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The advertisement features a photograph of the Model PS-100 probe station, a complex piece of scientific equipment with various mechanical components and a probe. The background is a gradient of blue. Text on the left includes 'NEW' in orange, 'Model PS-100' in large blue font, and 'Preconfigured Tabletop Probe Station' in smaller blue font. On the right, the 'Lake Shore CRYOTRONICS' logo is shown, with 'Lake Shore' in white and 'CRYOTRONICS' in blue. Below the logo, the tagline 'An affordable solution for a wide range of research' is written in white italicized font.

Realization of write-once-read-many-times memory device with O₂ plasma-treated indium gallium zinc oxide thin film

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A write-once-read-many-times (WORM) memory devices based on O₂ plasma-treated indium gallium zinc oxide (IGZO) thin films has been demonstrated. The device has a simple Al/IGZO/Al structure. The device has a normally OFF state with a very high resistance (e.g., the resistance at 2 V is $\sim 10^9 \Omega$ for a device with the radius of 50 μm) as a result of the O₂ plasma treatment on the IGZO thin films. The device could be switched to an ON state with a low resistance (e.g., the resistance at 2 V is $\sim 10^3 \Omega$ for the radius of 50 μm) by applying a voltage pulse (e.g., 10 V/1 μs). The WORM device has good data-retention and reading-endurance capabilities. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4862972>]

Write-once-read-many-times (WORM) memory devices could be used in high-speed, permanent archival storage application for videos, images, and other noneditable database. WORM memories based on organic materials, such as small molecules and polymers have been demonstrated.^{1–6} WORM devices have been also realized with various inorganic thin film materials, e.g., a WORM memory device was realized based on the charging-controlled modulation in the current conduction of an Al/Al-rich Al₂O₃/p-type Si diode^{7,8} and a WORM device based on conduction switching of a NiO thin film in a metal-insulator-metal structure fabricated on a flexible substrate was reported.⁹ In the present work, a WORM memory device based on O₂ plasma-treated indium gallium zinc oxide (IGZO) thin films is demonstrated. The device has a simple Al/IGZO/Al structure. Its memory operation is based on the switching from an OFF state to an ON state by applying a voltage pulse. The device has a normally OFF state with a very high resistance (e.g., the resistance at 2 V is $\sim 10^9 \Omega$ for a device with the radius of 50 μm) as a result of the O₂ plasma treatment on the IGZO thin films; and it can be switched to an ON state with a low resistance (e.g., the resistance at 2 V is $\sim 10^3 \Omega$ for the radius of 50 μm) by applying a voltage pulse (e.g., 10 V/1 μs). The WORM device exhibits good data-retention and reading-endurance capabilities.

The schematic of the WORM device based on IGZO thin film is illustrated in the inset of Fig. 1. A 30 nm Al₂O₃ layer was deposited on a p type Si substrate which server as the buffer layer by atomic layer deposition (ALD) process at 250 °C with 99% purity Trimethylaluminium (TMA). A 200 nm thick Al layer was then deposited on the Al₂O₃ layer by radio frequency (RF) magnetron sputtering to form the bottom electrode. After that, IGZO film was deposited onto the Al layer by RF magnetron sputtering of an IGZO target

with the mole ratio of In:Ga:Zn:O = 1:1:1:1 in a mixed Ar/O₂ ambient at a flow rate ratio of 10/1. During sputtering, the RF power was set at 100 W and the sputtering pressure was 3 mTorr. In order to investigate the influence of the thickness on the memory behavior of the WORM devices, IGZO thin films with the thicknesses of 50, 100, 200, and 400 nm were deposited, respectively. The deposited IGZO thin films were then subjected to an O₂ plasma treatment for 10 min at room temperature with a microwave plasma asher (PVA Tepla, 300 autoloader-pc). The O₂ plasma is generated by exciting the oxygen gas (O₂ flow rate = 820 ml/min, pressure = 1 mbar) at the frequency of 2.45 GHz with the power of 800 W. In our previous study, it was found that O₂ plasma treatment can greatly increase the resistivity of the IGZO thin film as a result of the reduction in the concentration of the oxygen vacancies in the IGZO thin film.¹⁰ The as-deposited IGZO thin film has a very low resistivity ($5.6 \times 10^{-3} \Omega\text{-cm}$); however, the O₂ plasma treatment for 75 s causes the resistivity increase to $1.9 \times 10^{-1} \Omega\text{-cm}$, and

