Highly Transparent ITO/HfO$_2$/ITO Device for Visible-Light Sensing

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ABSTRACT
Transparent visible-light sensors are of critical importance in invisible optoelectronic circuits as the interface between the optical and electrical domains. However, devices designed based on photocarrier generation for light sensing limit the transparency of the device in the visible region, as the optically active layer also passively absorbs light continuously. In this work, we present an all-transparent ITO/HfO$_2$/ITO device with the wide bandgap HfO$_2$ functioning as the resistive switching and the light sensing element. Electrically switching the resistive state of the device to a low-resistance soft-breakdown state is demonstrated to cause the wide-bandgap visible-light blind HfO$_2$ to become photosensitive. This allows us to optically functionalize the device for an optical response by electrical breakdown in the oxide and can be triggered on-demand. Apart from the on-demand optical response in the device, the inherent resistive switching properties of the HfO$_2$ device allow for integration of memory and optical sensing capabilities, presenting a novel phenomenon for optical sensing in invisible optoelectronics.

INDEX TERMS
Non-volatile optical memory, photosensor, ReRAM, transition metal oxides, transparent electronics.

I. INTRODUCTION
Advances in invisible electronics research have brought this futuristic concept in the past a big step closer to reality. Highly transparent transistor and memory devices have been successfully demonstrated [1]–[8]. Thin-film semiconducting oxides are excellent candidates for this purpose due to their facile large-area preparation methods and good mechanical elasticity, which made them particularly suitable for use on flexible substrates [1], [8]. Fullyrollable prototypes have been developed recently [9], [10]. Besides electrical functionality, it is also desirable to include optical functions to realize what is often called an invisible optoelectronic system. However, the development of transparent photosensitive devices is more challenging as compared to the classical opaque counterparts. To maintain optical transparency, only oxides with relatively large bandgap can be considered [11], [12], which limit detection to the ultra-violet regime. To extend the photoresponse into the visible-light range, various strategies have been explored. In one approach, photosensitive nanostructures [13]–[15] or plasmonic metal nanoparticles [16] are incorporated into the host oxide to modulate its photoactivity. Optoelectronic devices operating in the visible range have been demonstrated using p-Si/HfO$_2$ [17] and p-Si/SiO$_x$ [18] structures. However, owing to their reliance on the silicon substrate for their optical functionality limits their use in completely transparent circuits.

Another approach involves capping the wide-bandgap oxide with a thin visible-light-absorbing layer [19], [20]. Of-late, much attention has been paid to semi-transparent two-dimensional materials with good absorption characteristics (e.g. WSe$_2$ [21], MoS$_2$ [22], etc.). In these approaches, innovative means were sought to enhance light absorption while minimizing the loss of transparency. In an earlier work, we have found that after the soft electrical breakdown of SiO$_2$, illuminating it under visible light would restore the oxide back to the pre-breakdown state [23]. Time dependent dielectric breakdown stressing of the restored oxide showed comparable reliability performance as the pristine case, indicating that the breakdown oxide is structurally restored by the light. In this paper, we leverage on this phenomenological observation to demonstrate an all-transparent ITO/HfO$_2$/ITO...
resistive switching device with not only the HfO$_2$ displaying non-volatile resistive-switching memory characteristics, but also visible-light sensing and optical memory functionalities. The work highlights a possible alternative strategy for realizing high transparency and visible-light sensing, as well as non-volatile optoelectronic memory capability, altogether in a single device.

II. EXPERIMENTAL DETAILS
A quartz substrate was first rinsed with acetone, iso-propyl alcohol and deionized water and then blanket deposited with a 70-nm thick tin-doped indium oxide (ITO) bottom electrode (BE) in an AJA ATC-2200 UHV sputtering system at room temperature. This was followed by the blanket deposition of an approximately 10-nm thick HfO$_2$ layer in a CNT Savannah ALD reactor at 200 °C. The precursor was tetrakis (ethylmethylamino) hafnium and the oxidizing agent was H$_2$O vapor. Patterning for the top ITO top electrodes (TE) was carried out in a Micro Tech LW405B Laser writer. The patterned sample was then blanket deposited with a top ITO layer of a similar thickness as the bottom. Lift-off using Remover PG was then done to complete the top ITO electrode formation. Electrical testing was carried out at 300 K on a probe station equipped with a Keithley SCS4200 parameter analyzer. Illumination was provided by a Sugar CUBE ultra LED broadband white light source and spectrum dependence studies were performed using filters in tandem with the light source. The filters were noted to have wavelengths around 400nm and 700nm, corresponding to blue and red light respectively. (Fig. 1(a)).

