Solid Electrolytes Characteristics Based on Cu-Ge-Se for Analysis of Programmable Metallization Cell

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Programmable Metallization Cell (PMC) Random Access Memory is based on the electrochemical growth and removal of electrical nanoscale pathways in thin films of solid electrolytes. In this study, we investigated the nature of thin films formed by the photo doping of copper ions into chalcogenide materials for use in programmable metallization cell devices. These devices rely on metal ions transport in the film so produced to create electrically programmable resistance states. The results imply that a Cu-rich phase separates owing to the reaction of Cu with free atoms from chalcogenide materials.

Keywords : Programmable metallization cell, Solid electrolyte, Super-ionic region, Chalcogenide

1. INTRODUCTION

The layer of solid electrolyte which can be called a core of PMC presents more broad applications of amorphous chalcogenide material[1-3]. A super-ionic region that plays a role of a seed to form a route of conduction is formed if metallic ions are injected into the chalcogenide thin film in the state of amorphous which has very low conductivity.

A super-ionic region formed inside chalcogenide thin film plays a role that can flow or block current. PMC realizes a memory cell of completely different mechanism by using characteristics of electrolyte of chalcogenide thin film[5-7]. Semiconductors using amorphous chalcogenide material already bear fruits in PRAM. PRAM by principle forming on-state and off-state by inducing phase change between amorphous and crystalline materials of chalcogenide thin film is impending for commercialization.

Chalcogenide material is paid attention to as new material to be used for solar cells, thin film transistors and etc. as well as memory components, and especially the characteristic of electrolyte in solid state applied to PMC is thought to be possible for the application to super-minimized high-performance second batteries.

PMC components of Ge-Se doped with Ag ions were studied with help of the previous studies and copper was used for metallic ions taking into account of economy of components[7].

2. EXPERIMENTS

2.1 Manufacturing of bulk materials

$Ge_{25}Se_{75}$ bulkglass samples were prepared 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 hours, respectively. Then the contents of the ampoules were constantly stirred during these periods to achieve a complete homogenization of the constituents in the melt and quenched in water.

2.2 Manufacturing of PMC devices

As for manufacturing components, after the inert electrode(Ni, 1000 Å) to be used as lower electrode was attached in ratio of attachment of 5 Å/s on the p-type Si plate using an e-beam evaporator system, on that, SiO_2(2000 Å) to be used as insulation layer was attached using sputter.

After forming a pattern on the attached insulation, via-holes were formed using Reactive Ion Etching(RIE) system. On that, chalcogenide to be used as layer of solid electrolyte and Cu layer were attached without breaking out using e-beam evaporator system. The thickness of chalcogenide was attached by 1000 Å and Cu was attached by 200 Å. Ni to be used as upper electrode was attached to the manufactured sample using e-beam evaporation system after going through process of light diffusion on it.

For PMC, it goes through light diffusion process after chalcogenide and mobile metallic layer are formed before forming an upper electrode. Figure 1 shows a sectional drawing in the stage of light exposure of the manufacturing procedure. For light diffusion process, it was exposed to DPSS(Diode Pumping Solid State) laser(532 nm) and He-Ne laser(632.8 nm) which have different wave lengths in order to compare electrical characteristics of PMC memories according to light sources.

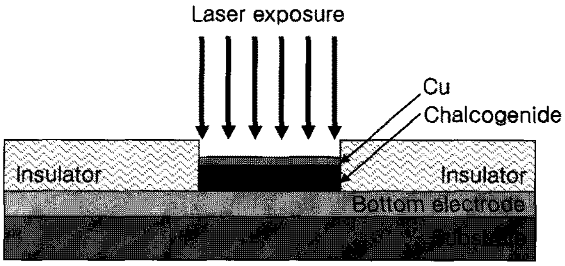

Fig. 1. Photo-doping process of Cu ions.

2.3 Photo-doping of activation ions

It has been known that light sensitivity is increased, index of refraction increases generally and efficiency of diffraction also increases because lattices are formed better than single chalcogenide thin film if a metal(Ag, Cu) is doped on chalcogenide hyaline material.

