Evidence of electrochemical resistive switching in the hydrated alumina layers of Cu/CuTCNQ/(native AlOx)/Al junctions
Nikolaus Knorr, Ameneh Bamedi, Zoi Karipidou, René Wirtz, Mustafa Sarpasan, Silvia Rosselli, and Gabriele Nelles

Citation: Journal of Applied Physics 114, 124510 (2013); doi: 10.1063/1.4823851
View online: http://dx.doi.org/10.1063/1.4823851
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/114/12?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Bipolar resistive switching characteristics in CuO/ZnO bilayer structure

Mechanism of resistive switching in Cu/AlOx/W nonvolatile memory structures

Electrical resistance switching in Ti added amorphous SiO x
Appl. Phys. Lett. 95, 162105 (2009); 10.1063/1.3243983

Endurance enhancement of Cu-oxide based resistive switching memory with Al top electrode

A comprehensive model for bipolar electrical switching of CuTCNQ memories
Evidence of electrochemical resistive switching in the hydrated alumina layers of Cu/CuTCNQ/(native AlOx)/Al junctions

Nikolaus Knorr,a) Ameneh Bamedi, Zoi Karipidou, René Wirtz, Mustafa Sarpasan, Silvia Rosselli, and Gabriele Nelles

Materials Science Laboratory, Sony Deutschland GmbH, Hedelfinger Strasse 61, D-70327 Stuttgart, Germany

(Received 22 May 2013; accepted 16 September 2013; published online 30 September 2013)

We have investigated bipolar resistive switching of Cu/CuTCNQ/Al cross-junctions in both vacuum and different gas environments. While the generally observed S-shaped I-V hysteresis was reproduced in ambient air, it was reversibly suppressed in well-degassed samples in vacuum and in dry N₂. The OFF-switching currents in ambient air peaked when approximately +2.6 V was applied to the Al electrode at low voltage sweep rates. OFF-switching at constant bias was accelerated in humid and oxygen-rich atmospheres. For unbiased samples stored in air, ON-state (R̂ON) and OFF-state (R̂OFF) resistances increased with time, and R̂ON surpassed the initial R̂OFF after approximately one week. Retention times were enhanced for samples stored in vacuum and those with a larger cross-junction area. We suggest that resistive switching occurs in a hydrated native alumina layer at the CuTCNQ/Al interface that grows in thickness during exposure to ambient humidity; ON-switching by electrochemical metallization of free Al and/or Cu ions and OFF-switching by anodic oxidation of the Al electrode and previously grown metal filaments.

I. INTRODUCTION

In recent years, a large variety of organic materials have been reported to exhibit voltage-driven bistable resistive switching properties that might be suitable for nonvolatile memory applications.1–5 However, the switching mechanisms are not well known, and the switching characteristics often cannot be well reproduced in other laboratories. Naturally, to improve performance and reproducibility, it is essential to find the parameters that are crucial to switching and to elucidate the switching mechanisms. One of the most intensively studied organic memory cell systems is a CuTCNQ film sandwiched between two metal electrodes, where CuTCNQ denotes the charge-transfer complex salt of the electron acceptor 7,7,8,8’-tetracyanoquinodimethane (TCNQ) with the electron donor Cu. Two different CuTCNQ crystal polymorphs have been identified: phase I is needle shaped and has a conductivity of 0.25 S cm⁻¹, and phase II is platelet shaped with a conductivity of 1.3 × 10⁻⁵ S cm⁻¹.6

The first report on reversible resistive switching of CuTCNQ films was published in 1979 by Potember et al.,7 and the principal switching characteristics have been reproduced by different research groups.8–24 The most experience has been gained with the Cu/CuTCNQ/Al layer system in which a layer of CuTCNQ crystals has typically been grown from the Cu bottom electrode and an Al electrode has been evaporated on top.7,9,10,12–14,16–18,21–23 I-V characteristics are of the bipolar S-type,3,25 with a sudden increase in conductance when a negative threshold voltage V̂ON is applied to the Al top electrode (“ON-switching”) and a more gradual decrease in conductivity is observed at the opposite polarity after surpassing a positive voltage V̂OFF (“OFF-switching”). In contrast to “hard” switching, where metal filaments bridge the entire gap between the metal electrodes, neither ON- nor OFF-states are ohmic for “soft” switched junctions investigated here.

The switching was initially ascribed to a reversible phase transition of the bulk semiconducting CuTCNQ material.7 However, V̂ON is not strongly dependent on the thickness of the CuTCNQ layer,9,12,14 and no evidence of switching in the bulk has been found for macroscopic pressed pellets.8 Several reports have suggested that the switching occurs predominantly at the CuTCNQ/Al interface.9,10,14,19,21,22 Impedance measurements indicate the action of mobile charge carriers at low frequencies.9 More recently, it has been proposed that the switching is based on an electrochemical metallization (ECM) mechanism in which the native Al oxide or hydroxide layer at the CuTCNQ/Al interface acts as an electrolyte through which Cu filaments can grow.21,22 However, the role of the oxide/hydroxide layer is under dispute. While several studies have reported the absence of switching for electrodes made of more noble metals,9,18,21 others have observed it, especially for extremely small electrode contacts.15,18,23 In the present study, we investigated the effects of the ambient atmosphere and the size of the junction area on the switching characteristics of Cu/CuTCNQ/Al junctions.

