

Resistive switching of rose bengal devices: A molecular effect?

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The resistive switching behavior of devices consisting of aluminum top electrode, molecular layer (rose bengal), and bottom electrode (zinc oxide and indium tin oxide) is examined. By measuring the current versus voltage dependence of these devices for various frequencies and by systematically varying the composition of the device, we show that the switching is an extrinsic effect that is not primarily dependent on the molecular layer. It is shown that the molecular layer is short circuited by filaments of either zinc oxide or aluminum and that the switching effect is due to a thin layer of aluminum oxide at the zinc oxide/aluminum interface. © 2006 American Institute of Physics.

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I. INTRODUCTION

Switching effects in layers of organic molecules have already been known for more than 30 years.^{1,2} Since then a wide variety of molecules such as tetracene,¹ anthracene,² polymethacrylate derivatives,³ phenylene ethynyls (known as Tour wires),^{4–8} bipolar diarylethenes,⁹ copper tetra(butylphenyl)porphyrin,¹⁰ and rotaxane¹¹ have been proposed as basic materials for molecular memories. Recently, layers of rose bengal (see Fig. 1) have been shown to switch resistively with high $R_{\text{off}}/R_{\text{on}}$ values (with R_{off} resistance in the high resistive state and R_{on} resistance in the low resistive state),^{12–16} but the switching mechanism is still under discussion. Possible explanations are a change in the electrical conjugation of the rose bengal molecule by electrochemical reduction,¹⁴ a twist of the upper benzene ring,¹² and the formation and breaking of metallic filaments. Similarly, some changes in the electrodes (e.g., by oxidation) or the interface between the electrode and the molecular film can cause the resistive switching.

To examine the switching behavior in more detail the elements of a rose bengal device are systematically replaced. In particular, current versus voltage (IV) characteristics of devices with different bottom electrodes, without any molecular layer and with a thin layer of aluminum oxide (Al_2O_3) between the top and bottom electrodes are shown.

II. EXPERIMENTAL DETAILS

To obtain layers of rose bengal (see Fig. 1), a solution of 100 mg rose bengal in 50 ml ethanol is spun onto zinc oxide

(ZnO) (doped with 1% Al) or onto indium tin oxide (ITO) bottom electrodes at different rpm resulting in varying film thicknesses (55–143 nm, measured by ellipsometry). For macroscopic measurements, circular aluminum pads (100 nm thick) with contact areas (0.013, 0.028, 0.067, and 0.233 mm²) are evaporated in an e-gun vacuum chamber at a base pressure of 10^{-7} mbar at a deposition rate of 0.1 nm/s.

For IV measurements, the voltage is applied with ZnO or ITO as cathode and the metal top electrode as anode by a voltage source (burstter Digistant 4462) for 2 s prior to current measurements. The applied voltage is increased in 0.1 V steps resulting in a frequency of a few millihertz (maximum voltage of ± 1.5 –2.5 V). High frequency measurements are taken by an Aixacct TF analyzer 2000.

The substrate and rose bengal film morphologies were studied by atomic force microscopy (AFM) in contact mode with Pt/Ir cantilevers employing a JEOL JSPM-4210. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) investigations were performed using the TOF-SIMS IV (ION-TOF GmbH, Muenster, Germany) equipped with a ²⁰⁹Bi ion source. Depth profiles were acquired in the positive as well as in the negative secondary ion mode using 25 kV Bi⁺

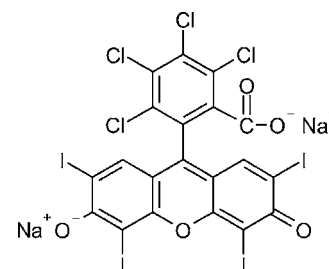


FIG. 1. Molecular structure of rose bengal.