In the present study, amorphous chalcogenide-line thin film doped with Cu was manufactured by formation of lattices of refraction and the study regarding the characteristics of waveguide was proceeded.

Light diffusion of Cu ions was induced using holography lithography methods as Fig. 2. Lattices of refraction were formed in a transmission-type holography method as Fig. 2 in a sample not gone through light diffusion.

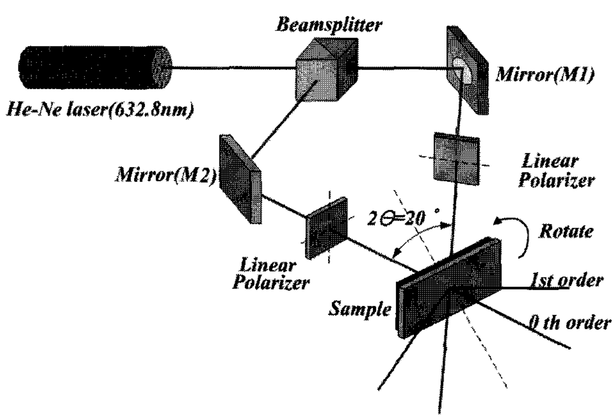

Fig. 2. Schematic views of experimental setup for formation of diffraction gratings.

In the experiment procedure above, a experiment to find out the characteristic of conductivity was proceeded by forming lattices of refraction using DPSS laser and He-Ne laser.

Figure 3 is a figure showing a cross section of a completed component.

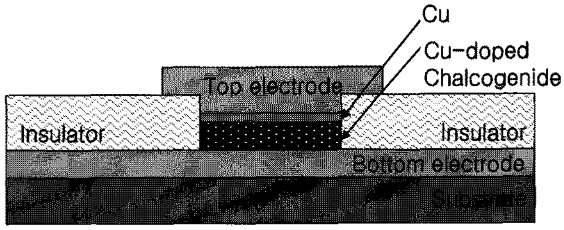

Fig. 3. Schematics of optical exposure process.

2.4 Electrical characteristics of PMC devices

For the electrical characteristic of PMC memory devices, the variation of resistance with varied voltage from -5 V to +5 V was measured using semiconductor parameter analyzer(SPA-agilent 4155B).

Positive voltage to the lower electrode and negative voltage to the upper electrode up to 0 V in reversed bias was applied individually and reversely at 0 V in forward bias, negative voltage to the lower electrode and positive voltage to the upper electrode was applied individually. This is done because bias direction affects formation and removal of the conducting path formed inside chalcogenide layers with voltage applied.

3. RESULTS AND DISCUSSIONS

3.1 Characteristics of Cu-doped PMC device

In the present study, a study on the characteristic of light diffusion of Cu to use PMC memory was executed. Efficiency of diffusion of Cu metal according to light sources was studied using DPSS laser and He-Ne laser as light sources used for light diffusion.

Figure 4 shows the relation curve of resistance-voltage of a Cu-doped $Ge_{25}Se_{75}$ component gone through a procedure of light diffusion by DPSS laser. As shown in the figure, it was manufactured in the state that initial resistance is high of about 10^9 Ω. Switching was confirmed as when positive bias was applied to the component, high resistance state was maintained and resistance decreased abruptly at 3.3 V. At this point, when negative bias was applied gradually, switching to high resistance state happened at -3.55 V.

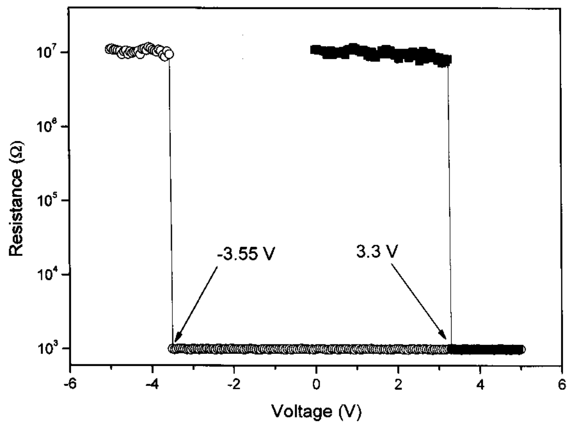

Fig. 4. Resistance-voltage plot of Cu-doped $Ge_{25}Se_{75}$ electrolyte exposed to DPSS laser. The voltage sweep was 0 V to +5.0 V to -5.0 V.

