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Investigation of the resistive switching in Ag_xAsS_2 layer by conductive AFM

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ABSTRACT

In this paper, a study of resistive switching in Ag_xAsS_2 layer, based on a utilization of conductive atomic force microscope (AFM), is reported. As the result of biasing, two distinct regions were created on the surface (the conductive region and non-conductive region). Both were analysed from the spread current maps. The volume change, corresponding to the growth of Ag particles, was derived from the topological maps, recorded simultaneously with the current maps. Based on the results, a model explaining the mechanism of the Ag particle and Ag filament formation was proposed from the distribution of charge carriers and Ag ions.

1. Introduction

Conducting-Bridge Random-Access Memory (CBRAM) or programmable metallization cell (PMC) shows a great promise for future non-volatile solid state memories [1]. Such A memory cell comprises a metal/insulator/metal (MIM) structure, in which a solid electrolyte is inserted between an active metal electrode (Ag or Cu) and an inert metal electrode (Pt or W) [2]. Chalcogenide compounds doped with Ag or Cu, such as Ag- or Cu- doped Ge-Se, Ge-S, have been commonly used as the solid-state electrolyte till now [3,4,5].

The doping of Ag or Cu species into a chalcogenide thin layer can be done by either co-sputtering or optically induced diffusion and dissolution (OIDD) [4]. OIDD is a mature technology to introduce Ag species into chalcogenide thin layer and has been widely studied for the step profile of Ag concentration by the Rutherford Back Scattering [5]. The mechanism for OIDD is currently understood as the counter diffusion of photo generated holes and Ag^+ ions within an ionic conductor [6]. However, OIDD may cause a deposition of Ag particles onto the surface of thin layer [7].

A resistive switching memory cell is based on a formation and dissolution process in the conductive filament, due to the redox reactions between active electrode and mobile ions [8]. When an active electrode (e.g. represented by a Ag thin layer) is positively biased during the set process, the following steps are involved: (i) oxidation of the Ag electrode; (ii) drift of Ag ions toward the inert electrode; (iii) reduction of Ag^+ ions; (iv) growth of the Ag filaments. Once the Ag filaments connect both electrodes, the memory cell will be switched from the high resistivity state to the comparably lower resistivity state. When the polarity is exchanged, the filaments can be electrochemically dissolved under a certain corresponding negative bias, changing the low resistivity state of the memory cell back to the high resistivity state [9].

The in situ growth of the conductive filament has been observed in previous literature by TEM, either from the top view of planar cell or from the cross-sectional view of a vertically aligned cell. Fruitful information has been obtained, including the direction of filament growth. In addition, a physic model for the filament growth was derived from experimental observations [10,11].

The study of surface modification has been done by STM, especially to Ag or Cu doped chalcogenide compound. Utsugi demonstrated a high resolution STM etching of Ag-S films, showing promising application on lithography and data storage [12]. Since then, Ohto and Tanaka reported a STM image of geometrical surface modification on the Cu(Ag)-chalcogenide glasses [13]. In addition, Hosaka et al. utilized scanning probe microscope (STM, AFM) to fabricate a magnetic domain on Pt/Co multilayer magnetic film, further proving the feasibility of SPM on data storage [14].

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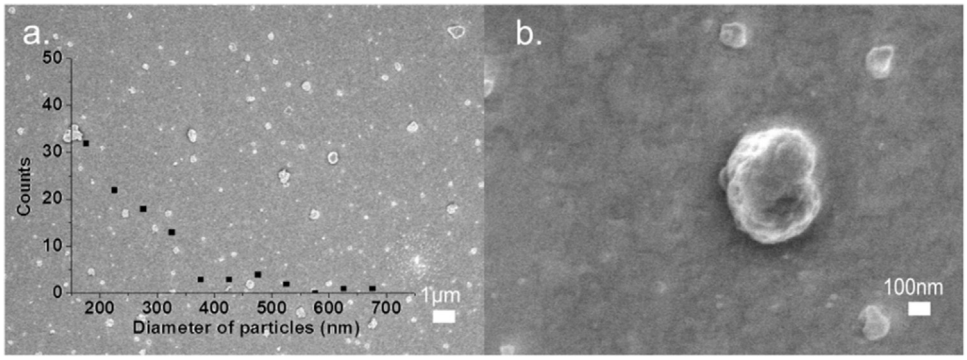

Fig. 1. (a) SEM image of Ag particles grown on the Ag_xAsS_2 layer by OIDD (the inset shows the Ag particle size distribution on the layer), (b) an enlarged SEM image showing Ag particle in detail.