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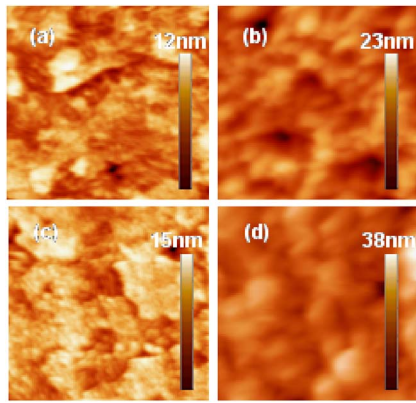


FIG. 2. (Color online) Morphological study of the investigated devices by atomic force microscopy (image sizes of $1 \times 1 \mu\text{m}^2$): (a) ITO substrate (roughness=1.6 nm), (b) ZnO substrate (roughness=3.9 nm), (c) ZnO/70 nm RB (roughness=1.9 nm), and (d) ZnO/143 nm RB/Al (roughness=4.9 nm).

(pulsed and bunched) primary ions for analysis ($150 \times 150 \mu\text{m}^2$) and 0.5 kV Cs^+ ions for sputtering ($300 \times 300 \mu\text{m}^2$).

III. EXPERIMENTAL RESULTS

The surface morphologies of ZnO and ITO, used as bottom electrodes, of rose bengal films spun onto a ZnO substrate, and of the Al top electrodes are shown in Fig. 2. The resulting surface roughness measured by atomic force microscopy on an area of $1 \times 1 \mu\text{m}^2$ is 3.9 nm (rms) for the ZnO and 1.6 nm (rms) for the ITO bottom electrode. The surface roughness of a 70 nm rose bengal film on ZnO is only 1.9 nm, while it increases to 4.9 nm for the deposited aluminum top electrode. These measurements prove that the rose bengal films cover the substrates homogeneously, and the aluminum top electrode is somewhat more uneven than the ZnO or ITO bottom electrode.

Figure 3 shows the *IV* characteristics of rose bengal layers with different thicknesses (143, 70, and 56 nm). The de-

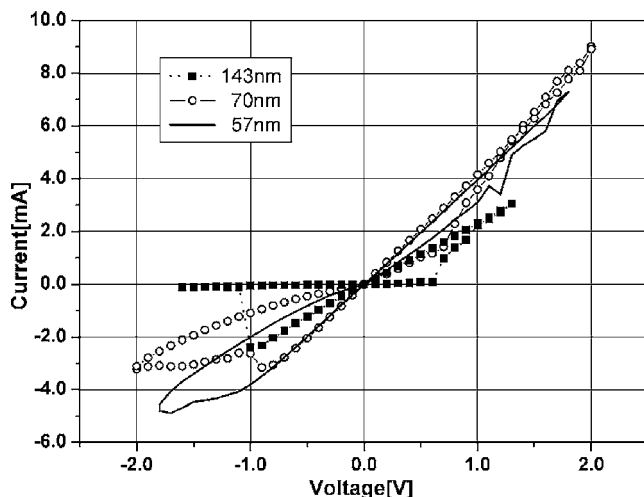


FIG. 3. *IV* characteristic of a layer of the rose bengal (143, 70, and 56 nm) on ZnO. All samples are contacted by an aluminum pads (contact area of 0.0288 mm^2). On switching occurs at positive voltages and off switching at negative values.

TABLE I. Characterization of the devices fabricated in this study.

Device	V_{on} (V)	V_{off} (V)	R_{on} (Ω)	R_{off} (at -0.3 V)	$R_{\text{off}}/R_{\text{on}}$
ZnO/143 nm RB/Al	0.65	-1.0	400	20 k Ω	50
ZnO/70 nm RB/Al	0.7	-1.1	242	1.1 k Ω	4.5
ZnO/56 nm RB/Al	1.0	-1.0	270	396 Ω	1.5
ZnO/143 nm RB/Ti	0.7	-2.0	250	1 k Ω	8
ITO/55 nm RB/Al	0.7	-0.9	412	2.88 k Ω	7
ITO/Al	0.8	-1.0	213	327 Ω	1.5
ZnO/Al	0.7	-1.5	163	200 Ω	1.2
ZnO/2 nm Al_2O_3 /Al	0.7	-1.0	240	400 Ω	1.7
ZnO/5 nm Al_2O_3 /Al	0.7	-1.5	214	1.16 k Ω	5.4

