Light-activated electroforming in ITO/ZnO/p-Si resistive switching devices

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Lock-in Amplifiers up to 600 MHz





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ABSTRACT

We report on light-activated electroforming of ZnO/*p*-Si heterojunction memristors with transparent indium tin oxide as the top electrode. Light-generated electron-hole pairs in the *p*-type substrate are separated by the external electric field and electrons are injected into the active ZnO layer. The additional application of voltage pulses allows achieving different resistance states that end up in the realization of the low resistance state (LRS). This process requires much less voltage compared to dark conditions, thus avoiding undesired current overshoots and achieving a self-compliant device. The transport mechanisms governing each resistance state are studied and discussed. An evolution from an electrode-limited to a space charge-limited transport is observed along the electroforming process before reaching the LRS, which is ascribed to the progressive formation of conductive paths that consequently induce the growth of conductive nanofilaments through the ZnO layer.

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The interest in resistive random access memories (RRAMs) has arisen as a promising alternative to conventional flash memories.^{1,2} The possibility to switch between two resistance states, namely, the high resistance state (HRS) and low resistance state (LRS), and retaining them without the necessity of any supplied voltage, opens a large range of potential applications in nonvolatile memories,^{3,4} even in logic and neuromorphic computing.^{5,6} The filamentary formation and partial destruction of conductive paths through a dielectric material have been established as the main mechanism of this resistive switching (RS) behavior, with electrochemical metallization (ECM) or valence change mechanism (VCM) being the most observed processes in metal oxides.^{7,8} In both cases, the out-diffusion of ions by electrical stress plays a crucial role in this structural and chemical modification.9-The first formation of these conductive nanofilaments (CNFs) takes place during the electroforming process, in which the LRS of the device is defined and it depends on the number and width of the CNFs.¹² In the case of polycrystalline materials, which usually present grain boundaries, these filamentary conductive paths are typically generated in these regions due to their initially defective nature. The abrupt and spontaneous formation of these

nanostructures under electrical stress has been used to obtain welldifferentiated resistance states, with the speed of the transition between them being on the order of picoseconds in some cases.¹⁴ However, this abrupt transition can be a drawback due to the permanent damages that some devices may undergo and consequently requiring to set a current compliance to avoid this occurrence. So far, some studies have focused on the control of the formation of the CNFs by using different values of the current compliance, which modifies the conductivity of the LRS and even enhances the endurance and the retention of the resistance states.^{15,16} Recently, light interaction has been proposed to modify the RS properties by either modulating the density of trapped electrons in heterojunctions¹⁷ or decreasing the Schottky-like barriers at rectifying interfaces.^{18,19} This effect has also been observed in solar cell-related materials such as perovskites, thus broadening their wealth of applications.^{20,21} Beyond these effects, an additional electron injection can facilitate the formation of oxygen vacancies, as observed in amorphous SiO₂.²² This effect has also been employed to influence the RS properties, where an additional current injection from the substrate, by means of photoconductivity, induces a decrease in the required voltage to switch to the LRS.²

In this work, we present the control of the CNF formation in pristine indium tin oxide (ITO)/ZnO/p-Si devices. The application of light photogenerates additional carriers in the p-Si substrate, which in combination with the applied voltages helps achieving a progressive growth of the CNFs. The application of subsequent current-voltage [I(V)] curves, progressively increasing the end-voltage, allowed controlling this CNF formation, thus achieving intermediate resistance states (IRS) at lower voltages, even without the necessity of setting a current compliance. Similar behavior has been observed using voltage pulses, recovering these IRS and achieving the same LRS.

