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Flexible Write-Once–Read-Many-Times Memory Device Based on a Nickel Oxide Thin Film


Abstract—A write-once–read-many-times (WORM) memory device based on conduction switching of a NiO thin film in a metal–insulator–metal structure is fabricated on a flexible substrate. The device can be switched from a low-conductance state (unprogrammed state) to a high-conductance state (programmed state) with the formation of conductive filament(s) in the NiO layer. The two memory states can be easily distinguished at a very low reading voltage. For example, at the reading voltage of 0.1 V, the current ratio of the state programmed at 3 V for 1 µs to the unprogrammed state is larger than 10⁴. The WORM device exhibits good reading-endurance and data-retention characteristics. The flexible device is promising for low-cost and low-power archival storage applications.

Index Terms—memory, NiO, switching, WORM.

WRITE-ONCE–READ-MANY-TIME (WORM) memory devices have been used in many types of permanent archival storage devices, such as the rapid archival storage of video images and radio-frequency identification tags, where high-power-consumption and large-volume magnetic or optical disk drives are not acceptable. Some studies on WORM memory devices based on polymer, small molecular materials, or hybrid inorganic/organic nanocomposites have been reported in recent years [1]–[6]. Recently, a WORM device based on AlN thin film containing Al nanocrystals, which is compatible with the silicon CMOS technology, was demonstrated [7], and it was also shown that Al-rich Al₂O₃ thin film can be used for the WORM applications [8], [9]. On the other hand, NiO has been reported for resistive-random-access-memory applications based on its conduction switching properties [10]–[12]. Conduction switching mechanism for the NiO film has been studied [13], [14]. The conductive filament (CF) concept has been popularly used to explain the conduction switching in NiO films. Joule heating is considered playing an important role in the formation and the rupture of CF in the NiO films [15], [16]. In this brief, a flexible WORM device based on conduction switching of a NiO thin film in a metal–insulator–metal (MIM) structure is fabricated on a flexible substrate. The device exhibits a large memory window at very low reading voltage, good reading endurance, and long data retention.

The starting material was the DuPont Melinex ST504 125 µm-thick polyester (PET) flexible substrate; 300-nm Au/270-nm Ni were deposited on the substrate by electron-beam vaporization as the bottom electrode. Then, a 100-nm polycrystalline NiO film was deposited on the bottom electrode by pulse laser deposition (PLD). The PLD was carried out with a NiO target of 99.9% purity in an oxygen environment of 0.5 pa at room temperature. The laser frequency was set to 3 Hz, and the voltage of the laser source was 21.5 kV; 300-nm Au/270-nm Ni with an area of about 0.25 mm² were deposited on the NiO thin film by electron-beam vaporization through a metal shadow mask as the top electrode. The device structure is illustrated in Fig. 1. In addition, to investigate the influence of NiO thickness on device performance, WORM devices with various NiO film thicknesses (150, 180, and 200 nm) were also fabricated. Electrical characterizations were carried out with a Keithley-4200 semiconductor characterization system by applying a voltage between the bottom and top electrodes and measuring the current. The current compliance was set to either 0.1 or 0.01 A.

Fig. 2 shows the current–voltage (I–V) characteristics of the WORM device obtained by sweeping the voltage from 0 to

Fig. 1. Schematic illustration of the WORM device fabricated on a plastic substrate.

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0.5 V. As shown in this figure, the device is in a low-conductance state initially, and the application of the voltage of 1 V for 1 ms leads to no significant change in the current conduction. However, the application of the voltage of 3 V for 1 ms leads to a huge increase in the current (e.g., the current measured at 0.1 V is increased by $\sim 5$ orders). This indicates that the conduction of the oxide film can be switched to a high-conduction state under a higher voltage as a result of the formation of CFs. WORM memory device can be realized based on the significant change in the current conduction. In other words, one memory state is represented by the low-conduction state (the unprogrammed state), and a high-conduction state (the programmed state) is achieved by applying a sufficiently high and wide voltage pulse (i.e., the writing voltage in the WORM operation). For example, the currents measured at a reading voltage of 0.1 V before and after the writing at 3 V for 1 ms represent two well-distinguished states. The current ratio of the state after writing to the state before writing is about $10^5$.

The switching behaviors observed in this brief can be explained with the CF model [15], [16]. At the initial state (i.e., the low-conductance state), no CF existed in the NiO film, and the current is at a low level of $\sim 10^{-8}$ A. A pulse of 3 V for 1 ms leads to the formation of CF in the NiO film as a consequence of Joule heating [15], [16]. Thus, a high-conduction state (the programmed state) is achieved. The formation of CF(s) is considered as the origin of the memory state switching in the NiO film. Thermal effect plays an important role in the formation and the deformation of the filament(s). In the programming process, the material and/or structure in certain regions/parts (e.g., ruptured filament) of the oxide film are modified by voltage-induced Joule heating, leading to the formation of CF.

