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Switching memory cells constructed on plastic substrates with silver selenide nanoparticles

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Abstract Programmable metallization cell (PMC) memory is a kind of next generation non-volatile memory that has attracted increasing attention in recent years as a possible replacement for flash memory. In spite of the considerable amount of research focused on the fabrication of non-volatile memories on plastic substrates with lightweight, thin, and bendable characteristics, there have been few studies on the fabrication of PCM memory on flexible substrates. In this study, we synthesized Ag_2Se nanoparticles (NPs) by a positive-microemulsion method and constructed PMC memories on plastic substrates with programmable layers formed by the spin-coating of the Ag_2Se NPs. To the best of the knowledge, this is the first attempt to construct PMC memory on plastic substrates by the spin-coating of Ag_2Se NPs. The Ag_2Se NPs synthesized in this study had a uniform size of 2 nm and interestingly showed α-phase (high temperature phase) stability at room temperature. Switching behaviors were observed through the voltage scanning on the fabricated memories with applicable switching voltages. However, the resistance ratios of the off-state to the on-state were quite small. The possible reasons for the α-phase stability of the Ag_2Se NPs at room temperature and the detailed memory characteristics will be described in this article.

Introduction

As one of the most promising candidates for non-volatile memory and as an alternative to flash memory, programmable metallization cell (PMC) memory has been widely researched recently, due to its key attributes such as its low voltage/low current operation, high speed, excellent scalability, retention, and endurance [1–4]. PMC memory is also called conductive bridge random access memory or electrolytic memory, because it uses the fast migration of cations in a solid-state electrolyte. That is, PMC memory functions by the build-up or break-up of a conducting path (or bridge) between the electrodes according to the polarity of the applied voltage. Various metal-chalcogenides with ionic conductivity have been studied as potential PMC materials [5–7]. Especially, silver selenide (Ag_2Se) is one of the widely investigated metal-chalcogenide materials for use in PMC memory, owing to its attractive properties [8–12].

Ag_2Se normally exists in the orthorhombic β-phase (low temperature phase) which is a narrow bandgap ($E_g = 0.07$ eV at -273 °C) semiconductor with high electrical conductivity [8]. On the other hand, at temperatures above 133 °C, the phase of Ag_2Se turns into the cubic α-phase (high temperature phase) which is a metallic compound with superionic characteristics [9]. This phase transition is known to be reversible [10] and, therefore, Ag_2Se has been widely investigated for use as a phase change material in non-volatile phase change random access memory [11]. In addition, there have been several attempts to apply the superionic properties of α-Ag_2Se to non-volatile switching memory or PMC memory [1, 12].

Ag_2Se thin films can be deposited by various methods [11, 13, 14]; however, they are generally high-cost, high temperature, and/or low throughput processes. Ag_2Se films can also be formed by the spin-coating of Ag_2Se nanoparticles (NPs). As one of the solution processes for film formation, the spin-coating of NPs enables the above-mentioned disadvantages of the other deposition methods

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to be overcome. More importantly, spin-coating enables films to be formed easily on plastic substrates at low temperature with high throughput, because it uses two essentially independent steps, namely, the synthesis of the NPs and the formation of the films [15]. There has been growing interest in the fabrication of electronic devices on plastic substrates, due to their lightweight, thin, and bendable features [16–18], and some researchers have reported on non-volatile memory devices fabricated on plastic substrates [19–21]. However, to the best of the knowledge, there have been no reports so far on the fabrication of PCM memory on a plastic substrate through the spin-coating of NPs, although a few studies have been conducted on the fabrication of PCM memory on a plastic substrate [22].

We constructed vertically stacked simple PMC memory structures on plastic substrates for the first time through the spin-coating of Ag_2Se NPs. Among the various methods suggested for the synthesis of Ag_2Se NPs [24–26], we used a positive-microemulsion method [23], because it can produce uniform-sized Ag_2Se NPs at low temperature. After the construction of the memory devices on the plastic substrates, we examined their electrical properties, in order to confirm the feasibility of Ag_2Se nanoparticle (NP)-based PMC memory as an emerging non-volatile memory technology.