Samples under study consist of an ITO/ZnO/p-Si metal-insulatorsemiconductor (MIS) device structure. Before the ZnO deposition onto the *p*-type Si substrate, a 400-nm-thick thermal SiO₂ layer was grown and etched using standard photolithography to define squared windows (60 \times 60 μ m²) in the field oxide. The ZnO layer was full-area deposited via radio frequency-magnetron sputtering, with a thickness of 60 nm, and subsequently annealed at 450 °C for 1 h under Ar flow. A second process of photolithography permitted the deposition of the ITO top electrode by electron-beam evaporation (EBE). Finally, fullarea Al was deposited by EBE as the bottom electrode. The structural characterization was carried out via transmission electron microscopy and Raman scattering measurements, indicating that ZnO exhibits a polycrystalline structure, and the results were published in a previous study on the same devices (see Ref. 24). The electrical characterization of devices was performed using an Agilent B1500 semiconductor device analyzer and a Cascade Microtech Summit 11000 probe station, supplying the voltage on the top ITO electrode and keeping the bottom contact grounded. Light excitation consisted in illuminating the device through the top ITO contact by means of a Nd:YAG continuous wave laser working at 532 nm with a power density of \sim 300 mW cm⁻².

Before the analysis of the effect of light on the electroforming process, a complete I(V) cycle in a pristine device under dark conditions was carried out, completing the electroforming and the first reset [see Fig. 1(a)]. An abrupt increase in the current can be observed around ~14 V, resulting in a switch to the LRS (a current compliance of 1 mA is required to avoid permanent damage to the device). The reset of the resistance state was carried out at negative voltages, obtaining an irregular curve in the range between -1.0 V and -2.5 V until the reset was completed. Successive I(V) characteristics were acquired in different but equivalent devices before, under, and after illumination to study the effect of light in the electroforming process. Cycling was done in a sequence with an end-voltage that was increased in each cycle up to 7 V. For comparison, a series of I(V) curves measured in the dark using another device were also recorded. In Fig. 1(b), the I(V)curves corresponding to the measurements without and under illumination are plotted. In the dark, the same I(V) characteristics were obtained in all cases, not reaching yet the electroforming and keeping the device in the pristine state to further study the effect of a combined application of light and voltage. These curves agree with the completed cycle under dark conditions obtained in the previously analyzed pristine device [see Fig. 1(a)]. Regarding the curves obtained under illumination, a clear increase in 5 orders of magnitude in current was obtained, with this effect being mainly ascribed to the injection into ZnO of electrons photogenerated within the p-Si substrate (although some electrons can also be promoted to the ZnO conduction band by direct absorption of photons at the ZnO/Si interface). After acquiring each curve under illumination, another curve was recorded in the dark



FIG. 1. (a) Complete first cycle of a device, acquired in the dark, showing the electroforming and first reset processes. (b) Sequence of I(V) characteristics increasing the end-voltage from 2 V to 7 V in the dark and under illumination. The colored arrows in (b) indicate the maximum voltage of each curve of the same color for the sake of a better comparison. (c) Curves obtained in the dark measured immediately after the acquisition of the corresponding curves under illumination shown in (b).

to observe possible permanent modifications in the I(V) characteristics [Fig. 1(c)]. In contrast to the curves in the dark obtained prior to illumination, where no modification of the I(V) characteristics was observed [see Fig. 1(b)], the curves acquired in the dark after

illumination present a clear variation, making the device more conductive and therefore exhibiting distinct resistance states. Curves until 2 V and 3 V present a similar line shape, consistent with the curves in the preillumination condition (at voltages lower than 0.75 V, displacement current dominates and charge accumulation takes place). However, the postilluminated I(V) characteristics at increasing endvoltage show a progressive increase in the current, with the illumination being responsible for this modification. As a consequence, charge accumulation no longer occurs, which suggests that illumination induces a modification of the charge transport mechanism through the device.

Analyzing more in detail the evolution of the postilluminated I(V) curves [see Fig. 1(c)], the first two curves (end-voltage of 2 V and 3 V) exhibit displacement current at voltages below 0.75 V, as well as accumulated charge in backward curves with a remnant voltage around 0.4 V. In addition, the pristine state presents asymmetrical I(V) characteristics with a clear limitation of the current at positive voltages, which can be ascribed to a Schottky-like conduction mechanism. However, this current limitation is altered in the two following curves acquired after illumination (end-voltage of 4 V and 5 V), which could be related to initial structural modifications caused by oxygen out-diffusion within the ZnO layer, therefore inducing an increase in conductivity. The two last curves (end-voltage of 6 V and 7 V) exhibit a totally different line shape, free of displacement current and accumulated charge, suggesting again another transport mechanism. This behavior can be ascribed to the existence of CNFs connecting directly both electrodes.

