electrodeposition of Cu was attempted. It should be noted that basic SAM characterizations, such as contact angle measurements or XPS, fail in the presence of a top metal layer and can therefore not be used to assess the potential damage to the SAM induced by the PLD step.

Electrodeposition of Cu employs the use of the Nb-STO substrate, immersed in a solution of a Cu^{II} salt, as the working electrode while applying a potential to the electrode that favors Cu^0 deposition. However, only in regions where the substrate is in direct electrical contact with the solution, either *via* defects in

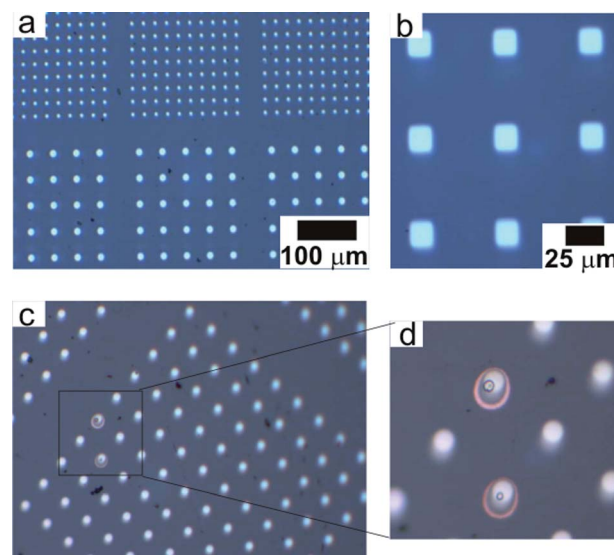


Fig. 2 Optical microscopy images of Pt top contacts on a TDP SAM-modified Nb-STO substrate after stencil deposition by PLD with a relatively high Ar background pressure (a and b) and after subsequent electrodeposition of Cu (c and d), with a zoom-in of a region where Cu growth was observed (d).

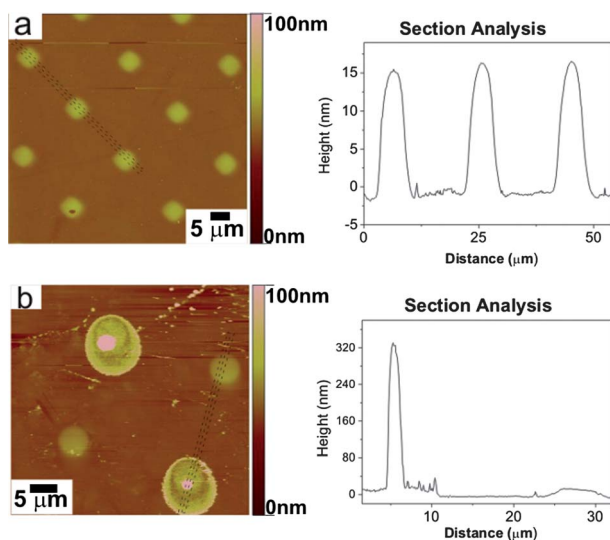


Fig. 3 Atomic force microscopy (AFM) height images, with section analyses, of Pt top contacts on a TDP SAM-modified Nb-STO substrate after stencil deposition by PLD with a relatively high Ar background pressure (a) and after subsequent electrodeposition of Cu (b) focused on a region where Cu growth was observed.

the SAM in the non-Pt-covered areas or *via* shorts in the Pt-covered areas, deposition is expected to occur.¹⁴

Fig. 2c and d and 3b show a Pt-patterned TDP SAM-modified Nb-STO surface after electrodeposition of Cu. Almost all of the features remained unchanged compared to before electrodeposition, which indicates that these Pt top contacts are not connected electrically to the underlying substrate. The few shorted features showed non-uniform Cu deposits of 30–300 nm in height (Fig. 2c and d and 3b). Less than 10 features out of 1000 showed shorts between the top contact and the substrate, as indicated by Cu growth, which indicates a yield of >99%.

