Characteristics on electrical resistance change of Ag doped chalcogenide thin film application for programmable metallization cell

Hyuk Choi · Ki-Hyun Nam · Yong-Woon Koo · Hong-Bay Chung

Abstract Programmable Metallization Cell (PMC) Random Access Memory is based on the electrochemical growth and removal of nanoscale metallic pathways in thin films of solid electrolyte. This paper investigates the resistance change characteristics with applied voltage bias on Ag/Ge–Se and Ag/As–Se chlacogenide thin film structure and describes the electrical characteristics of PMC-RAM made from these materials following annealing at 150 °C. As a result, it was obtained that $R_{\text{reverse}}/R_{\text{forward}}$ ratio which represent by reversible resistance change was about 10^6, which ratio value can be get a high sensing margin when PMC-RAM detect the data. PMC-RAM technology promises to be non-volatile, low current and potentially, low cost for the next generation of nonvolatile memory application such as RFID chip to replace EEPROM.

Keywords PMC (Programmable Metallization Cell) · ReRAM · Ag-doped · Chalcogenide · Amorphous

1 Introduction

Amorphous chalcogenide thin films have attracted much attention as a new advanced and replaceable technology material because of their interesting electrical, optical and thermal properties including resistance and reflectance change [1–2]. Especially, phase change nonvolatile memory is emerging as one of the candidate for the next generation of memory devices on amorphous chalcogenide thin film.

Phase change nonvolatile memory array based on chalcogenide material was originally reported from the beginning of 1970 [3].

Phase change nonvolatile memory utilize the electrical resistance difference between amorphous and crystalline state, while rewritable compact disk (CD)/digital versatile disk (DVD) take advantage of the optical reflectivity difference.

We have been studied the development of new composition of PRAM device for the low power, fast recording velocity, high sensing margin [4] and the improvement of hologram grating diffraction efficiency for 3D real-time optical information mass-memory storage medium on amorphous chalcogenide thin films [5].

As we have been studied the improvement of hologram grating diffraction efficiency on chalcogenide thin film with metallic Ag doped, it was found to need that the information recorded by a holographic method was reduced or erased by the thermal, optical and electrical erasing methods for the rewritable optical information device. Among predicted three methods, it was found that the electrical erasing effect of holographic data by electrical bleaching in amorphous chacogenide films is thought to be one of the promising rewritable technology for the optical recording of information with high stable holographic grating density [6]. Analyzing the basic mechanism, we investigated the resistance of Ag doped chalcogenide thin film varied by applied voltage bias direction from about 1 MΩ to several tens Ω. As well as the opposite direction voltage bias applied, the resistance value return to higher value.

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As the result of these resistance change effect, it was found that these effect were agree with Programmable Metallization Cell–RAM (PMC-RAM) [7].

It has been demonstrated that Programmable Metallization Cell (PMC) memory shows great promise as a future low energy non-volatile solid state memory [8]. The technology utilizes the electrochemical formation and removal of metallic pathways in thin films of solid electrolyte. Key attributes are low voltage/low current operation, high speed, excellent scalability, retention and endurance, and a simple fabrication sequence within the back-end-of-line (BEOL) flow.

Device formation involves the dissolution of mobile metal in a chalcogenide or oxide base glass to create a solid electrolyte. An oxidizable metal layer and an inert electrode formed in contact with the electrolyte film creates a device in which information is stored via electrical changes caused by the oxidation of the metal electrode and reduction of metal ions in the electrolyte.

If electrodes are formed in contact with this photodiffused layer, an anode which has oxidizable metal and an inert cathode, and a voltage is applied between them, the positively charged metal ions will migrate toward the cathode region. At small applied bias (much less than 1 V) in structures which are commensurate with state-of-the-art integrated device geometries, the ions will come out of the photodiffused layer at the cathode to rapidly form a stable metallic electrodeposit which may be made to extend from the cathode to the anode. The low resistance metal electrodeposit acts to short-out the relatively high resistance glass and hence the overall resistance of the structure can be reduced by many orders of magnitude via this non-volatile electrically stimulated deposition process. A reverse bias will cause electrodissolution of the metal link, returning the device to a high resistance state and this write–erase cycle may be repeated many tens of millions of times. This reversible switching effect is the basis of the programmable metallization cell (PMC) memory technology.