vices (ZnO bottom electrode, rose bengal, and aluminum top electrode) show resistive switching behavior with on switching (i.e., switching from the high resistive to the low resistive state) at positive and off switching (i.e., from the low resistive to the high resistive state) at negative voltages. On switching occurs for all three devices between 0.6 and 1 V and off switching at -1 V. The on state shows a linear *IV* characteristic, whereas the off state deviates from linearity at high voltages. For the ZnO/143 nm rose bengal (RB)/Al device the impedance of the off state is 20 k Ω and for the on state 400 Ω , resulting in a $R_{\text{off}}/R_{\text{on}}$ ratio of 50. Typical $R_{\text{off}}/R_{\text{on}}$ ratios for ZnO/143 nm RB/Al devices are obtained in the range of 2–50. All data (V_{on} , V_{off} , R_{on} , R_{off} , and $R_{\text{off}}/R_{\text{on}}$) for the devices fabricated in this study are summarized in Table I. It can be seen from Fig. 3 and Table I that R_{on} has almost the same value for all thicknesses of the rose bengal layer, while R_{off} increases with increasing layer thickness resulting in a higher $R_{\text{off}}/R_{\text{on}}$ ratio.

Substituting the ZnO bottom electrode by ITO, the switching can be observed as well (shown in Fig. 4). The *IV* characteristics are similar to the devices prepared on ZnO. The $R_{\text{off}}/R_{\text{on}}$ ratio of the device with a rose bengal layer of 55 nm is increased to the corresponding device on ZnO (7 compared to 1.5). This may be a material effect of the ITO bottom electrode, or the lower roughness of ITO allows to build up a more homogeneous and dense rose bengal layer,

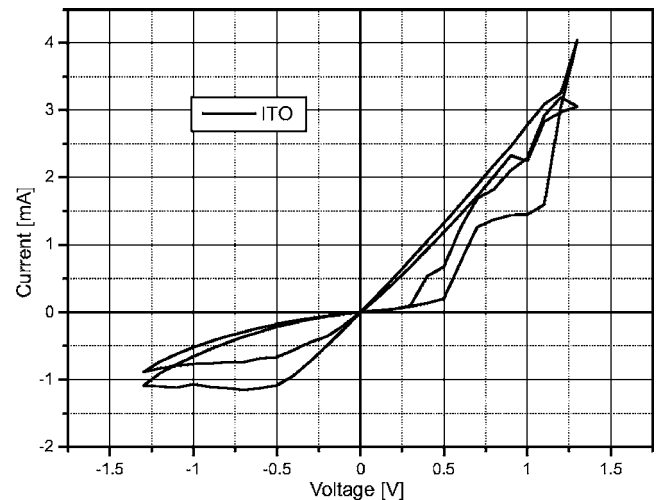


FIG. 4. *IV* characteristic of an ITO/55 nm RB/Al stack showing resistive switching. The contact area is 0.0288 mm^2 .

TABLE II. Frequency dependence of the switching voltages. Above 10 kHz the switching vanished. The device consists of an ITO bottom electrode, 85 nm rose bengal, and an aluminum top electrode (contact area of 0.066 mm²).

Frequency	V_{on} (V)	V_{off} (V)
100 Hz	0.64	-0.85
1 kHz	0.76	-0.8
10 kHz	0.65	-1.0
100 kHz

which is more insulating. Generally, the switching of devices with ZnO and ITO bottom electrodes shows the same distinct features: the on state is linear, whereas the off state deviates from linearity at higher voltages. This switching behavior is similar to the switching behavior of rose bengal devices described by Jakobsson *et al.*¹⁷ but shows significantly larger currents than the switching shown by Bandyopadhyay and Pal.¹³

For later applications, the switching speed of the devices is of fundamental interest. The frequency dependence of the switching voltages is shown in Table II. Up to 10 kHz, there is no significant change in the switching properties. Above 10 kHz the switching vanishes, giving a time constant of approximately 0.1 ms for the switching mechanism. This time constant is surprisingly large, pointing towards a switching mechanism that is not purely electronic.