Fig. 4 shows the XPS mapping of Pt and Cu on a Pt-patterned TDP SAM-modified Nb-STO surface after the Cu electrodeposition step on the region shown in Fig. 3b. The elemental spectra are shown in Fig. S3†. The red parts representing Cu match well with the elevated parts seen in the AFM (Fig. 3b). Similar to the AFM images, the Pt patterns (green) are much more uniform than the Cu patterns, and these do not contain any Cu.

In summary, optical microscopy, AFM and XPS all confirmed the formation of electrically isolated Pt top contacts on TDP-modified Nb-STO substrates with a near-perfect yield. Similar

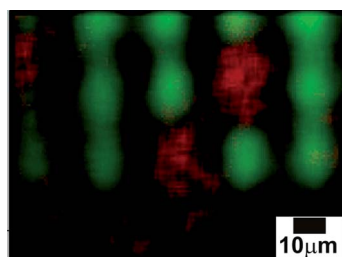


Fig. 4 XPS mapping showing the Pt-rich regions (green) and Cu-rich regions (red) (the resolution in the *x* direction is better than in the *y* direction because of the dispersive properties of the analyzer in the Quantera XPS).

attempts to fabricate Au top contacts on octadecanethiol-modified Au substrates yielded only 15% of isolated islands.¹⁴ The background pressure and sample target distance were similar to the conditions used here. Possible explanations of the higher success rate in our system may be the higher smoothness of the STO compared to the gold surface and a lower diffusivity of PLD-deposited Pt into monolayers compared to Au. Another difference may lie in the much higher resistivity ($\sim 35 \Omega \text{ cm}$) of the Nb-STO used here compared to gold ($\sim 2 \times 10^{-6} \Omega \text{ cm}$).

To investigate whether the low conductivity of Nb-STO could result in less Cu deposition even in the presence of shorts, control experiments were performed. Pt patterns were deposited on bare Nb-STO and on TDP SAM-modified Nb-STO by the same method (PLD, stencil deposition) but under harsher deposition conditions (lower Ar background pressure). Pt patterns after PLD are shown in Fig. 5a and b, and S4a and d†.

Optical images and AFM confirm the growth of Cu on all of the Pt top contacts deposited on bare substrates after electrodeposition (Fig. 5c, S4b and c†). On these substrates, the Pt patterns are in direct contact with the substrate. No Cu growth was observed on the bare substrate regions indicating the need of Pt features as nuclei to facilitate Cu growth. This experiment clearly proves that, if a Pt pattern is in contact with the bottom Nb-STO electrode, Cu growth occurs. In the case of Pt patterns deposited on TDP SAM-modified Nb-STO under relatively harsh deposition conditions, Cu growth was seen on most of the Pt islands after electrodeposition (Fig. 5d, S4e and f†), but Cu granules occurred with a lower density compared to the bare substrates. In this case, the SAM layer still acts as a barrier