Experimental

Synthesis of Ag_2Se NPs

Ag_2Se NPs were prepared by a positive-microemulsion method [23] as follows. First, 0.10 g of NaOH and 1.9 mL of linoleic acid (LA, $C_{17}H_{31}COOH$, Sigma-Aldrich Inc.) were dissolved in a mixture solution of de-ionized (DI) water (15 mL), ethanol (15 mL), and *n*-hexane (1 mL) to form a microemulsion. Then, 0.17 g of $AgNO_3$ dissolved in 5 mL of DI water was added to the solution while applying vigorous stirring. The solution quickly turned into a milky Ag^+-containing emulsion. 5 mL of Na_2SeSO_3 solution was injected into the solution. The Na_2SeSO_3 solution, as a selenium source, was prepared by sonicating selenium powder (0.40 g) and Na_2SO_3 (0.63 g) in de-ionized water (50 mL) for 1 h. The Ag^+-containing emulsion immediately changed from milky to black and was stirred for a long time. Then, 20 mL of *n*-hexane was added to destroy the microemulsion and extract the LA-coated Ag_2Se NPs into the oil phase. After the completion of the extraction, the oil phase containing the LA-coated Ag_2Se NPs was centrifuged to obtain Ag_2Se NPs after adding ethanol. In order to remove the LA residues on the surface of the NPs, the centrifuged NPs were washed several times by dispersing them in *n*-hexane and centrifuging the resulting dispersion with the addition of ethanol. Finally, the synthesized Ag_2Se NPs were re-dispersed in n-hexane for storage and their size and composition were confirmed by high-resolution transmission electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS) analyses, respectively. In order to examine their crystal structure, the Ag_2Se NPs were coated on Si substrates and annealed at 100 or 130 °C for 5 min in N_2 ambient. Then, the crystal structure of the NPs was characterized by X-ray diffraction (XRD) analysis.

Fabrication of Ag_2Se NP-based memory cells on plastic substrates

A polyethersulfone substrate was used as the plastic substrate for the fabrication of an Ag_2Se NPs-based memory cell in this study. A cross-linked poly-4-vinylphenol (C-PVP) buffer layer was formed on the substrate using the same procedures as those described in the previous study [15]. A bottom Au electrode was formed on the C-PVP layer using a photolithography process and a thermal evaporation method. Before the thermal evaporation process, UV/ozone treatment was applied to promote the adhesion between the substrate and the electrode and facilitate the lift-off of the photo-resist. A solution of *n*-hexane in which Ag_2Se NPs were dispersed was spin-coated on the substrate. Before the formation of the top Au electrode, the samples were annealed at 100 °C for 5 min in N_2 ambient. Then, the top Au electrode was formed on the Ag_2Se NP-layer in the same manner as that of the formation of the bottom electrode. The size of the contact area was $50 \times 50\ \mu m^2$. A cross-sectional schematic and an optical top-view image of the fabricated memory cell are presented in Fig. 1. The electrical characteristics were obtained for the fabricated memory cell with an Agilent 4155C semiconductor parameter analyzer. All measurements were made at room temperature in the dark in air.

Results and discussion

The HRTEM image of the Ag_2Se NPs synthesized in this study is shown in Fig. 2. Uniformly distributed crystalline NPs with a relatively uniform diameter of 2 nm are observed in the image. The composition of the NPs estimated from the EDS analysis corresponds to a ratio of Ag to Se of 2:1 (Se 34%, Ag 66%), indicating that the NPs synthesized in this study are stoichiometric Ag_2Se.

The XRD patterns of the as-synthesized and annealed Ag_2Se NPs are presented in Fig. 3. It can be seen in the figure that the peaks are considerably broader than those of the bulk powders or nanowires of Ag_2Se. The broadening of the XRD peaks is normally related to the smaller size of

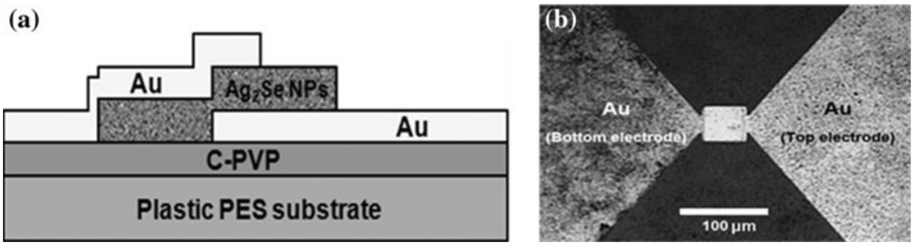

Fig. 1 **a** Cross-sectional schematic and **b** optical image of the fabricated vertically stacked Ag_2Se NP-based memory cell