In literature, the resistive switching behavior of devices of rose bengal is explained by two different conduction states of the rose bengal molecule. However, the low resistance and the linearity of the on state strongly suggest that the molecular layer does not take part in the conduction at all. Conduction in an organic layer would show a characteristic diode behavior that is governed by both charge injection at the electrodes and charge carrier mobilities. Especially, the large currents seen in Figs. 3 and 4 are not compatible with the charge carrier mobilities found in organic materials. Furthermore, the on state resistance does not show a significant dependence on the pad size of the aluminum top contact (pad sizes ranging from 0.013 to 0.233 mm² yield a range of on state resistances of 190–420 Ω). Therefore, Figs. 3 and 4 strongly suggest that, at least in the on state, the organic layer is short circuited, most probably by a metallic filament between the electrodes, so that the switching effect observed here cannot be molecular.

The observation of a short circuit in the on state is more general and does not depend on the top electrode material. When the aluminum top electrode is substituted by a titanium top electrode (Fig. 5), the same low resistance and linearity of the on state as for the aluminum top electrode are observed. However, a pronounced difference in switching voltages is observed. The off switching occurs for the ZnO/143 nm RB/Ti device in the range of -2 to -1.5 V in contrast to $V_{\text{off}} = -1$ V for a device with an Al top electrode. In Fig. 5 multiple cycles of resistive switching are shown, and the variations from cycle to cycle found for this device are comparable to the other devices of this study.

Furthermore, the aluminum top electrode is replaced by a gold electrode. As for the other metals, all devices with

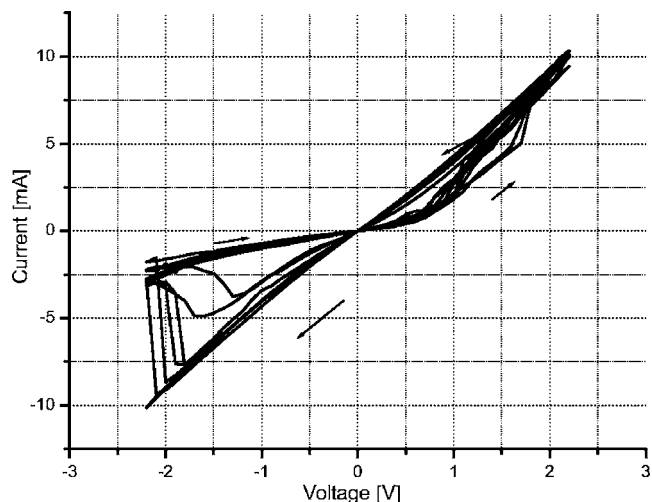


FIG. 5. *IV* characteristic of a ZnO/143 nm RB/Ti stack showing multiple cycles of resistive switching. The contact area is 0.0288 mm².

gold top electrodes (ZnO/140 nm RB/Au) prepared by either sputtering or evaporation techniques were short circuited, probably due to the migration of gold into the RB layer. Even with Au top electrodes prepared by microcontact printing, a method especially suitable for thin molecular films, the devices were short circuited showing a R_{on} of 150 Ω , comparable to the series resistance of our setup. But what is even more interesting in these devices is the absence of the switching effect. The *IV* characteristic of these gold top electrode devices always display a linear, Ohmic behavior without any switching to a higher insulating state. From these experiments it can be concluded that in the on state the molecular layer is short circuited for various top electrode materials. Furthermore, the occurrence of the off state and the switching effect is dependent on the redox potential of the electrode material. If gold as a noble metal which cannot be oxidized is used, the switching completely disappears.

This correlation of the switching effect with the oxidation of the top electrode is further confirmed by a control experiment that we conducted. In Fig. 6, the *IV* characteristic of a device is shown, where the molecular layer is completely omitted and aluminum is deposited directly onto ZnO. Even in this device, the switching persists, although the $R_{\text{off}}/R_{\text{on}}$ ratio is much lower than for the rose bengal devices. For ZnO bottom electrodes, on switching occurs at ~ 0.7 V and off switching at -1.5 V. If aluminum was deposited directly onto ITO, the switching voltages are slightly reduced to 0.8 and -1 V (the corresponding data are given in Table I).