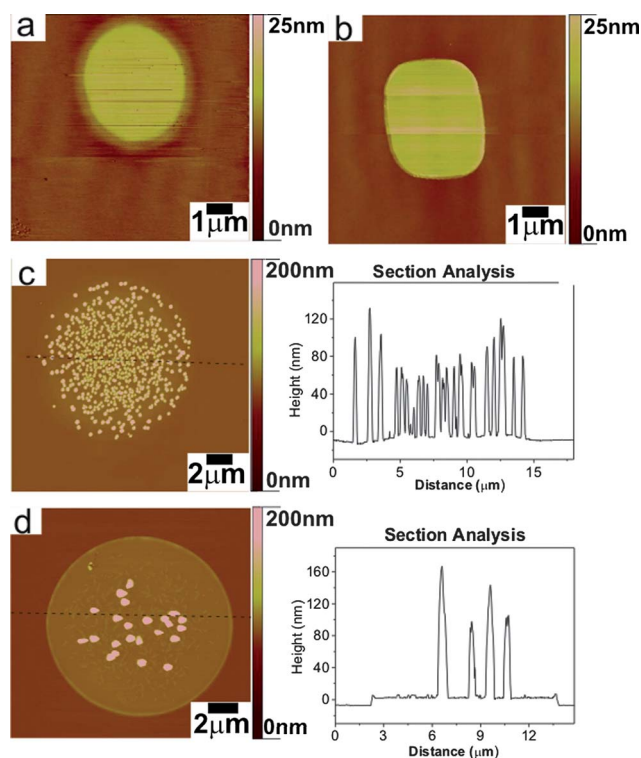


Fig. 5 AFM height images of Pt top contacts prepared by PLD on bare (a and c) and SAM-modified (b and d) Nb-STO substrates before (a and b) and after (c and d) subsequent electrodeposition of Cu.

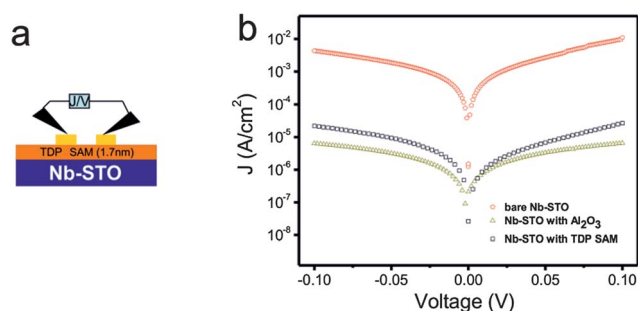


Fig. 6 (a) Schematic illustration of Pt top contacts and top contact-top contact measurement configuration on a TDP SAM-modified Nb-STO substrate. (b) J - V curves of bare, TDP SAM-modified and Al₂O₃-covered Nb-STO substrates measured through neighboring PLD-deposited Pt top contacts.

between the conducting substrate and the top contacts to some extent. In conclusion, deposition at relatively high background pressure enables the fabrication of isolated metal top contacts without damage to the underlying SAM.

Dielectric layers on Nb-STO

In order to assess the dielectric properties of a TDP SAM on the conducting Nb-STO substrate, the Pt PLD method was applied to create metal top contacts. Because of the high yield of the method, as discussed above, top contact-top contact J - V measurements could be performed, as described below, by contacting two neighboring Pt islands with a probe station (Fig. 6a). Pt patterns were deposited at high background pressure on bare and TDP SAM-modified Nb-STO substrates as described above (Fig. 1c). For comparison, Pt was deposited on a bare Nb-STO substrate and on a substrate modified with a thin (4 nm) inorganic dielectric Al₂O₃ layer.

Fig. 6b shows the J - V measurements of the bare and thin layer-modified Nb-STO substrates. The leakage current of the TDP SAM is 2–3 orders of magnitude less than that of the bare Nb-STO substrate. The SAM performs only slightly worse (2–5 times) than the more than twice as thick alumina layer. The nature of contact between the substrate, SAM and Pt, and whether the role of the SAM is purely an insulating layer or also modulating the electronic structure of the junction such as to eliminate the surface states are not known. To determine the electron transport mechanism and the function of the barrier, more experiments should be done, in a wider voltage range, with different SAM thicknesses (by using different adsorbates) and at different temperatures, but this is beyond the scope of the current study. The results presented here do, however, indicate that SAMs on a conducting single crystal metal oxide, while being extremely thin (1.7 nm), are robust and electrically insulating.

Conclusions

Stencil deposition combined with PLD allows creation of many features in a single deposition step. Increasing the background pressure enabled the metal top contact deposition without causing shorts in a near-perfect yield. The yield of non-shorted metal islands was much higher than that obtained for similar experiments on alkanethiol SAMs on gold. It was shown that this

difference is not due to the lower conductivity of the Nb-STO substrate. Electrodeposition of metals is a fast and easy way to check short-circuits of large numbers of top contacts. SAM modification resulted in a strong decrease of the leakage current. Thus alkylphosphate SAMs on conducting metal oxide substrates can be used as dielectric thin films and can withstand fabrication procedures to create metal top contacts.