A study on the memory performance has been conducted, as discussed below. Fig. 3(a) shows the current measured at a reading voltage of 0.1 V as a function of writing voltage for a fixed duration of 1 $\mu$s and (b) as a function of writing time for a fixed writing voltage of 3 V.

Fig. 4(a) shows the data retention characteristics of the device at room temperature. The currents measured at 0.1 V for the initial state (the unprogrammed state) and the state after writing (the programmed state) as functions of the waiting time are presented. Within the time frame of $1 \times 10^4$ s, the initial state and the state after writing do not show any significant degradation at the reading voltage of 0.1 V at room temperature. This indicates that the device has an excellent data retention capability, and it can be expected that a sufficient long retention time (e.g., ten years) is achievable. Fig. 4(b) shows the reading endurance of the WORM device. No significant degradation is observed after $10^5$ reading operations at 0.1 V for both the initial state and the state after writing. This indicates that, as the reading voltage of 0.1 V is far below the threshold voltage required for changing the initial state, the reading operation itself does not cause a significant impact on the memory states.
To test the flexible characteristic and mechanical robustness of the WORM devices fabricated on PET substrate, the substrate was repeatedly bent to form a semicircular shape for 100 times, and data-retention and reading-endurance characteristics of the devices after 100 times of bending were measured. No significant degradation caused by the bending was observed. Fig. 5(a) and (b) show the data-retention and reading-endurance characteristics after 100 times of bending, respectively. The programming and reading conditions here are the same as those used for the experiments of the unbent devices shown in Fig. 4. As can be observed in Fig. 5, although the devices have experienced 100 times of bending, their good data-retention and reading-endurance capabilities are maintained.

As shown in Fig. 6(a), the state written at +3 V for 1 µs does not revert to the state before writing (i.e., the initial state) after the application of 100 pulses of +0.6 V and 0.1 s. The current compliance is set to 10 mA in the writing process, i.e., in the operation of +3 V for 1 µs. This also explains why the reading operation at +0.1 V does not change the memory states as previously discussed. The current is reduced by more than 1 order (from ∼10 to ∼0.5 mA) to a new state after the application of the several pulses of +0.6 V and 0.1 s, and the new state does not show obvious change with the number of readings. The current ratio of the new state to the initial state is still larger than 3 orders. This confirms the irreversible of the writing process, and the WORM device based on the writing process always has a large window to distinguish the two memory states. If a larger current compliance is used during the writing operations, permanent CFs will be formed. In this case, the programmed state will be permanently maintained. In Fig. 6(b), the current compliance is set to 100 mA in the writing process, i.e., in the operation of +3 V for 1 µs. The application of 100 pulses of +0.6 V and 0.1 s does not have a significant impact on the permanent CFs, and thus, it does not cause a significant change in the current of the programmed state, as shown in Fig. 6(b).

The influence of the NiO film thickness on the device characteristics and memory performance has been investigated. Fig. 7 shows the minimum magnitude of a voltage pulse with the pulsewidth of 5 ms required for a successful programming as a function of the film thickness. Ten devices from different locations on the substrate were selected for the experiment. As shown in Fig. 7, the minimum magnitude of the voltage pulse increases as the thickness of NiO film increases. To maintain the electric field (in the order of 1 × 10^5 V/cm as estimated from Fig. 7) required for the programming switching, a larger voltage is of course needed for a thicker oxide. The current of the programmed state (measured at 0.1 V) is larger for a thinner oxide layer. For example, as shown in Fig. 8, although the currents before the writing are about the same for the two oxide thicknesses (150 and 200 nm), the current after the writing for the 150-nm oxide is about 1 order larger than that for the 200-nm oxide. Note that the writing voltage is 1.7 and 2.3 V for the 150- and 200-nm oxides, respectively, yielding about the same writing electric field (∼1.1 × 10^5 V/cm). A larger current of the programmed state for a thinner oxide layer could be due to the fact that the CF associated with the programmed state is shorter.
Fig. 6. Influence of the application of 100 pulses of $+0.6$ V and $0.1$ s on the programmed state with different current compliances in the writing process (i.e., in the operation of $+3$ V for $1$ $\mu$s). Current compliance of (a) 10 and (b) 100 mA.

Fig. 7. Minimum pulse voltage required for a successful writing as a function of NiO film thickness. The pulsewidth is fixed at 5 ms. Ten devices were measured for each NiO thickness.

In conclusion, a NiO film in the MIM structure is used to realize a flexible WORM memory device fabricated on a plastic substrate. The device can be switched from a low-conductance state (unprogrammed state) to a high-conductance state (programmed state) by applying a voltage pulse with sufficiently large magnitude and pulsewidth (e.g., 3 V and 1 $\mu$s). The two memory states can be easily distinguished at a very low reading voltage (e.g., 0.1 V). The WORM device exhibits good reading-endurance and data-retention characteristics. It is promising for low-cost and low-power archival storage applications.

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