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On the origin of bistable resistive switching in metal organic charge transfer complex memory cells

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Electrical characteristics of Cu:tetracyanoquinodimethane (TCNQ) devices with different electrodes were studied. The comparison of impedance spectroscopic measurements on devices with Al and Pt top electrodes proved the existence of a high resistive interface layer between Cu:TCNQ and Al. An equivalent circuit was modeled and the resulting values suggest that the interface layer is composed of naturally formed aluminum oxide. Devices with deliberately formed aluminum oxide and without Cu:TCNQ were fabricated and revealed a similar behavior. The authors propose that the switching effect in Cu:TCNQ thin film devices is a Cu ion based electrochemical effect occurring in a thin aluminum oxide layer. © 2007 American Institute of Physics. [DOI: 10.1063/1.2772191]

Resistive switching materials are promising for future high-density nonvolatile memory applications with good downscaling potential.¹ A lot of different organic material systems have been proposed for use in nonvolatile memories.² Here, we report on the bistable switching phenomena in charge transfer complex thin films consisting of copper as metal donor and tetracyanoquinodimethane (TCNQ) as organic acceptor. Potember *et al.* first reported electrical field induced resistive switching effects in Cu:TCNQ thin films sandwiched between copper and aluminum electrodes.³

Since then, several groups have observed this switching effect, however, often with different characteristics. Different theories have been proposed while the underlying mechanism is still not clear. Potember *et al.* postulated that a field induced solid-state reversible phase transition is responsible for this effect.³ The low impedance in the on state was attributed to an electrical field induced creation of neutral TCNQ.⁴ Gu *et al.* later expanded this theory by using a one dimensional model for overlapping donor and acceptor stacks in the crystalline structure.⁵ Heintz *et al.* showed the existence of two stable structural forms of Cu:TCNQ with distinctive different conductivities.⁶ Some other studies proposed interface effects to be responsible for the resistive switching effect.^{7,8}

In the present study, we conducted dedicated control experiments and impedance spectroscopical studies in order to elucidate the role of the TCNQ and the nature of the underlying switching effect. The studied devices were constructed as simple capacitorlike structures. Different bottom electrode materials were deposited on oxidized silicon wafer substrates with thin NiCr adhesion layers. The Cu:TCNQ thin films were prepared by a physical vapor deposition (PVD) process in a high vacuum chamber. By means of a thermal evaporation technique, Cu and TCNQ were simultaneously deposited with a ratio of 1:1. This PVD method has the advantage that Cu:TCNQ layers can be deposited on any bottom electrode material. Finally, a shadow mask with circular openings of

75 μm diameter was used to define the top electrode. More details on the deposition process are discussed elsewhere.⁹ Scanning electron microscopy on samples prepared by the simultaneous PVD process displayed dense and uniform Cu:TCNQ layers. These results were reproducible for the examined film thicknesses (30–300 nm). Infrared and UV-vis spectroscopic measurements were in good agreement to previously published results¹⁰ and confirmed the formation of a charge transfer complex. X-ray diffraction measurements on all samples revealed an amorphous structure of the Cu:TCNQ thin films.

All presented electrical measurements were made under ambient conditions until otherwise stated. The current-voltage (*I-V*) characteristics were measured with a Keithley 2410 sourcemeter. The impedance spectra in the frequency domain (100 Hz–10 MHz) were measured at zero dc bias with a voltage oscillation amplitude of 50 mV using a HP 4194A impedance analyzer.