Experimental

Materials

Polished substrates of (100) 0.5 wt% niobium-doped SrTiO₃ (Nb-STO) (1 × 10 × 10 mm³) were purchased from SurfaceNet GmbH, Germany. These substrates were cut into 5 × 5 mm² pieces with a diamond saw and cleaned by ultrasonication in acetone and ethanol for 30 min each. Tetradecylphosphoric acid (TDP) was supplied by A. Wagenaar and J. Engbersen (RUG, Groningen). The stencils were purchased from C2V (Enschede, NL), and fabricated according to a published procedure.³⁷

SAM formation

Oxygen plasma-cleaned Nb-STO substrates were immersed into a 0.125 mM TDP solution in 100 : 1 v/v hexane : isopropanol for two days at room temperature. Afterwards, the samples were rinsed with the solvent mixture, and dried under a flow of N₂.

Pulsed laser deposition of Pt and alumina

For Pt deposition, a Compex 205 KrF excimer laser of Lambda Physik emitting 25 ns pulses at 248 nm was used. Deposition pressures of 10⁻² mbar to 3 × 10⁻³ mbar were used with argon as the background gas. An argon flow was used from 0.2 to 7.5 ml min⁻¹ depending on the working pressure. A laser fluence of 5 J cm⁻² was used, with a spot size of ~1.95 mm². The laser beam entered the vacuum chamber at an angle of 45° with respect to the target normal. The substrate was placed parallel to the target at a distance of 48 mm. The pulse frequency was 5–10 Hz. The (99.99% pure) Pt target was obtained from Engelhard-CLAL (Drijfhout B.V.), Netherlands.

For alumina deposition, a deposition pressure of 10⁻¹ mbar was used with oxygen as the background gas. A laser fluence of 3 J cm⁻² was used, with a spot size of ~2.8 mm². The laser beam entered the vacuum chamber at an angle of 45° with respect to the target normal. The substrate was placed parallel to the target at a distance of 62 mm. The pulse frequency was 4 Hz.

Electrodeposition of Cu

The substrates after PLD were used as the working electrode and placed in an aqueous solution of CuSO₄ (10 mM) and H₂SO₄ (10 mM) as the electrolyte. A Pt mesh functioned as a counter electrode and a 3 M KCl Ag/AgCl (Radiometer Analytical REF321) reference electrode was used. The deposition was performed with a BANK Electrotechnik POS73 potentiostat. Cu deposition occurred at 0.05 V vs. reference potential at short-circuited islands.

Measurements

Atomic force microscopy (AFM). The morphology of the nanoparticle-covered surfaces was observed by a digital multi-mode Nanoscope III (Digital Instruments, Santa Barbara, CA) scanning force microscope, equipped with a J-scanner. All measurements were done at ambient in tapping mode.

Scanning Tunneling Microscopy (STM). The morphology of SAM modified Nb-STO was observed by an EasyScan 2 STM at ambient and at room temperature.

X-Ray Photoelectron Spectroscopy (XPS). Elemental composition was analyzed by a Physical Electronics Quantera Scanning X-ray Multiprobe instrument, equipped with a monochromatic Al K α X-ray source operated at 1486.7 eV and 25 W. Spectra were referenced to the main C1s peak at 284.80 eV.

Contact angle (CA). Measurements were done with a Krüss G10 goniometer equipped with a CCD camera. Contact angles were determined automatically during growth of the droplet by a drop shape analysis. Milli-Q water (18.4 M Ω cm) was used as a probe liquid.

Electrical measurements. The leakage current density–electric field (J – V) measurements were carried out by applying a dc bias voltage. Measurements of the leakage currents were performed using a Süss MicroTech PM300 Test Systems manual probe station equipped with a Keithley 4200 Semiconductor characterization system (Keithley Instruments GmbH/Germany) addressing the samples in a top contact–top contact configuration.

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