This result can be explained by considering that aluminum, which can be easily oxidized to Al₂O₃ and which has a more negative redox potential than zinc, indium, and tin (the different bottom electrode components), is oxidized by the oxidic bottom electrode. Therefore, an insulating layer of aluminum oxide is formed at the interface between bottom and top electrodes. Layers of aluminum oxide and of other metal oxides such as TiO, NiO, HfO₂, ZrO₂, and V₂O₅ have already been shown to exhibit bistable switching.^{18–25} Even in ultrathin layers of aluminum oxide (thickness below 1 nm), two conduction states were found,²² one Ohmic state

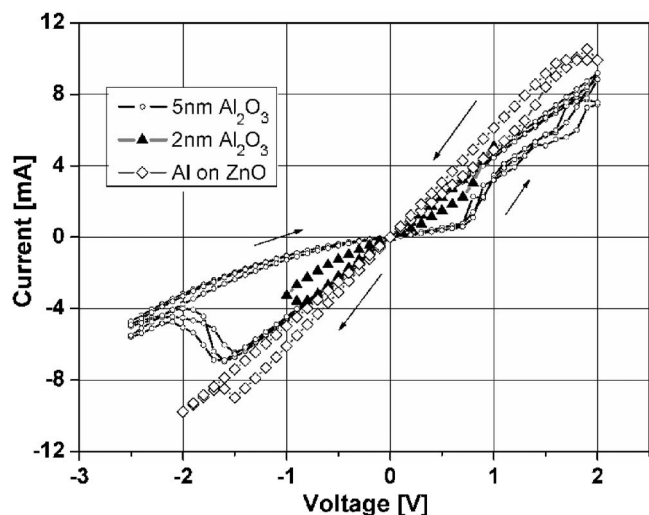


FIG. 6. Switching of devices consisting of ZnO/Al₂O₃/Al with thicknesses of aluminum oxide of 0, 2, and 5 nm, respectively. For all devices, the contact area is 0.0288 mm².

and one tunneling state. However, the transition between these two states in the ultrathin layers was not continuous and was probably triggered by external noise.

In literature, the switching in these oxides is often related to a dielectric breakdown and forming process in the oxide, which changes the phase or composition of the material between the electrodes. For example, Ansari and Qadeer²⁵ argued that titanium oxide (TiO_x) possesses different phases between TiO₂ and TiO_{1.75}. A change between these phases was proposed to be triggered by energy dissipation. Very often, it was assumed that the switching effect is localized in small spots (filaments).^{18,20,26} Besides this filament approach to explain switching in simple oxides, there are different theories such as current transport through two different defect states for the on and off states^{19,24} or the suppression of a tunneling barrier due to high currents.²²

To further verify that the switching effect we observe is strongly related to the switching of an oxide layer, another experiment was conducted. A 2 nm aluminum is sputtered onto ZnO and oxidized at an oxygen pressure of 200 mbar for 30 min. By repeating this step, a ~5 nm thick Al₂O₃ layer is grown. On top of the oxide, 80 nm of aluminum are sputtered. By this procedure, thin oxide layers of 2 and 5 nm, respectively, between the top and bottom electrodes are intentionally grown, which are argued to be responsible for switching. The result is shown also in Fig. 6. Switching occurs in a very similar fashion to the rose bengal devices: On switching occurs at positive and off switching at negative voltages. The on state is linear, whereas the off state deviates from linearity, and the on switching occurs at lower voltages than the off switching. This similarity of the switching of rose bengal devices and the aluminum oxide layer points to the same switching mechanism. Furthermore, even the same thickness dependence can be seen. A thicker aluminum oxide layer causes a higher resistance in the off state resulting in a higher $R_{\text{off}}/R_{\text{on}}$ (see also Table I).

In addition SIMS depth profiles of the layered system Al/143 nm RB/ZnO have been performed to investigate the