A similar experiment was carried out but using voltage pulses instead of I(V) sweeps. In this case, a train of 2 pulses was performed. The first pulse acted as writing voltage (V_w) with 1 s of duration, whose amplitude was varied from 1 V to 10 V; the second one was meant for reading the current of each resistance state for 0.5 s, which was set at $V_r = 1 V$ in all cases. This sequence of two pulses was repeated 10 times with 1 s of separation between each one, its schematics being represented in the inset of Fig. 2. As proceeded using I(V) curves, this sequence was applied before, during and after illumination for each $V_{\rm w}$. To analyze the influence of light, another device was submitted to the same pulsed sequence but only in the dark. In Fig. 2, the average current at V_r along the 10 pulses is plotted as a function of the different supplied $V_{\rm w}$ for both operation conditions, following the already described pulsed sequence. As observed, the reference device, biased in the dark, exhibits a constant value of the read current around 10^{-11} A for all $V_{\rm w}$ except at 10 V, when it shows a sudden increase in the current up to 10^{-5} A. In the case of experiments under illumination, the same values of the read current around 10^{-11} A are obtained at low $V_{\rm w}$ ($V_{\rm w} \leq 4$ V), after illuminating the devices. In contrast, a gradual increase in the read current in the range from 5 V to 8 V takes place, achieving a value of $\sim 10^{-5}$ A, which matches with the current obtained in the nonilluminated device at 10 V. This progressive current increase brings the device into intermediate resistance states (IRS), in good agreement with our observation when performing voltage sweeps.

To further elucidate the influence of light on the RS properties of the devices, it is interesting to study the charge transport mechanism evolution that the devices undergo when progressively switching from higher to lower resistance states. In order to analyze better this evolution, the I(V) curves of the different resistance states were fitted



FIG. 2. Representation of the average value of read current, along 10 pulses, obtained in the dark at $V_r = 1 V$, as a function of the different write voltage V_{w_r} without (black squares) and after (red circles) illumination. Three different regions can be observed in the second case: pristine, intermediate resistance states (IRS), and low resistance state (LRS). In the inset, a scheme of the applied voltage pulse train is illustrated.

according to the most general dependence of current on voltage in heterostructures,

$$I(V) = AV^{\alpha} \cdot \exp(BV^{\beta}), \tag{1}$$

with A and B being constants and α and β the potential dependence of the pre-exponential and exponential factors, respectively. The exponential factor is related to the conduction in materials with potential barrier profiles (like dielectrics or semiconductors), whereas the preexponential one is typically associated with conduction in materials with large carrier density, influenced by the profile of the electric field (like in degenerated semiconductors or metals). The curves and their corresponding fits are plotted in Fig. 3(a), where the resulting fitting parameters are also indicated. In the case of the three first curves, where the device is in intermediate states close to the HRS, only exponential contribution ($\alpha = 0$ and $\beta \neq 0$) is found. The value of β decreases when the end-voltage increases, which is consistent with a combination of a lower effect of the Schottky barrier on charge transport and the initial and progressive formation of CNFs. In contrast, the I(V) curves corresponding to the LRS show a value of $\alpha \approx 2$. This value is in agreement with a previous work carried out in the dark conditions on these same devices, where the space charge-limited current mechanism (SCLC) was determined to be dominant within the LRS in the accumulation regime (V < 0)²⁴ Please note that, in the present work, curves are taken in the inversion regime (V > 0), but the symmetry of the curves when the CNFs are formed suggests similar behavior in both polarities. Regarding the obtained value of $\beta \approx 0.5$ in the LRS, it could be ascribed to the Poole-Frenkel correction proposed by Murgatroyd, where the reduction of the effective trap level depth due to the external electric field is taken into account;²⁵ nevertheless, this contribution only affects at low voltages, with $I \propto V^2$ being the dominant dependence.