Figure 5 shows resistance change when voltage is applied to a Cu-doped $Ge_{25}Se_{75}$ component light-diffused by He-Ne laser. As shown in the figure, voltage for switching to on-state as shown as 4.55 V and voltage for switching from low resistance state to high resistance state was shown as -4.65 V. Comparing with the component of Fig. 4, the amplitude of switching voltage appeared relatively high.

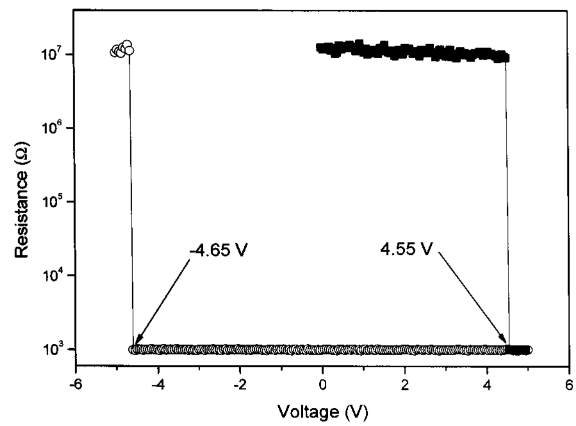

Fig. 5. Resistance-voltage plot of Cu-doped $Ge_{25}Se_{75}$ electrolyte exposed to He-Ne laser. The voltage sweep was 0 V to +5.0 V to -5.0 V.

This is thought to be affected by diffusion of Cu metal according to waves of laser on procedure of light diffusion into the inside of Cu-metal chalcogenide thin film, and in the case of a laser of long wavelength like He-Ne laser, the procedure of light diffusion is thought to be accomplished smoothly.

3.2 The devices formed with holographic diffraction gratings

Figure 6 shows an appearance of the surface of refraction lattices formed by holography method as Fig. 2 with light source of He-Ne laser using AFM.

Fig. 6. The AFM image of holographic diffraction gratings.

Figure 7 is a figure showing resistance change of a PMC device whose refraction lattices were formed using DPSS laser. The voltage for switching from initial high resistance state to on-state appeared as 2.95 V, and the voltage for switching from low resistance state to high resistance state appeared as -3 V. The amplitude of the switching voltage appeared relatively low comparing with the result of Fig. 4. This is thought to show that Cu ions are not diffused into chalcogenide thin film irregularly and it is made by regular diffusion like the shape of formed refraction lattices.

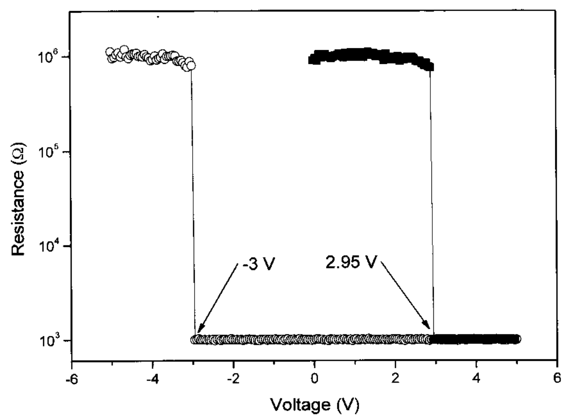

Fig. 7. Resistance-voltage plot of Cu-doped $Ge_{25}Se_{75}$ electrolyte formed diffraction gratings of DPSS laser.

Figure 8 is a figure showing resistance change of a PMC device whose refraction lattices are formed using He-Ne laser. The voltage for switching from initial high resistance state to on-state appeared as 3.8 V, and the voltage for switching from low resistance state to high resistance state appeared as -3.85 V. The characteristic of switching voltage was highly improved comparing with the result of Fig. 5, but it is thought to be affected by wavelength of light source seeing from the worse result than that by DPSS laser.