2 Experimental

A $Ge_{25}Se_{75}$ and $Ge_{30}Se_{70}$ bulk glasses was fabricated by a conventional melt quenching technique. The constituent elements Se and Ge weighed in given atomic-weight percentage ratios were sealed in evacuated quartz ampoules, which were then placed in a furnace and heated at 220, 650, and 1000 °C for 2, 2, and 24 h, respectively. Then the ampoules were constantly stirred during these periods to achieve a complete homogenization of the constituents in the melt and quenched in water. The PMC test structure for photo-doping process, represented schematically in Fig. 1, comprises a bottom inert electrode, the solid electrolyte,
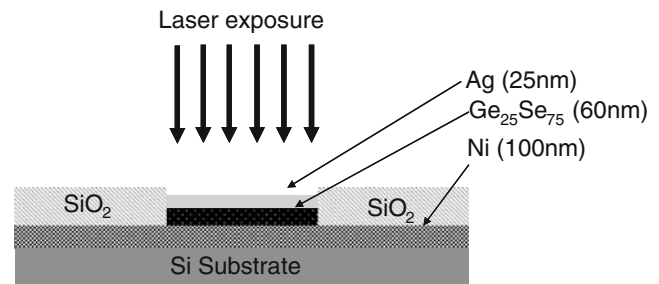

Fig. 1 Schematic process of photo-doping for PMC-RAM device

and a oxidizable metal layer. The electrodes are separated by a dielectric and a via in this layer defines the electrolyte area that contacts the bottom electrode.

To fabricate the test structures for the current work, a 100 nm thick nickel layer was deposited by electron beam evaporation on silicon dioxide grown on silicon substrates and covered with 100 nm of silicon dioxide. Vias ranging in diameter 100 μm were defined in this deposited dielectric using optical projection lithography and lift-off. The chalcogenide-based electrolyte was formed after via etch by depositing a 60 nm thick $Ge_{25}Se_{75}$ and $Ge_{30}Se_{70}$ base glass layer followed by a 25 nm thick layer of Ag, both by physical vapor deposition(thermal evaporation) under high vacuum (10^{-6} Torr) conditions.

The Ag was then dissolved into the base glass by photodissolution at room temperature using exposure to ultraviolet light from a 405 nm broadband source with an energy density at the wafer surface of 1 J/cm^2. Following dissolution, an additional 100 nm of Ag was added to ensure a continuous oxidizable source for electrodeposition and this also acted as the top electrode. A heat treated and non-treated film device was fabricated to accomplish the measurement of change of their electric field. The devices were annealed at 150 °C in N_2 with a few %O_2 (RTA, MILA-3000) for 15 min to assess the effect of relatively harsh annealing conditions on device performance. Figure 2 shows a completely PCM device after fabricated top electrode.

Electrical characteristics of the test devices were obtained by connecting the electrodes, via tungsten probes held in micromanipulators in a vibration and electromagnetic interference-isolated probe station, to a semiconductor parameter analyzer (SPA—Agilent 4155B). Voltage double
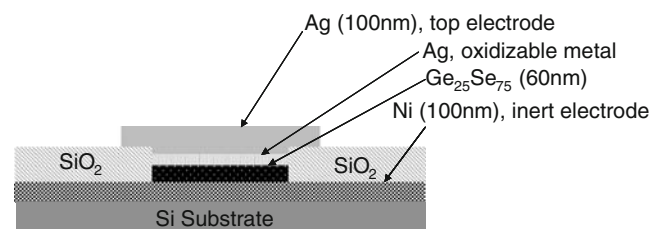

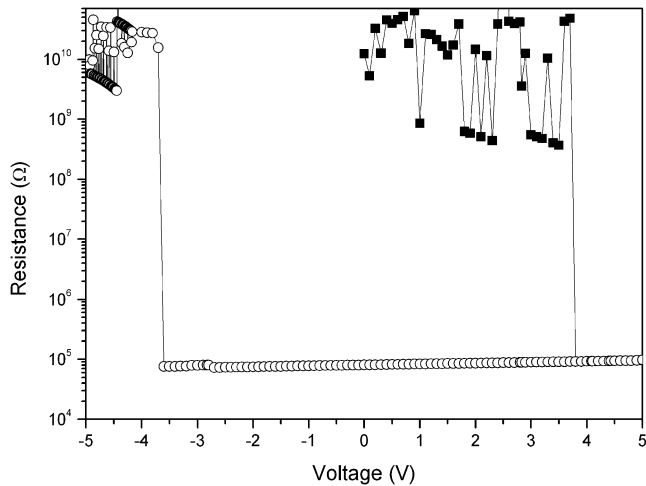**Fig. 2** Schematic cross-sectional view of completely PMC-RAM device

Fig. 3 Resistance-voltage plot of Ag-doped $Ge_{30}Se_{70}$ device at as-deposited. Voltage sweep is 0 to +5.0 to −5.0 V

sweeps were carried out starting at maximum reverse bias (Ni electrode positive, Ag electrode negative), sweeping through zero to an appropriate forward voltage (Ni electrode negative, Ag electrode positive), and sweeping back again through zero to the reverse bias starting point. The acquired data was saved in digital format for subsequent plotting and analysis.