In contrast to some studies reported in the literature that have only observed differences in the RS properties of ZnO when the device



FIG. 3. *I*(*V*) curves recorded after illumination with their corresponding fits following the general expression indicated in the inset. (b) Scheme of the device depicting the formation of CNFs due to the diffusion of the oxygen ions (blue circles) toward the top electrode when it is biased at positive voltage. The photogenerated electron-hole pairs formed within the Si substrate (red circles) enhance electron injection into the ZnO, which facilitates the formation of the CNFs. (c) Energy band diagram of the device structure, showing the band offset and bandgap (BG) energies corresponding to the involved materials.

is under illumination, but involving no permanent modifications after ^{5–28} the hereby analyzed devices exhibit different resistance states that, 18,2 after being illuminated. These results demonstrate that light strongly influences the formation of the CNFs during the electroforming process, obtaining different resistance states by adequately combining the applied voltage and the extra current induced via photoconduction. Indeed, the performed electrical characterization already gives information about the role of the device structure in its RS properties. In particular, the rectifying behavior observed in the inversion regime suggests the presence of a Schottky-like barrier at the interface between the ZnO layer and the p-Si substrate, whereas the remnant voltage around 0.4 V in this same pristine state confirms the existence of accumulated charge at this interface. On the one hand, some studies reported that, under illumination, the trapping and detrapping of optically generated charges in this region could influence on the RS behavior, for instance by inducing lower resistance states or lower set voltages.^{17,18} On the other hand, other authors proposed that the increase in the number of injected electrons due to carrier photogeneration in the substrate, together with electron trapping at intrinsic defects within the active layer, contributes to the creation of oxygen vacancies, crucial for the formation of the CNFs in metal oxides.²³ As a consequence of any of these hypotheses, the voltage at which the switch to the LRS is achieved, i.e., the voltage at which the CNFs are generated, is significantly reduced by the application of light.

It has been previously reported that the generation and stability of the CNFs depend not only on the applied voltage (i.e., the external electric field) but also on the current circulating through the material.²³ Indeed, the electron flow is responsible for breaking Zn-O bonds in order to free O²⁻ ions, whose diffusion toward the electrodes induces the formation of vacancy sites within the ZnO lattice that constitute the CNF. The fact that the ZnO presents polycrystalline morphology suggests that the breaking of Zn-O bonds takes place at grain boundaries, as has been reported in the literature, producing there the local formation of Zn-rich regions.¹³ In this regard, the utilization of light permits injecting an additionally photogenerated current from the substrate into the oxide material which, combined with the applied voltage, induces the structural changes into the ZnO layer [see Fig. 3(b)]. In the dark, the applied voltage is the main responsible for the electroforming process due to the low current that the device presents, typically requiring high voltages to switch to the LRS. At this high voltage, loosely bound oxygen ions move toward the ITO, thus inducing the sudden switch to a lower resistance state due to a high electrical stress of the material, achieving high currents. Therefore, this abrupt increase in current resulting from the formation of the CNFs can induce an undesired overshoot of current in the device, even working at lower voltages with short duration voltage pulses, and using a suitable compliance, which can lead to permanent damage within the structure. In contrast, the additional current injected from the Si substrate [following the energy band schematics in Fig. 3(c)] when illuminated allows achieving sufficient electrical stress at lower voltages, thus providing gradual oxygen ions drift without triggering the sudden formation of the whole CNF, even when forming a considerably large number of them. However, during illumination, the increase in current may induce some defects at the ZnO/ITO interface and/or deeper into the ITO contact.

We have hereby shown that, in the ITO/ZnO/*p*-Si devices under study, the progressive and stable CNF generation during the electroforming can be achieved by means of two different approaches: the progressive increase in the end-voltage in consecutive I(V) curves and the usage of voltage pulses (which reduce the required electroforming voltages from 10 V to 5 V), which avoid the constant stress of the device under illumination and thus prevent a sudden switch to the LRS. These presented protocols therefore give the possibility to control the formation of the CNFs, permitting to tune the resistance into intermediate states and thus obtaining a quasianalog behavior, thanks to the adequate addition of light to the applied voltage.

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