II. EXPERIMENTAL METHODS

Bottom electrodes of a 2 nm Ti adhesion layer (99.99% purity; Umicore) and a 250 nm Cu layer (99.999% purity; Umicore) were deposited by electron beam (e-beam) physical vapor deposition at a rate of 0.3 nm s⁻¹ in a vacuum of 10⁻⁶ mbar through shadow masks with single openings of 100 μm × 8 mm on 1 cm² pieces of Si wafers (p-doped Si with a 400 nm SiO₂ top layer; Silicon Materials). CuTCNQ charge-transfer crystals were grown from the Cu bottom electrodes by a dry solid-gas phase corrosion reaction process.8,9,10,12–14,16–18,21–23 The observations were carried out in a high-vacuum system using a two-electrode configuration of Cu/CuTCNQ/Al (0.7–1.5 μm) cross-junctions.9,10,12–14,16–18,21–23 The biasing voltage was applied to the Al electrode at low voltage sweep rates. OFF-switching at constant bias was accelerated in humid and oxygen-rich atmospheres. For unbiased samples stored in air, ON-state (R̂ON) and OFF-state (R̂OFF) resistances increased with time, and R̂ON surpassed the initial R̂OFF after approximately one week. Retention times were enhanced for samples stored in vacuum and those with a larger cross-junction area. We suggest that resistive switching occurs in a hydrated native alumina layer at the CuTCNQ/Al interface that grows in thickness during exposure to ambient humidity; ON-switching by electrochemical metallization of free Al and/or Cu ions and OFF-switching by anodic oxidation of the Al electrode and previously grown metal filaments.
between the Cu electrodes and hot TCNQ vapour.\textsuperscript{17,18,20,22} The samples were positioned in the center of a hole cut in an Al cup, which was placed on a hot plate. The plate was heated to 205°C, and fresh TCNQ powder (Aldrich) was arranged circumferentially around the sample inside the Al cup. The cup and sample were then covered with a glass bowl (10 cm in diameter) to prevent air convection and improve temperature stability. The glass bowl rapidly filled with green TCNQ vapor, and the Cu electrodes turned purple-black in color. A reaction time of 10 min was long enough to ensure homogenous CuTCNQ crystal growth and short enough to avoid consumption of a major fraction of the Cu electrode.

Top electrodes of Al (400 nm thick; 99.9% purity; Umicore) were e-beam evaporated on top of and perpendicular to the Cu/CuTCNQ electrodes through shadow masks with either eight openings of 100 μm × 8 mm or three openings of 400 μm × 8 mm, yielding eight or three crossed junctions with active areas $A$ of approximately 0.01 mm$^2$ or 0.04 mm$^2$, respectively. The samples were taped into chip carriers (68LCC-1.27 mm-24.11 mm; AAT Aston), and the sample electrodes were connected to the chip carrier electrodes by bonding thin Al wires. The working junction yield was approximately 90%, with ON- and OFF-state junction-to-junction and sample-to-sample resistance variations smaller than a factor of two. Using an e-beam evaporator for the relatively thick Al electrodes was crucial for reproducibility of the switching characteristics. Al evaporation from resistively heated crucibles resulted in reduced working junction yields and frequently strongly increased junction resistances. Additionally, the Al electrode resistances were varied substantially and frequently surpassed 100 kΩ, compared to the approximately 10 Ω resistance of the e-beam electrodes. Apparently, the Al electrodes formed by resistive heated evaporation did not bridge the CuTCNQ crystals well and established electrical contact to only a small fraction of the junction area. Scanning electron microscope (SEM) images were taken with a Carl Zeiss LEO 1530 instrument.

$I$-$V$ curves were obtained at room temperature with an HP 4142B Modular DC Source/Monitor controlled by a PC running LabVIEW software. The bias was applied to the Al top electrodes, while the Cu bottom electrodes were connected to ground. The current compliance was set to 10 mA. The switching characteristics were not well reproduced without current compliance, presumably due to hard switching and material disintegration from resistive heating of the junctions at high currents. The bias of the $I$-$V$ curves shown in Figs. 3 and 4 is the control software bias prior to application of the current compliance, i.e., it is higher than the true junction bias for complied currents. For the current measurements, the samples were either placed in an aluminum box that was filled with ambient air of approximately 30% relative humidity (RH) or flushed with different gases or inserted into a vacuum Dewar (Oxford) pumped to 10$^{-6}$ mbar. N$_2$ gas was moistened to nearly 100% RH by streaming through either deionized water or a 5% H$_2$O$_2$ aqueous solution in a fritted glass aspirator at a low flow rate. Junction resistances $R_{ON}$ and $R_{OFF}$ were determined from voltage ramps to $-0.1$ V. At such low voltages, $I$-$V$ curves were approximately ohmic and no resistance changes of the junctions were caused by the read-out.