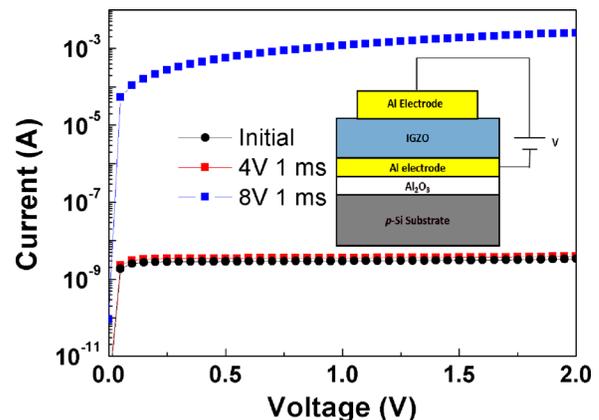


FIG. 1. I-V characteristics of the WORM device before and after the application of voltage pulses. The inset shows the schematic diagram of the Al/IGZO/Al WORM device structure.

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the resistivity is extremely high (the resistivity is too high to be measured with a four-point probe) after the plasma treatment of 10 min. The increase in the resistivity is due to the large decrease in the free electron concentration in the IGZO thin films, e.g., the electron concentration decreases from $1.3 \times 10^{21} \text{ cm}^{-3}$ of the as-deposited film to $2.2 \times 10^{18} \text{ cm}^{-3}$ after the O_2 plasma treatment of 75 s. The XPS measurement shows that the O_2 plasma treatment can greatly reduce the concentration of the oxygen vacancies which act as donors in the IGZO thin film.¹⁰ With the O_2 plasma treatment, the resistance of the OFF state of the WORM device is very high such that the OFF-state current is very low, which is very useful to the operation of the WORM device. Finally, the top Al electrode was deposited using RF magnetron sputtering and patterned into circular pads with radius of $50 \mu\text{m}$ by photolithography and lift-off process. The electrical characterization of the devices was carried out with a Keithley 4200 semiconductor characterization system at room temperature.

Figure 1 shows the current-voltage (I-V) characteristics of the device as fabricated and after the applications of voltage pulses of 4 V/1 ms and 8 V/1 ms, respectively. The I-V characteristics were measured by sweeping the voltage from 0 to 2 V. The device is initially in the high-resistance state (i.e., the OFF state) with the current at the order of nA. As shown in the figure, there is no significant change in the current conduction after the application of the voltage pulse of 4 V/1 ms. However, the current drastically increases after applying the voltage pulse of 8 V/1 ms. For example, the current measured at 2 V increases from $3.92 \times 10^{-9} \text{ A}$ to $2.52 \times 10^{-3} \text{ A}$ (~ 6 orders) after the application of the voltage pulse; and the current then remains at the same order (10^{-3} A) in the repeating voltage sweepings. This means that the device can be switched from a high-resistance state (the OFF state) to a low-resistance state (the ON state) by applying a voltage pulse. The ON state can be maintained without returning back to the OFF state in the subsequent positive or negative voltage sweepings. The irreversible switching is ideal for the WORM device application.

Resistance switching has been observed in many metal oxide systems, and various switching mechanisms such as cation migration or conductive filament (CF) of oxygen vacancies have been proposed.^{11–15} The switching between a high-resistance state and a low-resistance state is generally reversible. However, in the present work, the switching from the OFF state to the ON state in the O_2 plasmas-treated IGZO layer is non-reversible. A plausible mechanism is shown in Fig. 2. Before O_2 plasmas treatment, there is a high

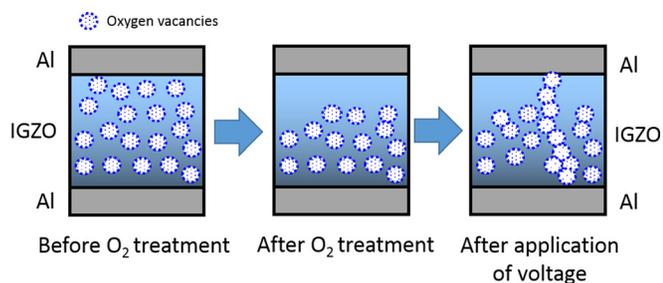


FIG. 2. Schematic illustrations of the changes in oxygen vacancies in the IGZO layer as a result of O_2 plasmas treatment or the application of a writing voltage.

concentration of oxygen vacancies in the as-deposited IGZO film, thus, the film's resistivity is very low. Oxygen plasma is known to contain various excited oxygen species, including O^+ , O_2^+ , and O^* .¹⁶ During the O_2 plasma treatment, oxygen radical atoms diffuse into the IGZO layer from the surface, reaching tens of nanometers in depth to fill the oxygen vacancies.^{17,18} This greatly reduces the free electron concentration in the film's surface region, and thus the OFF state is observed. However, when a voltage is applied to the device, some of the lost oxygen vacancies in the surface region are regenerated as a result of electrochemical reactions under the influence of electric field. With the formation of CFs by the oxygen vacancies connecting the two electrodes, the ON state is achieved.