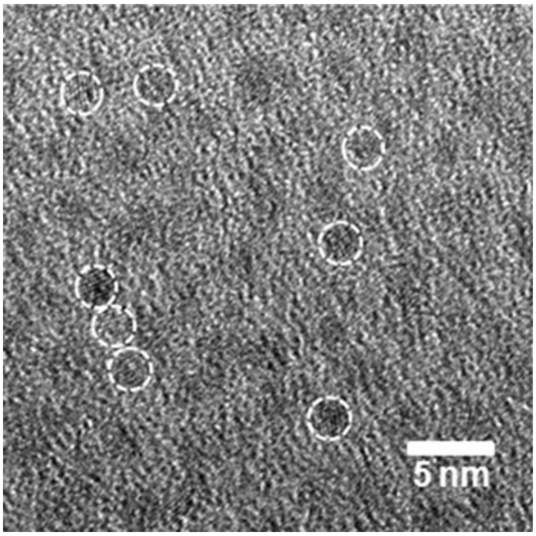

Fig. 2 HRTEM image of the Ag_2Se NPs synthesized by a positive-microemulsion method. The clearly observed NPs are indicated by *white circles*

the particles. Although the small size of the NPs synthesized in this study (about 2 nm) results in the broadening of the XRD peaks, their crystal structure can be roughly identified. For the as-synthesized Ag_2Se NPs, the broad peak at a 2θ value of about 33° can be indexed as the merged (112) and (121) peaks of the β-phase (low temperature phase) from the JCPDS data (no. 20-1041). The β-phase is the only phase generally observed in the as-synthesized Ag_2Se nanostructures [23, 25, 26]. However, interestingly, there are other peaks that cannot be indexed as β-Ag_2Se at 2θ values of about 36° and 45°. These peaks can be indexed as the (200) and (211) peaks of α-Ag_2Se (high temperature phase) from the JCPDS data (no. 76-0135). The formation of α-Ag_2Se is noteworthy, because β-Ag_2Se is thermodynamically stable at room temperature [27]. However, it has also been reported [28] that the α-phase exists in Ag_2Se film when its thickness is below 15 nm. Since the size of the synthesized NPs in this study is as small as about 2 nm, the existence of α-Ag_2Se is possible, while the co-existence of the α-phase and β-phase is not clearly understood. The stability of the α-phase at room temperature is a very desirable characteristic for PMC applications, because it has superionic properties, as described above. In the XRD pattern, there is an additional Ag (111) peak at a 2θ value of about 38° (JCPDS data, no. 04-0738). It was reported that metallic Ag specks appear when orthorhombic β-Ag_2Se is transformed into cubic α-Ag_2Se [29]. When the film is annealed at 100 °C for 5 min, the intensity of the α-Ag_2Se peaks increases, while that of the β-Ag_2Se peak decreases. This implies that the phase transformation from β-phase into α-phase occurs during annealing, while the reverse phase transformation (α to β) occurs less during cooling to room temperature. Since it is generally believed that the complete reverse phase transformation (α to β) occurs during cooling, our observation is unusual. However, a recent study [12] reported that Ag_2Se nanowires consist predominantly of α-phase with some β-phase after they are heated over their phase transition temperature and subsequently cooled to room temperature, possibly due to the small domain size and/or the large contribution of the surface energy of the nanowires. In addition, after the Ag_2Se NPs are annealed at 100 °C, the intensity of the Ag peak increases. This may be attributed to the phase transition of the Ag_2Se NPs. The newly observed peak at a 2θ value of about 43° in the pattern of the annealed Ag_2Se corresponds to metallic Ag (200). There is no distinct difference between the film annealed at 100 °C and that annealed at 130 °C except for the growth of the Ag peaks. Based on these XRD results, during the fabrication of the memory cell, the spin-coated Ag_2Se NPs were annealed at 100 °C for 5 min in N_2 ambient prior to the formation of the top electrode, in order to maximize the fraction of α-phase in the NPs-based film.

The electrical characteristics of the vertically stacked memory cell were examined in terms of the current (I) versus applied voltage (V) in the range of −1 V to 1 V. The I–V curves obtained by repeated voltage scanning are presented in Fig. 4. The I–V curves reveal the representative switching behavior of the PMC memory device. The switching behavior is of interest, because the electrodes of the memory cell are made of an inert metal (i.e., Au). In general, PMC memory devices have metal source layers (e.g., Ag or Cu) sandwiched between the electrodes or their electrodes consist of one metal source electrode (e.g., Ag or Cu) and another inert metal electrode [2, 5, 6], although there have been few reports showing switching behavior without any metal source layer [11, 12]. In the case of the memory cell, it may be that the metallic Ag observed in the

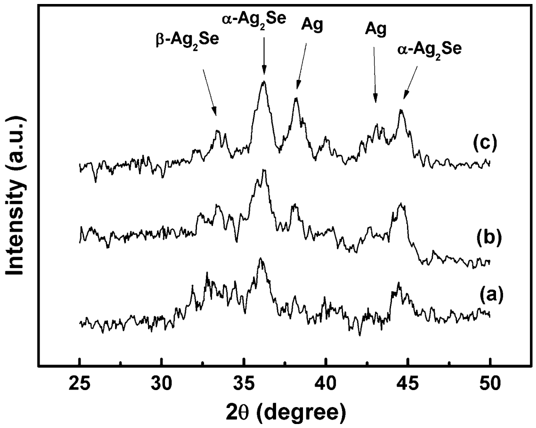

Fig. 3 XRD patterns of (*a*) the as-synthesized Ag_2Se NP-based thin film and the films annealed (*b*) at 100 °C or (*c*) at 130 °C