Samples with identical Cu:TCNQ thin films with a thickness of 200 nm and varying electrode materials (Cu, Al, Au, Pt) were electrically characterized. The different devices showed strongly diverse behavior depending on the electrode materials. Memory cells with aluminum top electrodes generally display the lowest conductivity in the pristine and the off state of all tested setups. Resistive switching could be observed in combination with any of the tested bottom electrode materials. Memory cells with a Cu bottom electrode and an Al top electrode exhibited the most stable and reproducible behavior. This is also by far the most common electrode setup published in literature. A typical *I-V* curve for such a memory cell is shown in Fig. 1(a). Samples with other bottom electrode materials display qualitatively comparable characteristics. All samples were initially in the high resistive state (HRS) and display a bipolar switching behavior. By application of a more negative voltage than the threshold voltage ($V_{\text{th,off-on}}$) to the Al top electrode the memory cell was switched abruptly to the low resistive state (LRS). The memory cell could be switched back by application of a positive voltage greater than $V_{\text{th,off-on}}$. The ratio HRS/LRS is between 100 and 1000. Both conductance states display a

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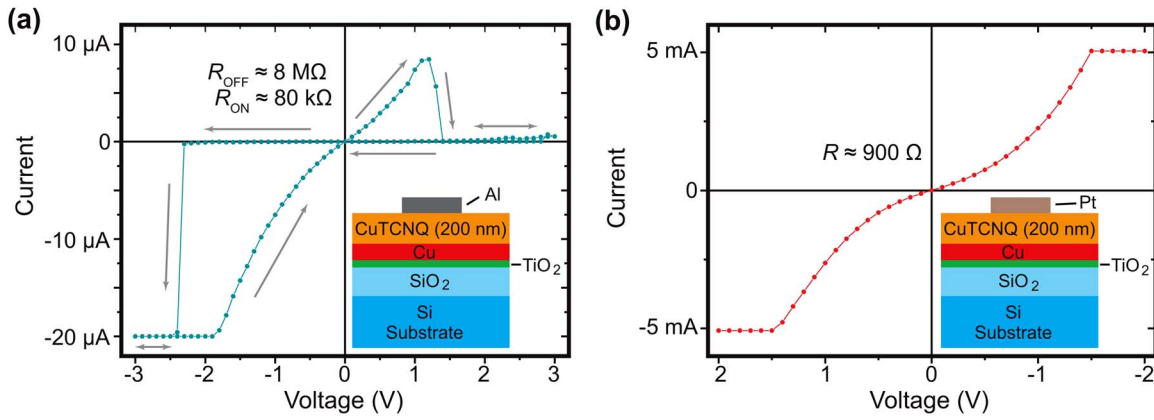


FIG. 1. (Color online) I - V characteristics for different electrode setups. (a) Sample with Cu bottom electrode (BE) and Al top electrode (TE). Current compliance (CC) set to 20 μ A. (b) Sample with Cu BE and Pt TE. CC set to 5 mA.

nonlinear current-voltage behavior with an approximately exponential characteristic. Measurements on devices with an inverse setup (Al/Cu:TCNQ/Cu) confirmed the polarity dependence (on switching: positive voltage applied to Cu electrode). Memory cells with noble metal top electrodes generally display completely different characteristics with an order of magnitudes higher conductivity. Samples with Au top electrodes were all in an extreme low resistance state (a few ohms). We attribute this to the migration of Au atoms during the top electrode evaporation process. A typical I - V curve for a sample with Cu bottom electrode and Pt top electrode is shown in Fig. 1(b). The conductance is at least 50 times better than the LRS of devices with Al top electrode and hence in better accordance to results published by Melby *et al.* on bulk Cu:TCNQ.¹¹ He observed semiconducting properties with low resistivity values on synthesized Cu:TCNQ bulk crystals. Samples with other bottom electrode materials display comparable characteristics. Temperature-dependent measurements revealed that the conductance behavior is thermally activated. The experiments with different electrode materials indicate that in the examined devices with Al top electrodes the resistance is dominated by the interface to the top electrode.