### III. RESULTS

Fig. 1 shows SEM images of the top and cross-sectional views of Cu/CuTCNQ/Al junctions. The CuTCNQ crystals were of the needle-shaped type with diameters in the range of 10 nm to 100 nm, with a height of approximately 15 μm. Their structure at the top was highly branched and interconnected,

![SEM images of Cu/CuTCNQ/Al junctions. (a) Top view. Scale bar: 50 μm. (b) Zoom on Cu/CuTCNQ crystals. Scale bar: 1 μm. (c) Zoom on Al covered crystals. Scale bar: 1 μm. (d) Cross-section broken along Al electrode. Scale bar: 5 μm.](image-url)
reminiscent of a neuronal network. The crystals that were coated with Al during Al top electrode evaporation had increased diameters of approximately 200 nm to 400 nm. No continuous layers of Al were formed on top of the CuTCNQ crystals, except for small patches at the edges of the Al electrode areas [Fig. 1(d)].

Fig. 2(a) shows the $I$-$V$ curves of different junctions for a freshly prepared sample in ambient air with $V_{ON} \approx -4$ V and $V_{OFF} \approx +3$ V. $R_{ON} \approx 1$ kΩ and $R_{OFF} \approx 100$ kΩ, where $R_{ON}$ and $R_{OFF}$ are the resistances of the ON- and OFF-states, respectively. The voltage sweep rate ($v = dV/dt$) was 830 mV s$^{-1}$. A value of $V_{OFF} \approx +3$ V has also been observed in Refs. 9, 19, and 23. In particular, the switching characteristics of $V_{ON} \approx -4$ V, $V_{OFF} \approx +3$ V, and $R_{ON} \approx 5$ kΩ reported in Ref. 23, where an e-beam was also used for electrode evaporation, match well with those observed here. However, in that study, the CuTCNQ crystals were grown out of Cu bottom electrodes in a TCNQ electrolyte. In contrast, in Refs. 21 and 22, where no e-beam was used, $R_{ON} \approx 10^{5}$ Ω. While CuTCNQ crystals were grown from a hot gas TCNQ phase in Ref. 22, layers of CuTCNQ were grown by simultaneous vapor deposition of Cu and TCNQ in Ref. 21. All of those studies had comparable junction areas, which were on the order of $10^{-2}$ mm$^2$. The strong variation in $R_{ON}$ among the different studies provides further evidence that the quality of the Al top electrode and its contact to the CuTCNQ layer strongly affect the $I$-$V$ characteristics, while different CuTCNQ layer preparation methods, which yield different crystal sizes,10,12 seem to have no decisive effect.

Fig. 2(b) shows $I$-$V$ curves for the same sample as in Fig. 2(a) after storage in high vacuum for 18 days. Their shapes were strongly modified: almost no hysteresis was observed at negative voltages, and negative currents were as high as or even higher than the ON-state currents for the junctions measured in air. For positive voltages, the hysteresis was shifted to lower voltages and higher currents, with a peak at approximately $+3$ V. Furthermore, the currents increased again at higher voltages, in contrast to the continual drop observed for the junctions measured in air. We observed similar curves for samples that were thoroughly degassed in dry N$_2$.

After subsequent storage of the sample for one week in ambient air, voltage sweeps were applied to the junctions for a third time, yielding $I$-$V$ curves that resemble those of the pristine junctions measured in air, except with an increased $R_{OFF} \approx 500$ kΩ, $V_{ON} \approx -5$ V, and a slightly increased $R_{ON} \approx 1.5$ kΩ. Whereas we ascribe the increase in $R_{ON}$ to repeated cycling [see Fig. 3(a)], we ascribe the increases in $R_{OFF}$ and $V_{ON}$ to the storage time in air, as discussed below. A strong increase in $R_{OFF}$ by orders of magnitude for samples exposed to ambient air for the first time after preparation, without breaking the vacuum, was also reported in Refs. 10, 14, and 22. In Ref. 10, the increase in resistance was also studied after exposure to N$_2$, O$_2$, and H$_2$O vapor. While no strong effect was observed for either N$_2$ or O$_2$, $R_{OFF}$ increased by approximately one order of magnitude after exposure to 3 mbar of H$_2$O for 20 min. In Ref. 23, the disappearance of the hysteresis in vacuum and dry N$_2$ gas and its reappearance in air and O$_2$ gas vapor were reported for Cu/CuTCNQ/Al$_2$O$_3$/Au junctions with 200 nm Al$_2$O$_3$ interlayers evaporated between the CuTCNQ layers and Au top electrodes. However, the $I$-$V$ curves shown in this context seem to be of the hard-switched type.