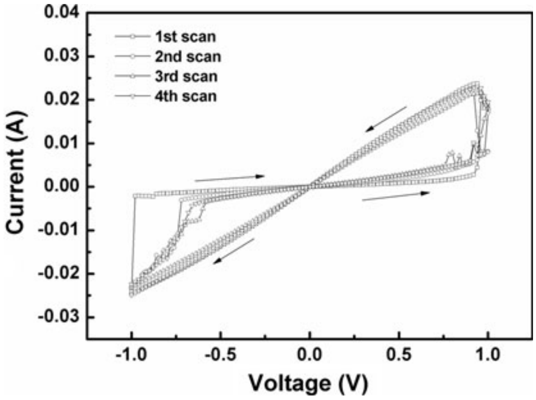

Fig. 4 The *I*–*V* curves obtained by repeated voltage scanning the range of -1 to 1 V. Every scan starts at 0 V in the positive direction

XRD pattern of the Ag_2Se NPs annealed at 100 °C (Fig. 3) acts as a metal source, resulting in the switching behavior. Now, let us explain the switching behavior in detail. The voltage was first applied in the positive direction (0–1 V). Below a voltage of about 0.9 V, the cell maintains its high-resistive off-state ($R_{off} = 5.4 \times 10^2$ Ohm). At a voltage of about 0.9 V, instantaneous switching from the off-state to the low-resistive on-state ("write" in terms of device operation) occurs. This implies that a conducting bridge between the top and bottom electrodes is built-up by the migration of Ag ions. Then, the voltage was applied in the negative direction (1 to -1 V). The cell remains its on-state ($R_{on} = 3.7 \times 10$ Ohm) until the applied voltage reaches -1 V. However, as soon as the voltage is applied in the positive direction (-1 to 0 V), the immediate switching from the on-state to the off-state ("erase" in terms of device operation) occurs, resulting from the break-up of the conducting bridge and the dissolution of Ag into the solid-state electrolyte matrix. These switching characteristics were repeatedly observed during the voltage scanning with R_{off}/R_{on} ratios of about 4 (for the third scan) $\sim$14 (for the first scan). These R_{off}/R_{on} ratios are relatively small compared to those reported in other studies, in which ratios about 5–6 orders of magnitude higher were obtained. The reason for the small ratio obtained herein is not understood and further investigations are needed to clarify this and to increase the ratio to a level suitable for the application of the devices as non-volatile memories. In addition, the "write" (about 0.9 V) and "erase" voltages (about -1 V) are higher and lower than the generally reported values of below 0.4 V and above -0.4 V, respectively [2, 30, 31]. For logic applications, a high switching voltage of over 1 V between the two states is desirable, because the switching voltage should be higher than the operation voltage of logic circuits [3]. Therefore, the memory cells fabricated in this study are more applicable to logic circuits in terms of the switching voltage. These high "write" voltage and low "erase" voltage may be caused by the relatively slow Ag migration in the film composed of Ag_2Se NPs. That is, even if the Ag ions migrate relatively freely in α-Ag_2Se [32], the interfaces constructed between the NPs may obstruct the free migration of Ag ions, resulting in a decrease of the migration speed and, consequently, the slowdown of the build-up or break-up speed of the conductive bridge in the film composed of Ag_2Se NPs.

Conclusions

Ag_2Se NP-based PMC memory devices were constructed on plastic substrates by the spin-coating of Ag_2Se NPs. The Ag_2Se NPs synthesized by a positive-microemulsion method have a uniform size of about 2 nm. The XRD analysis of the as-synthesized and annealed NPs revealed that the Ag_2Se NPs exist mainly in the form of a superionic α-phase at room temperature giving them the potential to be used as a PMC material. From the repeated voltage scanning on the PMC memory cell, *I*–*V* curves showing the representative switching behavior of PMC memory were obtained with applicable "write" and "erase" voltages of about 0.9 and -1 V, respectively, due to the restriction of the free migration of the Ag ions at the interfaces of the NPs. However, the resistance ratios of the off-state to the on-state are as small as 4–14 with a scan-to-scan variation. Although this ratio needs to be improved and the other memory characteristics, such as the retention and endurance, still need to be investigated, this study is meaningful in that it confirms, for the first time, the feasibility of fabricating PMC memory devices on plastic substrates by the spin-coating of Ag_2Se NPs.

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