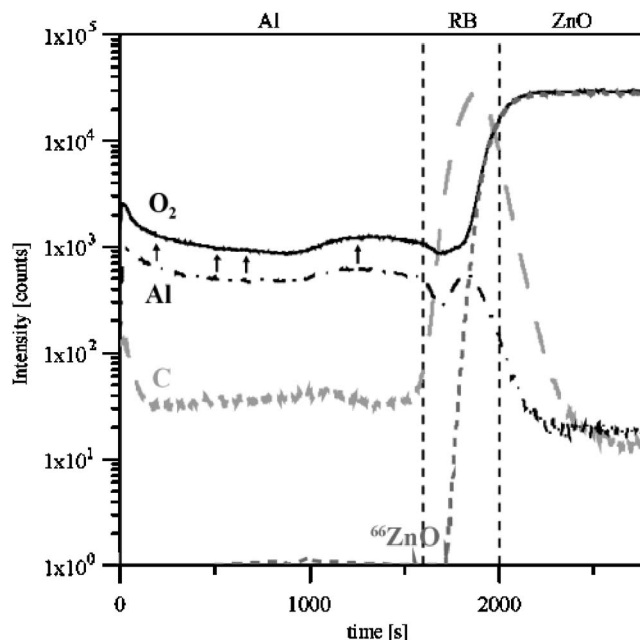


FIG. 7. Depth profile of a Zn/143 nm RB/Al device taken by TOF-SIMS immediately after preparation.

interface between Al/RB and RB/ZnO, respectively, and to gain information on the composition of the RB layer. This sample was studied immediately after preparation and one month after deposition. For comparison Al was deposited directly onto ZnO. Figure 7 shows the depth profile of the fresh RB sample. The O content within the Al is roughly stable and relatively high with respect to the Al. The hump at the beginning of the measurement is due to Al₂O₃ at the surface. Surficial Al₂O₃ is also obvious for the Al/ZnO sample, but within the Al top electrode material the O content is clearly lower compared to the Al and the RB samples. Therefore the high O content can be attributed to the specific properties of the rose bengal layer. In addition the Al top electrode is probably oxidized to some extent already during deposition. One month after deposition (Fig. 8) the oxygen content within the RB layer decreases. The small hump at the Al/RB interface indicates the oxygen movement from the RB layer into the aluminum. This is a clear evidence for the oxidizing properties of rose bengal and indicates the formation of Al₂O₃ at the Al/RB interface.

IV. DISCUSSION

The results presented here can be explained by the following model. The low on state resistance and the linear behavior of the current in the on state suggest that the molecular layer is short circuited. Furthermore, the switching of the control device, in which the molecular layer is omitted, excludes a molecular origin of the switching.

There are several ways of how the organic layer can be short circuited so that it does not take part in the conduction process. First of all, analogous to a breakdown mechanism of Al₂O₃ (Ref. 27) at high electric fields, aluminum ions can migrate through the sample and short circuit the organic layer. Similarly, already during the deposition of the top electrode, aluminum ions can punch through the molecular layer.

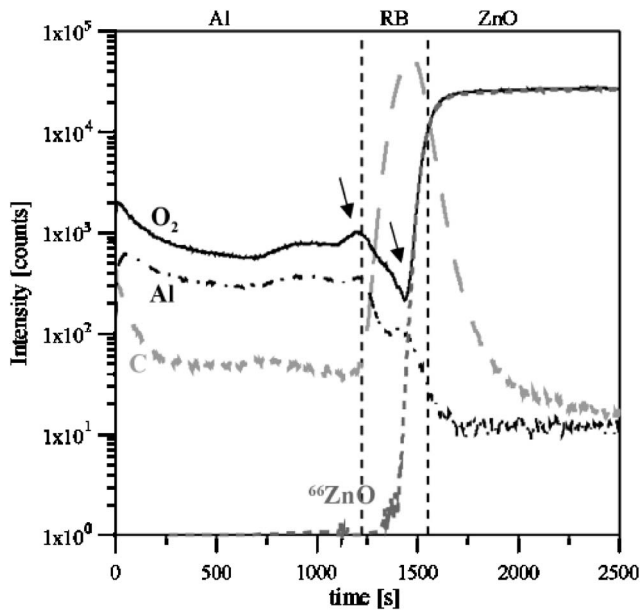


FIG. 8. Depth profile of a Zn/143 nm RB/Al device taken by TOF-SIMS one month after deposition.

Alternatively, it is also possible that needles or filaments of ZnO grow through the sample and short circuit the device.

Either of these explanations results in paths of aluminum or ZnO that bypass the organic layer. These metallic paths can form filaments that can form and break and thereby exhibit two conduction states: an Ohmic on state and an isolating state, in which the filaments are broken.