Fig. 3(a) shows the evolution of the $I$-$V$ curves for immediate repeated cycling. The strong decrease in $R_{OFF}$ in the second and all subsequent voltage sweeps was presumably caused by nanoscopic morphological changes in the switching layer attributable to the formation and only partial subsequent dissolution of metallic filaments during the first sweep.26 As the number of sweeps increased, the currents and the hysteresis at both polarities, particularly the positive polarity, continually decreased. It should be noted that this behavior is in strong contrast to the trends observed in Fig. 2(b) for storage in air versus vacuum, where currents increased and the positive voltage hysteresis was maintained to some degree. Thus, different mechanisms were evidently at work. The mechanism evident in Fig. 3(a) might be related to material fatigue due to electrode corrosion20 and decomposition of the CuTCNQ material.8

Figs. 3(b) and 3(c) show the impact of $v$ on the $I$-$V$ characteristics for different $A$. For $A = 0.01$ mm$^2$ [Fig. 3(b)] in the negative bias range, the ON- and OFF-state currents were not strongly affected by $v$. In the positive bias range, the currents and the hysteresis increased at higher values.
of \( v \). \( V_{\text{OFF}} \), which is defined as the bias where the transition from positive to negative curvature occurs, decreased with increasing \( v \) and reached approximately +2.7 V for \( v = 9.8 \text{ mV s}^{-1} \). For \( A = 0.04 \text{ mm}^2 \) [Fig. 3(c)], negative voltage \( \text{OFF-state currents before switching and ON-state currents were also not strongly affected by } v \). \( V_{\text{ON}} \), however, shifted from approximately −5 V at high \( v \) to approximately −4 V at lower \( v \). The irregular \( \text{ON-switching currents for } v = 9.8 \text{ mV s}^{-1} \) are assumed to reflect the irregular growth of metal filaments.\(^{27}\) The value of \( R_{\text{OFF}} \approx 5 \text{ k}\Omega \) is lower than in Fig. 2(a) because of the previous sweeps and the larger junction size of \( A = 0.04 \text{ mm}^2 \). Interestingly, the value of \( R_{\text{ON}} \approx 1 \text{ k}\Omega \) is comparable to the \( A = 0.01 \text{ mm}^2 \) results. For the \( A = 0.01 \text{ mm}^2 \) sample in the positive voltage range, the currents and the hysteresis increased at higher values of \( v \). Because curvature transitions approximately coincide with current peaks, \( V_{\text{OFF}} \) can be defined by the bias of the peak currents. \( V_{\text{OFF}} \) decreased with increasing \( v \) and reached approximately +2.6 V for \( v = 9.8 \text{ mV s}^{-1} \).

Fig. 4 shows the log-log plots of the retention of \( R_{\text{ON}} \) and \( R_{\text{OFF}} \) in freshly prepared, pristine junctions stored for time \( t \) in air [Figs. 4(a) and 4(c)] and in vacuum [Fig. 4(b)], immediately after switching in air using half-cycle voltage sweeps with the same parameters used in Fig. 2. For samples stored in air with \( A = 0.01 \text{ mm}^2 \) [Fig. 4(a)], \( R_{\text{ON}} \) and its slope in the log-log plot, i.e., the asymptotic power law exponent \( \alpha \), increased continuously with \( t \). \( \alpha \) increased from an initial value of +0.04 to +0.8 and +2.0 for the two different junctions. In contrast, \( R_{\text{OFF}} \) first decreased slightly, with a minimum at \( t \approx 10^3 \text{s} \), and then increased continually at higher \( t \). The value of \( \alpha \) reached approximately +1.0 at \( t = 10^4 \text{s} \). \( R_{\text{ON}} \) surpassed the minimal \( R_{\text{OFF}} \) after approximately \( 10^5 \text{s} \) to \( 10^6 \text{s} \), implying that the bistability of the junctions is semivolatile, with a retention time of about one week. For the \( A = 0.04 \text{ mm}^2 \) sample stored in air [Fig. 4(c)], the retention time was increased to several weeks, due to a higher initial \( R_{\text{OFF}}/R_{\text{ON}} \), as well as a lower \( \alpha \), which reached 0.3 to 0.6 at \( t = 10^6 \text{s} \) for \( R_{\text{ON}} \) and \( R_{\text{OFF}} \). The general trends were the same for the sample stored in vacuum [Fig. 4(b)], with the difference of a reduced \( \alpha \approx 0.2 \).
system as a so called ECM cell, also referred to as Conductive Bridging (CB) cell or Programmable Metalization Cell (PMC) in the literature. ECM rely on electrochemically active electrode metals, the drift of mobile cations in an ion conducting layer, and the discharge of the ions at the counter-electrode leading to a growth of metal dendrites, which form a highly conductive filament in the ON state of the cell. Upon reversal of the polarity of the applied voltage, an electrochemical dissolution of these filaments takes place, resetting the system into the OFF state. The focus of the following discussion is on the nature of the ion conducting layer that is bridged, its behavior under exposure to environmental humidity, as well as the OFF-switching mechanism.