3 Results and discussion

Figure 3 shows a representative resistance–voltage plot of Ag-doped $Ge_{30}Se_{70}$ electrolyte at as-deposit. The voltage sweep was 0 to +5.0 to −5.0 V and the current limit is 50 μA. The device switches at 3.76 V from an off-state resistance, R_{off}, above 10^{10} Ω to an on-state resistance, $R_{on}=$ 90 kΩ, more than six orders of magnitude lower for this programming current. The device transition to a high
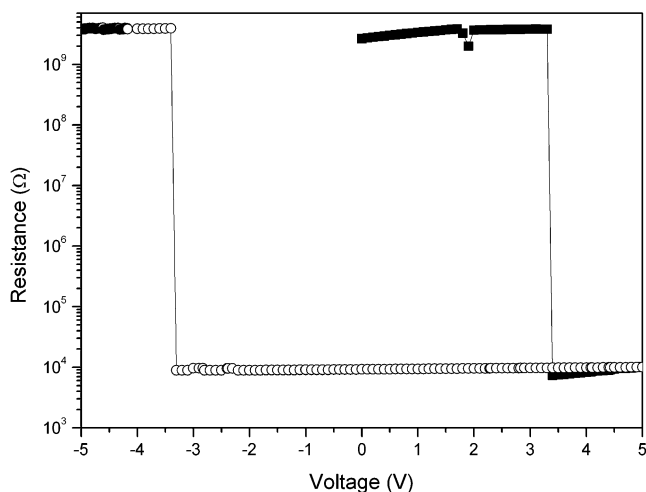

Fig. 4 Resistance–voltage plot of Ag-doped $Ge_{30}Se_{70}$ device which has been annealed at 150 °C. Voltage sweep is 0 to +5.0 to −5.0 V

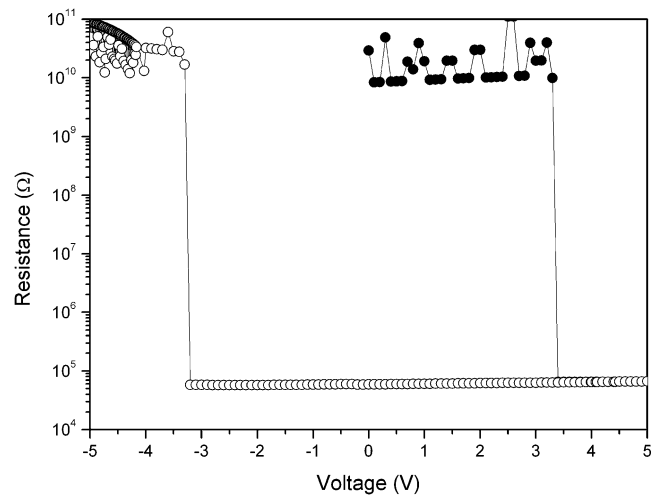**Fig. 5** Resistance–voltage plot of Ag-doped $Ge_{25}Se_{75}$ device at as-deposited. Voltage sweep is 0 to +5.0 to −5.0 V

resistance state occur at −3.69 V. Continuing the negative sweep, the off resistance remains above 10^{10} Ω as the voltage is swept out to −5.0 V.

It was reported that a metallic thin film formed amorphous chalcogenide which is irradiated by light is showing physical and chemical changes by doping and diffusion methods by ion or atom of metal. This phenomenon is called "Photo-doping." At 1990, Kolobof and Elliott tried to examine this phenomenon in a thin film through electrical resistance change. In this case, because of VAPs' doping by electrical combine of defect-pair of chalcogenide thin film which is diffused by photo-dissolution of Ag ion in the chalcogendie, the electro-resistance is sharply decrease and maintain low resistance state by the irradiation of induced light. We used an electrical energy to induce Ag ion to diffuse beside optical energy.