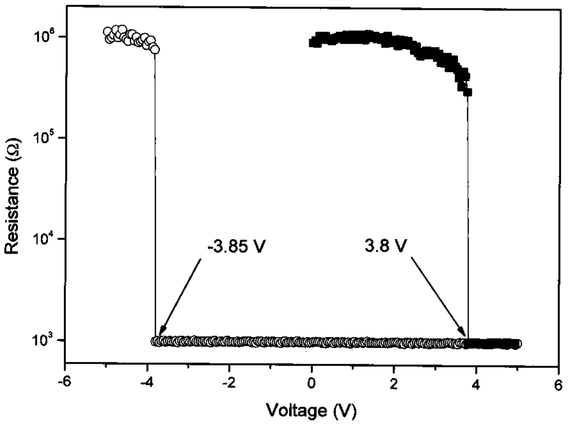

Fig. 8. Resistance-voltage plot of Cu-doped $Ge_{25}Se_{75}$ electrolyte formed diffraction gratings of He-Ne laser.

4. CONCLUSION

In the present study, we measured the electrical characteristics of a PMC component using amorphous chalcogenide $Ge_{25}Se_{75}$ and Cu. And also components were manufactured applying a method to form holographic refraction lattices to light diffusion of Cu ions and the characteristics were measured. Cu ions injected into the inside of thin film form super-ionic region playing a role to enable current to flow in amorphous chalcogenide thin film and become a core to make them have a characteristic of electrolyte.

It was confirmed that components manufactured with DPSS laser with relatively short wavelength have better switching characteristic than He-Ne laser which has a long wavelength, and seeing from the fact that they have different electrical characteristics individually according to wavelengths of light sources, the conclusion could be obtained that wavelengths influence diffusion of Cu ions.

Also, light diffusion of Cu ions was tried applying a method forming holography refraction lattices. From Fig. 6, cross stripes with regular intervals are seen to be formed in different colors. The formed refraction lattices have different index of refraction by the light counterbalancingly interfered with the light supplementally interfered, and it can be thought that when Cu ions are diffused into the inside of chalcogenide thin film, they show better switching characteristics as super-ionic region is formed in the shape with regularity.

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REFERENCES

[1] J. Hajto, P. J. S. Ewen, R. E. Belford, and A. E. Owen, "Interference grating fabrication in spin-coated As_2S_3 films", Thin Solid Films, Vol. 200, p. 229, 1991.

[2] M. N. Kozicki, S. W. Hsia, A. E. Owen, and P. J. S. Ewen, "Pass - a chalcogenide-based lithography scheme for I.C. fabrication", J. Non-Cryst. Solids Vol. 137-138, p. 1341, 1991.

[3] T. Kawaguchi, S. Maruno, and S. R. Elliott, "Photoinduced surface deposition of metallic silver in Ag---As---S glasses: effect of addition of other elements", J. Non-Cryst. Solids, Vol. 212, p. 166, 1997.

[4] M. N. Kozicki, C. Gopalan, M. Balakrishnan, M. Park, and M. Mitkova, "Non-volatile memory based on solid electrolytes", Proceedings of the 2004 Non-Volatile Memory Technology Symposium, p. 10, 2004.

[5] R. Symanczyk, M. Balakrishnan, C. Gopalan, T. Happ, M. Kozicki, M. Kund, T. Mikolajick, M. Mitkove, M. Park, C.-U. Pinnow, J. Robertson, and K.-D. Ufert, "Electrical characterization of solid state ionic memory elements", Proceedings of the 2003 Non-Volatile Memory Technology Symposium, p. 17-1, 2003.

[6] M. N. Kozicki, M. Park, and M. Mitkova, "Nanoscale memory elements based on solid state electrolytes", IEEE Trans. Nanotechnology, Vol. 4, No. 3, p. 331, 2005.

[7] H. Choi, S. M. Koo, W. J. Cho, Y. H. Lee, and H. B. Chung, "Properties on electrical resistance change of Ag-doped chalcogenide thin films application for programmable metallization cell", J. of KIEEME(in Korean), Vol. 20, No. 12, p. 1022, 2007.