Effects of environmental humidity on resistive switching thin-film devices have recently been studied by several groups. Wu et al. observed that switching in carbon/fluorene/TiO2/Au junctions is completely inhibited in dry atmosphere and concluded that conductance increase is mainly caused by bias induced reduction of hydroxylated TiO2 sites. Knorr et al. observed pronounced current increases for increased ambient humidity in Cu/poly(3-hexylthiophene)/Au junctions and device degradation by crystal formation on the Cu bottom electrode and explained it by electrochemical reactions caused by field-absorbed water in the junctions. Tsuruoka et al. observed an increase in |V_{on/off}| with reduced ambient air pressure in Pt/SiO2/Cu junctions and explained it in terms of varying ion mobility along grain boundaries in the oxide layer by formation of hydrogen-bonded water networks as well as ionization of Cu at the anode interface due to chemical oxidation via residual water in the oxide layer. Tappertzhofer et al. studied the impact of ambient humidity on cyclic voltammetry (CV) currents and electromotive force in Pt/SiO2/Cu junctions. In Off-state junctions, they observed CV Cu oxidation and reductions peaks, strong increase of CV currents with H2O partial pressure, as well as a strong dependence of open-circuit voltages on ion concentrations in the junctions and on H2O partial pressure. They concluded that ambient water is mainly supplying the required counter charge for anodic Cu oxidation by its reduction rather than enhancing ion mobility in SiO2 thin films. Yang et al. observed device degradation and first increased and later on (t > 10^6 s) decreased R_{OFF} with storage time in humid atmosphere of Mo/SiO2/Pt/Pt junctions. In contrast, R_{ON} and V_{on/off} were not strongly affected. They explained the increase in R_{OFF} in terms of moisture penetration via nanoporosity and dielectrophoresis in the films triggering Mo oxidation and SiO2 reduction. Device degradation and deterioration in switching uniformity and retention characteristics were effectively prevented by sealing the junctions with a dense Al2O3 layer.

B. General conclusions from the experimental results

We draw the following conclusions from the experimental observations in Sec. III: The junctions are switched reversely, without the application of bias, from a high resistance state (R_{HRS}) to a low resistance state (R_{LRS}) by removal from the ambient air and thorough degassing in a vacuum or in dry N2 (Fig. 2). Because the negative bias currents in a vacuum [Fig. 2(b)] are comparable to the ON-state currents shown in Fig. 2(a), it is presumably the resistance difference

IV. DISCUSSION

A. Literature results on ambient humidity effects in resistive switching thin-film devices

The metal filament based resistive switching mechanism proposed in Refs. 21 and 22 classifies the Cu/CuTCNQ/Al system as a so called ECM cell, also referred to as Conductive Bridging (CB) cell or Programmable Metalization Cell (PMC) in the literature.

FIG. 5. I(t) decay at +6 V immediately after ON-switching using negative voltage half-cycles in different atmospheres. (a) In dry N2 gas. Red lines: 1st I(t) curves. Black lines: 5th I(t) curves after 4 cycles of ON- and OFF-switching. (b) Black lines: Same as in (a). Colored lines: 7th I(t) curves, after flushing the measurement box with different gases after cycle 5.

at long times and increased retention times, as defined above, of approximately 10^6 to 10^7 s.

Fig. 5 shows the effect of different ambient gases on the OFF-switching currents at constant positive bias. Pristine samples were placed inside a measurement box flushed with dry N2 gas and switched repeatedly ON and OFF. ON-switching was achieved using negative voltage half-cycles with the same parameters as in Fig. 2, and OFF-switching was achieved using a constant applied bias of +6 V for 10^7 s. For the OFF-switching I(t) curves, the currents continually increased from the 1st to the 5th cycle from approximately 0.6 mA to approximately 2 mA at t = 10^6 s; the value of x at long times increased from 0.21 to 0.15 for the same cycles [Fig. 5(a)]. Upon flushing the measurement box with dry O2, moistened N2, or H2O2-moistened N2, the decay of I(t) was accelerated, particularly for H2O2-moistened N2 [Fig. 5(b)]. Whereas x was constant at approximately 0.9 at 10^3 s in H2O and H2O2-moistened N2. The second, not the first, cycles in the changed atmospheres, i.e., the overall 7th cycles, are shown because the junctions needed some operation time to adapt to the new ambience, i.e., the first, cycles in the changed atmospheres, i.e., the overall 7th cycles, are shown because the junctions needed some operation time to adapt to the new ambience. For higher overall 7th cycles, are shown because the junctions needed some operation time to adapt to the new ambience. For higher overall 7th cycles, are shown because the junctions needed some operation time to adapt to the new ambience. For higher overall 7th cycles, are shown because the junctions needed some operation time to adapt to the new ambience.
between the HRS and the LRS that is switched by the applied voltage, i.e., \( R_{\text{ON}} \approx R_{\text{LRS}} \) and \( R_{\text{OFF}} \approx R_{\text{HRS}} \). Therefore, the ON-switching does not occur primarily in the CuTCNQ or in the un-hydrated native aluminium oxide (AlOx) layer because the resistances of the two layers, as present in vacuum, are too low (e.g., the resistance of a bulk 15 \( \mu \text{m} \) thick and 0.01 \( \text{mm}^2 \) large film of phase 1 CuTCNQ is 15 \( \Omega \)), both layers are stable in vacuum (the reaction of metallic Al with oxygen is highly exothermic; neither AlOx nor CuTCNQ has been reported in the literature to decompose in vacuum), and no pronounced switching was observed in vacuum for well-degassed samples [Fig. 2(b)]. This observation also excludes ambient-air-assisted switching of the two layers as present in vacuum. Rather, the switching occurs prevalently in either an additional layer introduced in ambient air or in AlOx or CuTCNQ layers with increased resistance that have been modified in ambient air. We suggest the following mechanisms.