In order to further examine the interface properties, impedance spectra of the test structures were recorded on devices with top electrode areas of 0.018 mm². The thin film impedance (Z_{TF}) of samples shown in the inset of Fig. 1(b) can be described by a simple equivalent circuit consisting of

a parallel connection of a capacitance (C_{TF}) and a resistance (R_{TF}),

$$Z_{TF} = \frac{R_{TF}}{1 + \omega^2 R_{TF}^2 C_{TF}^2} - j \frac{\omega R_{TF}^2 C_{TF}}{1 + \omega^2 R_{TF}^2 C_{TF}^2}. \quad (1)$$

With the assumption of a simple parallel plate capacitor the measurements result in a dielectric constant of $\epsilon_r = 1.26$. The resistivity calculates to $\rho \approx 20 \Omega \text{ m}$ with linear assumption. Measurements on identical samples with the only difference being the top electrode material, Al instead of Pt, displayed distinctive different results. The frequency dependence of the real and imaginary part of the impedance is shown in Fig. 2 for the HRS (a) and LRS (b). For this kind of memory cell, we extend the simple model used in Eq. (1) by a second RC element in series with the first one, as shown in the inset of Fig. 2. One such element represents the conducting, homogeneous bulk with the interface to the Cu bottom electrode. In a first approach, we can set the values of this element to the results of the Cu/200 nm Cu:TCNQ/Pt memory cells ($R_{TF} = 1000 \Omega$, $C_{TF} = 2 \times 10^{-12} \text{ F}$). The second element represents the interface to the Al top electrode ($R_{IF,TE}$, $C_{IF,TE}$). For this model, the real and imaginary parts of the impedance can be calculated to

$$\text{Re}\{Z_{\text{model}}\} = \frac{R_{TF}}{1 + \omega^2 R_{TF}^2 C_{TF}^2} + \frac{R_{IF,TE}}{1 + \omega^2 R_{IF,TE}^2 C_{IF,TE}^2}, \quad (2)$$

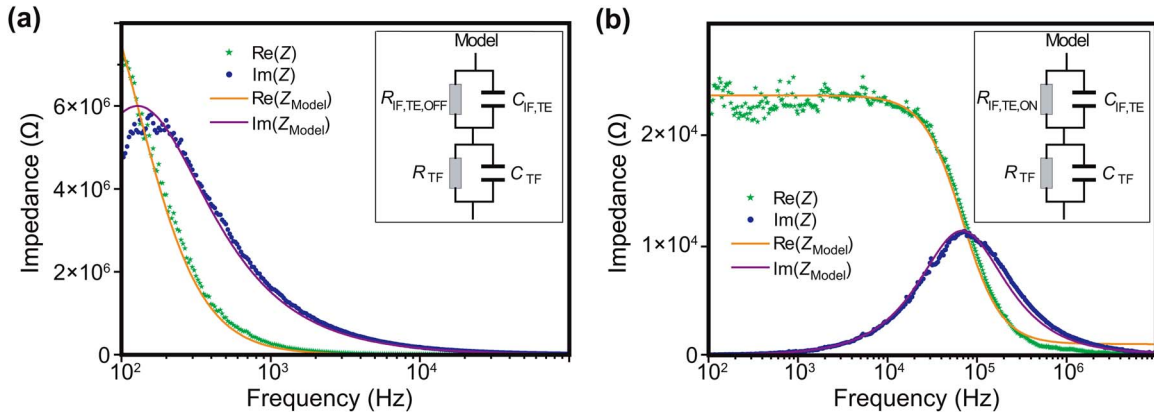


FIG. 2. (Color online) Frequency dependence of the real and imaginary parts of the impedance of a sample with Cu BE, a 200 nm Cu:TCNQ layer, and Al TE. (a) Memory cell in HRS. (b) Memory cell in LRS.

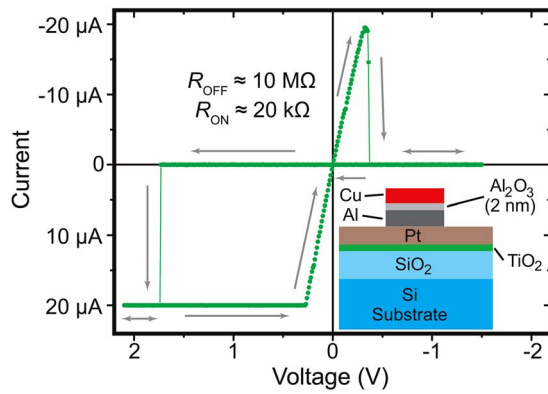


FIG. 3. (Color online) I - V characteristic for a sample with Al BE, a 2 nm thin Al_2O_3 instead of 200 nm Cu:TCNQ, and a Cu TE. CC set to 20 μA .