Figure 3 shows the influence of the application of a voltage pulse (i.e., writing the WORM memory) on the current of the device measured at 2 V. Figure 3(a) shows the current as a function of the pulse voltage with pulse duration fixed at $1 \mu\text{s}$. As can be observed in the figure, the writing of the WORM device has a threshold voltage of $\sim 7 \text{ V}$ (note that the threshold voltage depends on the pulse duration as well as the IGZO film thickness). When the writing voltage is lower than $\sim 6 \text{ V}$, the device remains at the initial high-resistance state with the current of $\sim 10^{-9} \text{ A}$; the current drastically increases to $\sim 10^{-4} \text{ A}$ when the voltage reaches $\sim 7 \text{ V}$, and it further increase to $\sim 10^{-3} \text{ A}$ at the pulse voltage of 10 V. This indicates that the ON state can be easily achieved with a voltage pulse of greater than 7 V (for the

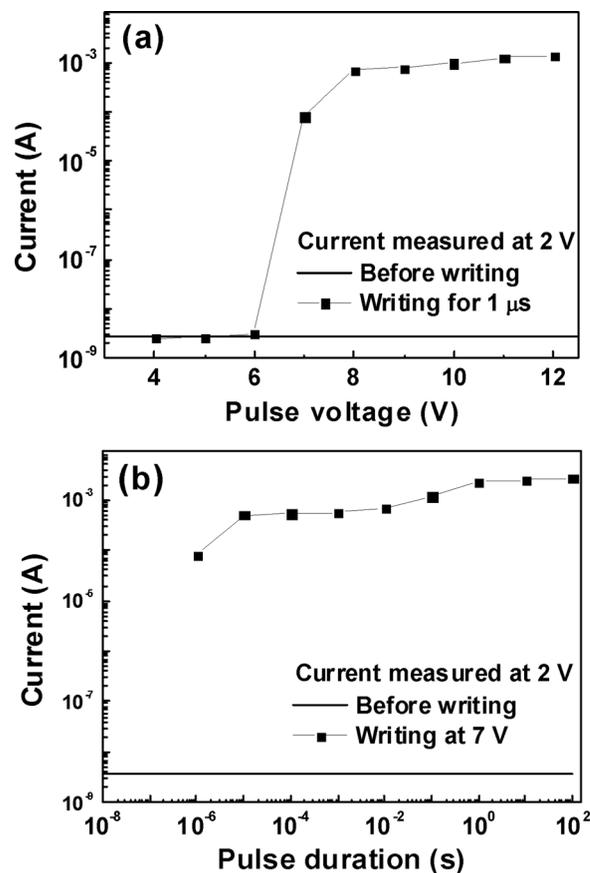


FIG. 3. Device currents measured at 2 V as a function of either (a) the pulse voltage with the pulse duration fixed at $1 \mu\text{s}$ or (b) the pulse duration with the pulse voltage fixed at 7 V.

pulse duration of 1 μs). Figure 3(b) shows the current as a function of the pulse duration for the pulse voltage fixed at 7 V. The device shows a high-speed writing performance. As can be seen in the figure, the pulse duration of 1 μs results in an increase in the current by about ~ 4 orders at the pulse voltage of 7 V, which provide a memory window large enough for the memory operation (note that for the same increase in the current, a shorter pulse duration is required for a high pulse voltage, as suggested by Fig. 3(a)). Also as expected, a longer pulse duration results in a larger increase in the current (and thus a larger memory window).

Figure 4(a) shows the data-retention performance of the WORM devices. The currents of both the OFF state (i.e., the state before writing) and the ON state (i.e., the state after writing) were measured with a reading voltage of 2 V at room temperature. The OFF state current measurement was first measured for 10^5 s. Subsequently, a voltage pulse of 8 V with 1 μs duration was applied to switch the device from the OFF state to the ON state; then the current of the ON state was measured in the time frame of 10^5 s. It is observed that there is no significant change in the OFF state currents and only a very small reduction in the ON state currents after 10^5 s. The predicted current ratio of the ON state to the OFF state (the memory window) is still larger than 4 orders after 10 yr. The reading endurance of the WORM device has been also characterized, as shown in Fig. 4(b). No significant degradation is observed for the OFF and ON states after 10^6 readings at 2 V, showing an excellent reading endurance.