C. Hydration of the native AlOx layer and its growth in a humid atmosphere

The surface of metallic Al electrodes is rapidly oxidized in contact to oxygen, even at very low oxygen partial gas pressures. The reaction is self-limiting and results in complete coverage of a dense AlOx layer of a few nm thickness. When a well-degassed sample with Al electrodes is exposed to ambient air, the dry hygroscopic native AlOx layer rapidly adsorbs several monolayers of water from the ambient, dissociating a fraction of the water molecules.\(^3\) The CuTCNQ layer does not restrict the water adsorption because of its high porosity. With time, the adsorbed water reacts with the outer part of the AlOx layer, forming increasingly hydrated forms of aluminum, such as AlOOH, Al(OH)\(_3\), and alumina gels of higher water content. Possible reactions are as follows: Al\(_2\)O\(_3\) + 3H\(_2\)O \(\rightarrow\) 2AlOOH; Al\(_2\)O\(_3\) + H\(_2\)O \(\rightarrow\) 2AlO\(_2\); and AlOOH + 2H\(_2\)O \(\rightarrow\) Al(OH)\(_3\).\(^3\) Such reactions are well known to occur on Al immersed in water or exposed to humid air and have been studied by X-ray photoelectron spectroscopy and other techniques.\(^3\) The AlOx layer hydration is accompanied by an increase in thickness due to water uptake. The increase of the resistance of the junctions to electronic current flow, as observed in the increase of \( R_{\text{OFF}} \) in Fig. 2(c) relative to Fig. 2(b), can thus be explained by a thickening of the insulating AlOx layer. Thinning of the nonhydroxide fraction of the AlOx layer that faces the metallic Al layer, through the growth of a gelatinous hydroxide layer, reduces its function as a gas and ion barrier; this effect possibly results in further oxidation of the metallic Al and diffusion of Al ions, which become hydrated as they enter the gel.\(^3\) Possible reactions are as follows: 2Al + 1.5O\(_2\) \(\rightarrow\) Al\(_2\)O\(_3\); 2Al + 3H\(_2\)O \(\rightarrow\) Al\(_2\)O\(_3\) + 3 H\(_2\); 2Al + 2 H\(_2\)O \(\rightarrow\) AlOOH + 1.5H\(_2\); Al + 3H\(_2\)O \(\rightarrow\) Al(OH)\(_3\) + 1.5H\(_2\); and 4Al + 3O\(_2\) + 6H\(_2\)O \(\rightarrow\) 4Al(OH)\(_3\).\(^3\) In this way, the resistances of the junctions may continually increase and reach very high values with time as observed in Figs. 4(a) and 4(c).

D. Water loss from the hydrated native AlOx layer in a vacuum

The oxide and hydroxide phases of Al are in hydrothermal equilibrium with each other and differ only by the loss of water.\(^3\) Their equilibrium depends on the temperature and the partial pressures of H\(_2\)O. The phase diagram is not well established because of the low transition rates of the different phases.\(^3\) Low water vapor pressures and high temperatures favor Al\(_2\)O\(_3\), whereas low temperatures and high partial water vapor pressures favor hydroxides. For example, in the final step of the production of alumina in the Bayer process, Al(OH)\(_3\) is calcinated by heating to high temperatures and decomposes to anhydrous Al\(_2\)O\(_3\), giving off water vapor in the process. Similar reactions occur on hydrated Al surfaces, even at room temperature, on a long time scale under a low partial pressure of water vapor.\(^4\) Thus, the reduced \( R_{\text{OFF}} \) values in vacuum, as shown in Fig. 2(b), are presumably caused by the loss of water and the reduction in thickness of the hydrated AlOx layer. Whereas the increase in junction resistance in ambient atmosphere discussed in Sec. IV C might be alternatively explained by extended oxidation of the Al electrode only, which is diffusion limited and has logarithmic time dependence, too, the pronounced and reversible decrease in junction resistance in vacuum excludes this explanation because oxidation of metallic Al is highly exothermic and not reversible.

E. ON-switching: Filament growth in the hydrated native AlOx layer by cathodic metallization of mobile ions

We now address the bias-induced switching mechanisms. Junctions are presumably switched ON at negative bias by ion metallization at the Al cathode, resulting in metal filament growth through the hydrated AlOx layer.\(^2\) It should be noted that not only Cu ions may be involved in the process, as previously proposed,\(^21,22\) Al ions, which are present in large numbers and are comparatively free to move in the hydrated AlOx layer, may also be involved.\(^5\) The hypothesis that the presence of Cu is not necessary for switching is supported by the observation of soft switching in Al/AI0x/Al junctions made by Fisher and Giaever during their famous period of research on tunneling barriers. They found that “at constant voltage, the current increases when the oxidized electrode is negative, and decreases when the oxidized electrode is positive.”\(^54\) Pollack and Morris further studied this effect in 1964.\(^55\) They observed that the retention time of the ON- and OFF-states is approximately 20 min at 300 K; that the ON-switching time increased and the change in conductance decreased at reduced temperature; that ON- and OFF-states could be quenched by cooling to 70 K; and that similar switching characteristics can also be achieved on samples with counter-electrodes of Pb, Cu, and Au, instead of Al. They concluded that “These transient effects are probably related to the ionic transient effects observed in amorphous oxide films except that instead of observing ionic conductance directly, it is the effect of the ionic motion on the barrier parameters and therefore on the tunnel currents that is observed.”