III. RESULTS AND DISCUSSION
Fig. 1(b) shows a photograph of the fabricated sample. The active area (enclosed in dashed lines) has good optical transparency relative to the plain quartz substrate. Scanning electron microscopy shows an array of top ITO electrodes (Fig. 1(c)). The HfO$_2$ is 10 nm thick, as confirmed by high-resolution cross-sectional transmission electron microscopy (Fig. 1(d)). The quality of the HfO$_2$/ITO interfaces was checked using electron dispersive spectroscopy (EDS). Relatively sharp interfaces, with no intermixing of the elements, are evident from EDS results (Fig. 1(e)). X-ray photoelectron spectroscopy (XPS) analysis of the sandwiched HfO$_2$ reveals a Hf:O ratio of 1:1.7 (not shown). The oxygen deficiency may be ascribed to the n-type ITO known for its oxygen “scavenging” property [24].

The typical bipolar resistive switching (RS) of the device was investigated by applying bias voltages to the TE while the BE was grounded. After electroforming, the device exhibits bipolar resistance switching, as shown in Fig. 2(a) [25].

Initially, the pristine device was in the high resistance state (HRS) before applying any bias. When a positive bias was applied on the ITO TE, the device switches from the HRS to the low-resistance state (LRS) at a voltage of 1.3 V, which is called the SET process. When a negative bias is applied to the ITO TE, the device switches back to its HRS state at the voltage of −0.9 V, which is called the RESET process. In addition, the transmittance spectra of the ITO/HfO$_2$/ITO structure was measured, as shown in Fig. 2(b). The average transmittance, including the glass substrate, exceeds 85% in the visible wavelength region of 400-800 nm. The ITO/HfO$_2$/ITO structure is thus a good candidate for a fully transparent resistive random-access memory (RRAM) device. Bipolar switching is commonly ascribed to a vacancy filament, which can be alternately ruptured or reformed via oxygen exchange with the electrode [26], [27]. The RS mechanism of the device, which includes the formation and rupture of the conductive filament for the device, is illustrated in figure 3. The CF forms into a conical shape, where the thicker part of the filament is on the cathode side while the thinner part is on the anode side [26]. Therefore, during the electroforming or SET process, the RS region is feasibly closer to the interface of ITO TE and the HfO$_2$ layer in the ITO/HfO$_2$/ITO device, as shown in Fig. 3(a). When a positive voltage is applied to the ITO TE, oxygen vacancies are generated in the HfO$_2$.
layer and migrate toward the ITO BE to form conical shape filament. When positive voltage is applied on ITO TE, oxygen vacancies \((V^{2+}_o)\) are generated in the HfO\(_2\) layer and migrate toward the ITO BE while oxygen ions drift toward the ITO TE and are transformed into oxygen ions \((O^{2-})\), creating a conical shape filament \([26],[28]\). This process is called the reduction process. The device changes its state from HRS to LRS. It is noted that from the reaction, the oxygen vacancies with two electrons \(V^{••}_o\) along with two electrons \(V^{••}_o\) are neutral oxygen \([29]\).

\[
O + 2e^- = V^{••}_o + O^{2-} \quad \text{(Reduction process)} \quad (1)
\]

During the reset process, when a negative voltage is applied on ITO TE, oxygen ions migrate back to the ITO BE and recombine with the oxygen vacancies \((V^{••}_o)\), resulting in the rupturing of the CF at the ITO/HfO\(_2\) interface and the device switches back to the HRS, as shown in Fig 3(b). The oxidation process occurring at the ITO/HfO\(_2\) interface can be expressed as follows \([29]\).

\[
V^{••}_o + O^{2-} = O + 2e^- \quad \text{(Oxidation process)} \quad (2)
\]