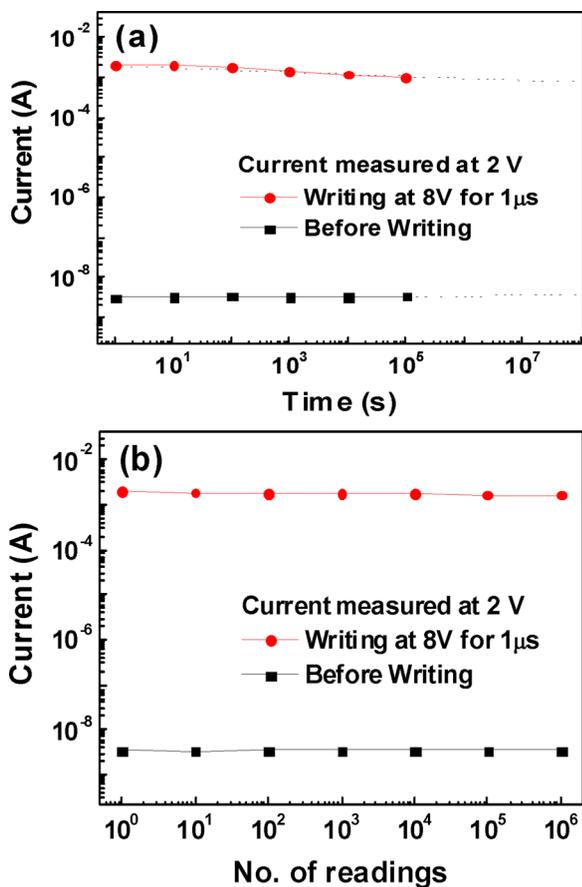


FIG. 4. (a) Retention characteristic of the OFF and ON states; and (b) reading endurance of the OFF and ON states. The current is measured at 2 V.

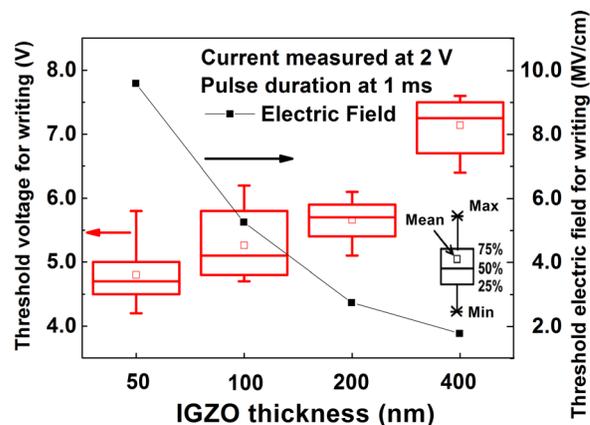


FIG. 5. Threshold voltage and corresponding electric field for writing for the pulse duration of 1 ms as a function of the IGZO film thickness. For each thickness, ten devices at different locations on a die were measured.

The influence of the IGZO film thickness on the threshold voltage of writing (i.e., the minimum pulse voltage required to produce a current increase by 4 orders for a given pulse duration) has been examined. Figure 5 shows the threshold voltage as a function of the film thickness for the pulse duration of 1 ms. As expected, the threshold voltage decreases with decreasing film thickness. However, as shown in the same figure, the corresponding electric field increases as the film thickness decreases, indicating that a larger electric field is required for a thinner IGZO layer to switch from the OFF state to the ON state. This observation can be explained as follow. As pointed out early, O_2 plasma treatment reduces oxygen vacancies in IGZO surface layer.¹⁰ The impact of the reduction in oxygen vacancies in a thinner IGZO layer would be more significant than that in a thicker IGZO film with the same amount of O_2 plasma treatment on the surface. The CFs connecting the top and bottom electrodes are more difficult to formed in a thinner IGZO layer due to the reduction of oxygen vacancies in the surface region. Thus, a high electric field is required for switching from the OFF state to the ON state to occur in a thinner IGZO layer.

In conclusion, a WORM memory device based on a simple Al/IGZO/Al structure with good performance has been demonstrated. Its memory operation is based on the switching from an OFF state to an ON state by applying a voltage pulse. The device has a normally OFF state with a very high resistance due to the reduction of oxygen vacancies in the film surface region by the O_2 plasma treatment. An ON state is achieved when CFs connecting the two electrodes are formed due to the regeneration of the lost oxygen vacancies in the IGZO surface region under the influence of the applied field. A sufficiently large memory window (e.g., with the ON/OFF current ratio of $\sim 10^4$) can be achieved by applying a low-voltage pulse (e.g., 7 V) with short duration (e.g., 1 μs). The WORM memory has good data-retention and reading-endurance capabilities.

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