F. OFF-switching by anodic oxidation

The increase in currents and their shift towards higher voltages with \( v \) observed in Figs. 3(b) and 3(c) at positive
bias resembles the typical characteristics of electrochemical CV measurements. In CV, currents increase as the potential reaches the redox potentials of the reactive species present in the electrochemical cell and frequently decrease at higher potentials due to depletion of the reactive species close to the electrode surface. The peak positions are dependent on $\nu$. For example, peak currents are proportional to the square root of $\nu$ if they are limited by the diffusion of species to the electrode surface.\textsuperscript{57} At low voltage sweep rates ($\nu < 10 \text{ mV s}^{-1}$), quasi-steady-state conditions are typically reached, and currents peak at approximately the redox potentials of the reactive species.

The change in curvature from positive to negative for positive voltage ON-state currents in Fig. 3(b) can be interpreted as a transition from current flow dominated by semiconductance of the CuTCNQ layer to current flow increasingly limited by the insulating hydrated AlO$_x$ layer, which is less and less bridged due to electrochemical dissolution of the metal filaments. The effect is even more pronounced in Fig. 3(c), where the observed current peaks are similar to those found in CV, with the difference that the currents are predominantly electronic, rather than ionic. It is difficult to specify the dominant redox reactions occurring at $+2.6 \text{ V}$ because no reference electrode was used and because reactions kinetics are limited by ion diffusion in the hydrated AlO$_x$ layer. Possible anodic half reactions are $\text{Al} + 3\text{OH}^- \rightarrow \text{Al(OH)$_3$} + 3\text{e}^- \quad$ and $\text{2Al} + 9\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}_2\text{O} + 6\text{e}^-$. Water may be catalytically reduced at CuTCNQ and bare Cu surface by the following complementary reactions: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$; $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$; and $6\text{H}_2\text{O}^+ + 6\text{e}^- \rightarrow 3\text{H}_2 + 6\text{H}_2\text{O}$. The enhanced OFF-switching observed in Fig. 5 when ambient water and oxygen are present thus indicates an increased relevance and vapor pressure due to capillary condensation.\textsuperscript{60} Water absorption rapidly filled with liquid water even well below its saturation vapor pressure due to capillary condensation.\textsuperscript{60} Water absorption is further enhanced, also for hydrophobic materials, when high electric fields are present in the porous material; this is because the high dielectric constant of water causes ambient water to be attracted towards places of greatest field density. Depending on the relative humidity and the film thickness and hydrophilicity of the materials, nanometer-spaced gaps are filled by an applied bias of a few V. The effect has been well studied for field-induced water meniscus adsorption at the probe of an atomic force microscope (AFM).\textsuperscript{61–64} It has been employed for the nanoscale anodic oxidation of Si, other semiconductors, and metals, where the AFM probe was used as a cathode and the adsorbed water meniscus provided the electrolyte.\textsuperscript{65} For metal-filament-based switching, as in electrochemical metallization cells, water molecules may be field adsorbed to the extremely high fields present at the apexes of the growing nanoscopic filaments from trace water in the ambient material—even for encapsulated junctions or well-degassed junctions measured in vacuum. The attraction of water to high electric field centers inside a porous material has been referred to as dielectrophoresis\textsuperscript{66,67} in Ref. 33.

A native oxide layer, which is often present in organic thin film devices with easily oxidized metal electrodes such as Al, is therefore under strong hydration pressure and is assumed to contain an ample amount of moisture in biased thin film junctions with access to ambient humidity, especially when additional porous films are present, or small electrode areas have been used so that moisture can penetrate form the lateral sides. These criteria are met for the Cu/ CuTCNQ/Al junctions studied here. In Ref. 23, where sharp metal tips were used to contact Cu/CuTCNQ layers in ambient air, field-adsorbed water menisci may have promoted local oxidation and hydration even for more noble metals due to the high electric fields at the pointed probes. Indeed, the $V_{\text{OFF}}$ of $-1.8 \text{ V}$ for Pt, $-1.2 \text{ V}$ for Au, $+2.8 \text{ V}$ for Cu, $+1.4 \text{ V}$ for In, and $+3 \text{ V}$ for Al observed in Ref. 23 for the pressed probe measurements are to some degree, with the exception of Cu, correlated to the half reaction potentials of the metals under, for example, acidic conditions (e.g., $\text{Au} \rightarrow \text{Au}^+ + \text{e}^- \quad$ with $-1.7 \text{ V}; \quad \text{Pt} \rightarrow \text{Pt}^2+ + 2\text{e}^- \quad$ with $-1.2 \text{ V}; \quad \text{Cu} \rightarrow \text{Cu}^+ + \text{e}^- \quad$ with $-0.5 \text{ V}; \quad \text{In} \rightarrow \text{In}^{3+} + 3\text{e}^- \quad$ with $+0.3 \text{ V}; \quad \text{and Al} \rightarrow \text{Al}^{3+} + 3\text{e}^- \quad$ with $+1.7 \text{ V}$).\textsuperscript{68}