However, our results favor a different explanation of the switching, schematically shown in Fig. 9. In the on state the molecular layer is short circuited due to paths of either aluminum or ZnO. This implies that the resistance of the device in the on state is determined by the metallic path and thus independent of the molecular layer or thickness variations of the molecular layer. But, at least in the off state, a complete short circuit is avoided since at the contact of these paths with the opposite electrode, the aluminum is oxidized. This oxidation is analogous to the oxidation of an aluminum electrode which is directly deposited onto ZnO or ITO. But in the case of a rose bengal layer located between the ZnO and Al electrodes, the oxidation of the Al electrode is enhanced due to the oxidation properties of rose bengal. Dyes such as rose bengal are known²⁸ to sensitize oxidation and it is found that

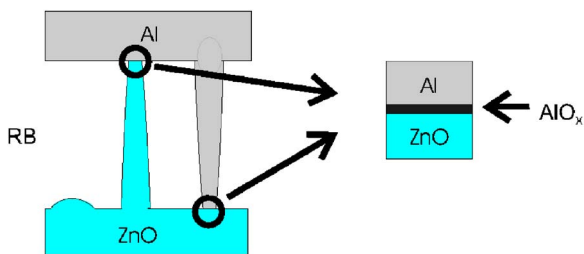


FIG. 9. (Color online) Proposed model to explain the switching effect. The molecular layer is short circuited by either ZnO or Al filaments. At the Al/ZnO interface a thin layer of aluminum oxide is formed. Thereby, the switching is an effect of a thin aluminum oxide layer (compare Fig. 5) and thus not molecular.

singlet oxygen, a very reactive intermediate, is responsible for such processes.^{29,30} If the thickness of the rose bengal layer in the device is increased, the oxidation of the aluminum electrode will be enhanced, and thus the insulating Al_2O_3 layer will grow resulting in a higher R_{off} value. A 2 nm thick Al_2O_3 layer can be formed by normal oxygen and an even thicker layer will be formed by the more reactive singlet oxygen. Because a thin layer of Al_2O_3 exhibits almost identical switching behavior as the rose bengal devices (see Figs. 3 and 6), the whole switching as observed in Fig. 3 is explained by the switching of a thin layer of Al_2O_3 at an Al/ZnO interface and is thus not a molecular effect.

However, although rose bengal does not directly originate the switching effect, it still has an indirect contribution. The $R_{\text{off}}/R_{\text{on}}$ ratio has been found to increase with increasing rose bengal layer thickness. Probably, the rose bengal layer (as well as other organic molecules) affects the redox mechanism of metal filaments. This also leads to an increase in the $R_{\text{off}}/R_{\text{on}}$ ratio with increasing rose bengal layer thickness.

V. CONCLUSIONS

We have shown that rose bengal thin films sandwiched between a ZnO or ITO bottom electrode and aluminum or titanium top electrode show resistive switching. By leaving out the molecular layer and depositing aluminum directly onto ZnO, we are able to exclude the molecular layer to generate the switching.

It is proposed that filaments of either aluminum (titanium) or ZnO grow through and short circuit the molecular layer. At the interface of ZnO and aluminum (titanium), a thin layer of aluminum oxide (titanium oxide) is formed. Due to the strong similarity of the switching of the rose bengal devices to the switching of an Al_2O_3 layer and due to the enhanced Al_2O_3 signal at the RB/Al interface obtained with TOF-SIMS, it is suggested that the switching is completely extrinsic, i.e., generated by the thin aluminum oxide layer at the interface.

However, it has to be noted that the results presented here do not exclude that rose bengal can show a molecular switching effect in other experimental setups. In fact, in the on state the molecular layer is short circuited by metallic filaments so that any molecular effects will be masked. Therefore, no conclusion about the molecule and its ability to switch can be drawn. Furthermore, the magnitude of the currents shown here is higher than observed by Bandyopadhyay and Pal.¹³ They also observed switching in rose bengal devices contacted by different top electrodes, e.g., mercury top electrodes,¹⁶ which hints that the effect they observed has a different origin. However, the switching effect observed in our devices is a more general mechanism which may be in operation in other molecular devices also.

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