The schematic structure of the ITO/HfO\(_2\)/ITO transparent device under the white light illumination is shown in Fig. 4(a). The ITO/HfO\(_2\)/ITO device was switched to LRS condition in the dark when a positive DC bias was applied to the ITO TE with a current compliance (CC) of 500 \(\mu\)A as shown in Fig. 4(b), represented by the blue curve labelled pre-illumination SET. The transition to the LRS was verified by a subsequent positive voltage sweep shown by the red curve labelled pre-illumination LRS. Following this, the current was measured with time under a constant read voltage of 0.2 V, which is shown in Fig. 4(c). The current was measured in the dark prior to any illumination and was observed to be stable without degradation. Following this, the response to light was studied in the succeeding step. The light was turned on at 5 s, and it can be easily observed that the current showed a near-instantaneous drop and the device changes its resistance state from LRS to HRS. This phenomenon suggests that light illumination led to the disruption of CF in the oxide layer, because the oxygen vacancies have been shown to be able to recombine with the oxygen ions under light illumination \([30]\). The oxygen ions are theorized to be hindered from recombining with the electrically generated vacancies by virtue of an energy barrier in the LRS. In the presence of illumination, light provides the required energy to enable the interstitial ions to recombine with the generated vacancies. This causes the filament to be ruptured which is understood as the conductive path between the top and bottom electrodes being disrupted, resulting in an optical reset process. Due to light-mediated recombination of the oxygen-ions with the vacancies, the CF path is disrupted reverting the device to the HRS. This is observed in Fig. 4(c) as the sudden drop in current upon illumination \([30]\). To verify the transition from the LRS state to the HRS following the illumination, a positive voltage sweep was conducted verifying this, as shown by the green curve in Fig. 4(b) labelled post-illumination SET.

The multiple visible light sensing cycles for ITO/HfO\(_2\)/ITO device are shown in Fig. 4(d), where multiple SET and RESET cycles can be repeatedly produced by subjecting the device alternately to a positive DC voltage sweep and visible-light irradiation, respectively. Both the LRS and HRS states are highly stable for more than 120 cycles and the ON/OFF ratio of the device was found to be around 6 orders.

Following the observation of light mediated negative conductivity change in the device, further experiments were conducted using colored filters in tandem with the white light source to determine if the response to light persists throughout the visible spectrum. For this, we chose two filters corresponding to 400 nm (blue) and 700 nm (red) as representing the bounds of the visible light regime and conducted endurance tests. The blue curve in Fig. 5(a) shows that when blue light (65 mW/cm\(^2\)) is turned on at \(\sim 5\) s, the current suddenly drops and the device switches from LRS to HRS. After the blue light RESET, the same device is switched back to LRS again by an electrical sweep. Following the electrical set, for the optical test, the red filter is connected to the illuminator and the device response to red illumination is observed. The red curve in Fig. 5(a) shows that when red light
is of the order of $30 \mu$A.

As highlighted in the figure, we note that the response time parameter analyzer connected via a Stanford Research Systems SR560 low noise pre-amp, is shown in Figure 5 (c). As highlighted in the figure, we note that the response time is of the order of 30 $\mu$s.

For the photoresponse experiments conducted at a measuring bias of 0.2 V, there was no return to the current compliance observed on turning off the light source [Fig. 4(c)]. We further studied the effect of the measuring bias on the optical reset to determine if the reset to HRS persists after the illumination is turned off or if the device switches from the HRS to LRS in the absence of illumination at higher measuring biases. For measuring biases up to 1.2 V, we observe that the reset state persists even after the illumination is turned off but at 1.2 V, we observe that turning off the illumination results in the device returning to LRS, as shown in Fig. 5(d). For several test cases up to 1.2 V measuring bias (not presented here), there was no such current rise to compliance observed barring the expected fluctuation and increase in current arising from using a larger voltage. For a measuring bias of 1.2 V, the device was observed to show multiple cycling between bi-stable HRS and LRS states. The HRS persisted for as long as the device was illuminated followed by a return to LRS in darkness when the illumination was turned off. This suggests the possibility for a dual use-case of the device as either a permanent light-based reset device or a transient light-based current quenching device depending on the applied measurement bias. Such a feature would enable us to either have a device with in-built optical to electronic memory or an always-on continuous measurement optoelectronic sensor.

**IV. CONCLUSION**

A transparent ITO/HfO$_2$/ITO resistive switching device that responds to visible light is demonstrated. The response is in the form of a quenching of the high-leakage current of the device’s low resistance state when it is illuminated by visible light. The devices show excellent endurance characteristics as well as a high ON/OFF ratio and a fast response time, which we believe can be further improved through material and architecture improvements. The presented results of the photoresponse strongly suggests that the process involves a light-assisted reconstruction of the electrically generated defective oxide network. Further investigation into the material and device characteristics within the near infrared region may reveal exciting avenues of application arising from plasmonic absorption in the oxide layers. These findings, coupled with the response in the visible region, inherent memory capabilities of the RRAM device, the on-demand photoresponse of the device and multiple operating schemes dependent on the measurement bias may pave the way for the development of fully CMOS compatible transparent oxide-based devices with not only non-volatile electrical memory but also integrated on-demand optical sensing and memory functionalities.

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