**G. Field-adsorption of water**

Finally, we would like to emphasize the relevance of capillary condensation and field absorption of water to the operation of thin film devices in general and resistive switching devices in particular.\textsuperscript{31} When some degree of porosity, such as the voids in amorphous polymers or metal oxides,\textsuperscript{35} is present in thin films, the pore space in any hydrophilic materials is rapidly filled with liquid water even well below its saturation vapor pressure due to capillary condensation.\textsuperscript{60} Water absorption is further enhanced, also for hydrophobic materials, when high electric fields are present in the porous material; this is because the high dielectric constant of water causes ambient water to be attracted towards places of greater field density. Depending on the relative humidity and the film thickness and hydrophilicity of the materials, nanometer-spaced gaps are filled by an applied bias of a few V. The effect has been well studied for field-induced water meniscus adsorption at the probe of an atomic force microscope (AFM).\textsuperscript{61–64} It has been employed for the nanoscale anodic oxidation of Si, other semiconductors, and metals, where the AFM probe was used as a cathode and the adsorbed water meniscus provided the electrolyte.\textsuperscript{65} For metal-filament-based switching, as in electrochemical metallization cells, water molecules may be field adsorbed to the extremely high fields present at the apexes of the growing nanoscopic filaments from trace water in the ambient material—even for encapsulated junctions or well-degassed junctions measured in vacuum. The attraction of water to high electric field centers inside a porous material has been referred to as dielectrophoresis\textsuperscript{66,67} in Ref. 33.

A native oxide layer, which is often present in organic thin film devices with easily oxidized metal electrodes such as Al, is therefore under strong hydration pressure and is assumed to contain an ample amount of moisture in biased thin film junctions with access to ambient humidity, especially when additional porous films are present, or small electrode areas have been used so that moisture can penetrate form the lateral sides. These criteria are met for the Cu/ CuTCNQ/Al junctions studied here. In Ref. 23, where sharp metal tips were used to contact Cu/CuTCNQ layers in ambient air, field-adsorbed water menisci may have promoted local oxidation and hydration even for more noble metals due to the high electric fields at the pointed probes. Indeed, the $V_{\text{OFF}}$ of $-1.8 \text{ V}$ for Pt, $-1.2 \text{ V}$ for Au, $+2.8 \text{ V}$ for Cu, $+1.4 \text{ V}$ for In, and $+3 \text{ V}$ for Al observed in Ref. 23 for the pressed probe measurements are to some degree, with the exception of Cu, correlated to the half reaction potentials of the metals under, for example, acidic conditions (e.g., $\text{Au} \rightarrow \text{Au}^+ + \text{e}^- \quad$ with $-1.7 \text{ V}; \quad \text{Pt} \rightarrow \text{Pt}^2+ + 2\text{e}^- \quad$ with $-1.2 \text{ V}; \quad \text{Cu} \rightarrow \text{Cu}^+ + \text{e}^- \quad$ with $-0.5 \text{ V}; \quad \text{In} \rightarrow \text{In}^{3+} + 3\text{e}^- \quad$ with $+0.3 \text{ V}; \quad \text{and Al} \rightarrow \text{Al}^{3+} + 3\text{e}^- \quad$ with $+1.7 \text{ V}$).\textsuperscript{68}

**V. CONCLUSION**

In conclusion, a hydrated AlO$_x$ layer was shown to be a previously poorly identified ion conducting layer in which redox reactions causing reversible bipolar resistive switching can take place. This interpretation supports the recent suggestion in Ref. 69 that S-shaped switching is often caused by ambient-water-assisted redox reactions. From an applied point of view, the results presented here introduce a trade-off in the performance of the bipolar memory cell under study: while retention times are increased in dry conditions and for larger electrodes, the ON/OFF conductance ratios and the storage densities, respectively, are reduced. Further improvement in performance may be achieved by further elucidating the relevance of the CuTCNQ layer to switching mechanisms. Although Cu:TCNQ crystals may not necessarily be chemically involved in the redox-reactions during switching, they presumably can support switching because of several crucial properties. These include their high porosity, enabling good access of ambient water and oxygen to the interior of the junctions; their open three-dimensional network structure, increasing the interfacial CuTCNQ/Al area; their limited conductance, acting as a series resistor that limits
current flow during ON-switching; their small size and spikiness, catalyzing chemical reactions by providing high local electric fields and nucleation centers for gas formation; and their elasticity, acting as “moving electrodes”—as utilized in Al/air batteries—and maintaining electrical contact with the Al electrode, even at an advanced stage of corrosion.

ACKNOWLEDGMENTS

The authors acknowledge the valuable suggestions on electrochemical reactions provided by Bill Ford.