$$\text{Im}\{Z_{\text{model}}\} = \frac{\omega R_{\text{TF}}^2 C_{\text{TF}}}{1 + \omega^2 R_{\text{TF}}^2 C_{\text{TF}}^2} + \frac{\omega R_{\text{IF,TE}}^2 C_{\text{IF,TE}}}{1 + \omega^2 R_{\text{IF,TE}}^2 C_{\text{IF,TE}}^2}. \quad (3)$$

The fitted curves for both the real and imaginary parts of the impedance are shown in Fig. 2 for HRS (a) and LRS (b). The fitting results in $R_{\text{IF,TE,off}} = 1.2 \times 10^7 \Omega$ for HRS and $R_{\text{IF,TE,on}} = 22.5 \text{ k}\Omega$ for LRS. The value of the capacitance is constant in both states ($C_{\text{IF,TE}} = 1.04 \times 10^{-10} \text{ F}$). Calculated with the assumption of a parallel plate capacitor model, this results in a quotient of $\epsilon_{\text{r,IF,TE}}/d_{\text{IF,TE}} = 0.52 \text{ nm}^{-1}$ for the unknown thickness and dielectric constant of the interface. The result calculates to an interface layer of a few nanometer thickness and a dielectric constant between 1.5 and 3. These values match to an interface layer of naturally oxidized aluminum between Cu:TCNQ and the aluminum top electrode. This Al oxide film may be formed by oxygen adsorbed and entrapped by the Cu:TCNQ layer and the *ex situ* deposition of the Al, which is the typical process of the Cu:TCNQ cells reported in the literature. These results are in good accordance to previously published results on resistive switching in rose bengal molecular devices.¹² The switching in these devices is attributed to the formation of a thin aluminum oxide layer between the top electrode and molecular layer. Cölle *et al.* proposed a similar mechanism for spin-coated polymeric films.¹³

To verify our assumption, we fabricated *in situ* samples without Cu:TCNQ with only a thin ($\approx 2 \text{ nm}$) aluminum oxide film between the electrodes. The aluminum bottom electrode was sputtered through a shadow mask on top of a continuous Pt layer. The surface of the aluminum was then controlled oxidized by UV treatment in oxygen atmosphere (50 mbars). Finally the Cu top electrodes were sputtered. The device setup is shown in the inset of Fig. 3. The current voltage characteristic (Fig. 3) is remarkably similar to the Cu:TCNQ devices [Fig. 1(a)]. Endurance measurements displayed a better switching stability for devices with Cu:TCNQ (≥ 1000 cycles) and a better yield than for samples with only a thin aluminum oxide layer

(≤ 50 cycles). It is important to note that the on switching occurs for a negative voltage polarity applied to the Al electrode in all cases. This is well known for resistively switching electrochemical metallization cells and reflects the drift of Cu ions through the amorphous aluminum oxide layer, the cathodic reduction, and growth of Cu filaments toward the anode.^{14–17} First results of further control experiments with an aqueous solution of CuSO_4 top electrode suggest that aluminum oxide represents the electrolyte which mediates a Cu ion based electrochemical switching.

In conclusion, we confirmed earlier reports^{7,8,13} about the decisive role of a thin interfacial aluminum oxide layer at the Al electrode by these experiments. We supplement this theory by additional experiments which indicate that the switching effect in Cu:TCNQ thin film devices could be a Cu ion based electrochemical effect, i.e., the devices could be described as electrochemical metallization cells, where the aluminum oxide represents the electrolyte. The Cu:TCNQ layer appears to be a suitable spacer, which possibly stabilizes the reversible switching by acting as a Cu ion buffer. However, the TCNQ does not appear to be essential for the switching process.

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