As a result, it maintained low resistance state (a bond of Ag^+ ion—VAPs) at forward bias and high resistance state
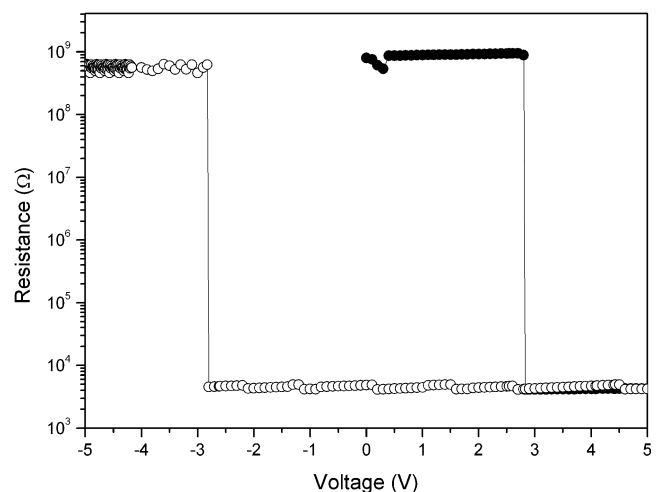

Fig. 6 Resistance-voltage plot of Ag-doped $Ge_{25}Se_{75}$ device which has been annealed at 150 °C. Voltage sweep is 0 to +5.0 to −5.0 V

(Ag^+ density change by the destruction of bond) at reverse bias. We induced Ag doping phenomenon by electrical energy at amorphous chalcogenide thin film.

Figure 4 describes a resistance–voltage plot of Ag-doped $Ge_{30}Se_{70}$ electrolyte which has been annealed at 150 °C for 15 min in N_2/O_2. An initial resistance value was 10^9 Ω at fabricated device. Until initial 3.32 V, it was changed near initial resistance value while at 3.31 V shown sharply changed resistance of about 8 kΩ in the same time of voltage apply. The low resistance state was maintained until 5 V. Repeatedly, the device switches at -3.34 V from an on-state resistance above 8 kΩ to an off-state resistance, 10^9 Ω.

Figure 5 gives an example of resistance–voltage plot of Ag-doped $Ge_{25}Se_{75}$ electrolyte at as-doped. An initial resistance value of fabricated device was 10^{10} Ω. For forward bias experiment, it decreased resistance about 60 Ω at 3.26 V. When it was applied reverse bias, it could explore a change of resistance about 10^{10} Ω at -3.23V in same device. The voltage bias switched the device from its off-state resistance above 10^{10} Ω to an on-state around 60 kΩ, a difference of over six orders of magnitude. This result showed that the Ag-doped $Ge_{25}Se_{75}$ devices could also be switched with low voltage bias compared to Ag-doped $Ge_{30}Se_{70}$. It is considered that it is relatively more effective photo-doping efficient at Ag-doped $Ge_{25}Se_{75}$ devices.

Figure 6 shows a resistance–voltage plot of Ag-doped $Ge_{25}Se_{75}$ electrolyte which has been annealed at 150 °C for 15 min in N_2/O_2. The voltage sweep ran from 0 to 5.0 to -5.0 V and the current limit was 50 µA as before. The device is operating even after this harsh anneal but it is clear that the off state resistance is smaller at -0.5 V than in the case of different devices and the write threshold has been reduced from 3.26 to 2.76 V. We believe that excess Ag diffusion in the electrolyte from the oxidizable electrode is largely responsible for these effects.

4 Conclusion

We have investigated the new type of Programmable Metallization Cell–RAM (PMC-RAM) using metallic Ag-doped amorphous chalcogenide $Ge_{25}Se_{75}$ and $Ge_{30}Se_{70}$ thin films for the next generation of nonvolatile memory applications. As a result, the technology stores data in a Ag based chalcogenide thin film. These devices have excellent switching characteristics application for programmable metallization cell. We have confirmed that switching characteristics of as-doped PMC devices but off-state resistance was unstable. A as-doped PMC device annealed at 150 °C also exhibit good switching characteristics with a lower.

Finally, the Ag-doped $Ge_{25}Se_{75}$ devices, annealed at 150 °C, could also be switched with low voltage bias (-2.83, $+2.76$). Especially, the most obvious difference between this result and that obtained from the $Ge_{30}Se_{70}$ devices were that the on-state resistance is lower for Ag-doped $Ge_{25}Se_{75}$ device.

This PMC-RAM technology promises to be non-volatile, low current and, potentially, low cost for the next generation of non-volatile memory applications such as RFID chips to replace EEPROM.

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