Previous literature reported that also a conductive atomic force microscopy (c-AFM) can be utilized for an investigation of the resistive switching cell. Schindle et al. introduced a conductive AFM image of topographical and current map on the $Ag/Ge_{0.3}Se_{0.7}$ bilayer thin film, which the conductive area is in spot shape [15]. And Pradel et al. showed a similar conductive AFM images of current and topographical map with conducting spot and non-conducting boundary on $Ag/Ge_{0.25}Se_{0.75}$ thin layer [16]. However, in both these papers, Ag doping and diffusion within the chalcogenide layer leading into creation of conductive filaments was achieved purely by applying a bias on the layer using c-AFM tip [15,16].

In the present work, however, we utilized a c-AFM to study an influence of the applied bias on the evolution of the cell morphology, in particular on the non-conductive region within Ag_xAsS_2 layer. Based on the obtained topological maps and evaluated spread current maps, a model explaining the formation of conductive regions and surface particles is proposed forward.

2. Experiment

For the preparation of the thin layers, silica glass was utilized as the starting substrate. Approx. 300 nm thin Ag layer and 165 nm thin AsS_2 layer were evaporated sequentially. The as-deposited insulating AsS_2 thin layer on Ag layer was then modified into an ion-conducting Ag_xAsS_2 layer by OIDD process through the light emitted from a Hg lamp for 20 min under N_2 atmosphere (purity 4 N). Herein, the Ag electrode was used as the source of Ag ion within photo-diffusion process.

Morphology of the thin layers (cells) was investigated by a scanning electron microscope (JEOL JSM7500F), and further analysed by ImageJ software. The resistive switching of the cells was evaluated by a conductive atomic force microscope (AFM Solver Pro M, NT-MDT; Russia) with a silicon probe coated with the Cr/Pt layer, scanning first from 10 mV to 100 mV and then from −10 mV to −100 mV with bias step 30 mV. The probe was defined as the negative electrode and Ag layer as positive electrode. The current flow in this work was considered from the positive electrode to the negative electrode. The tapping mode was selected to investigate i) the in situ surface morphology of the memory cell, in particular volume changes and ii) the spread currents. The screened area had a size of $3 \times 3\ \mu m^2$. The scanning frequency was 0.6 Hz with a resolution 256×256 pixels and the duration of bias was set as 0.3 ms.

3. Results and discussion

Fig. 1 shows the surface morphology of the cell. As one can see, the surface consists of Ag particles (with different dimensions) grown on the Ag_xAsS_2 layer by the OIDD process. Based on the particle size evaluation, shown in Fig. 1a, it can be seen that counts of particles decrease (from more than 30 to less than 5) with the increasing diameter of particles (from less than 200 nm to more than 650 nm). Moreover, the particles are uniformly distributed over the surface of whole cell. Fig. 1b shows an enlarged image of the Ag particles. From these observations, it can be deduced the Ag particles grow up with a different speed or different growth time upon the illumination (using OIDD).

Fig. 2 shows a sequence of topographical maps and spread current maps recorded on the surface of Ag_xAsS_2 in various periods of the switching cycle. In the 2D topological map shown in Fig. 2a, it was recorded before any external bias was applied to the cell. Three extra-large spots can be distinguished that represent Ag particles created on the Ag_xAsS_2 layer by OIDD. However, the corresponding spread current map in Fig. 2a revealed induced current without applied bias. The current flows in both defined positive and negative direction, due to photo generated surface charge (electrons, holes, etc.), in the similar way as xerographic photoreceptor within copying machines [17].

Fig. 2b corresponds to the case, when a bias of 70 mV was applied to the cell. It can be seen that almost no volume change occurred under this bias. However, the corresponding spread current map shows an apparent current increase, compared with the map in Fig. 2a, where current flows mainly around the Ag particles. The recorded current in this case stems form a number of trapped electrons due to the fact that the sample was exposed on a daily light for a short time between the OIDD process and the c-AFM measurement (to set up the tip). It is not yet a current that could be assigned to the initial stage of the filament growth.

Fig. 2c corresponds to the case, when a bias of 100 mV was applied to the cell. Compared with results of Fig. 2a and b, a whole range of new particles with different size appeared on the surface. In addition, the initial 3 spots were also expanded in size. In our opinion, these changes can be attributed to reduction of the Ag ions (from Ag_xAsS_2 layer) on the cells surface due to applied bias [18]. In addition, the current increased considerably compared to the 70 mV bias shown in Fig. 2b. By comparison of maps in Fig. 2c, one can see that the current flows not through the newly grown surface particles, but rather around. This is likely due to the fact, that at this surrounding area, newly grown Ag filaments are presented within the Ag_xAsS_2 layer. In other words, the current map shows dark regions exactly on the same areas, where particles are present. However, the conductive and nonconductive region in current map shows an opposite distribution, compared with that in literature introduced above [15,16], as the current flows through spots, rather than through the edges of spots. Obviously, such difference might be caused by the Ag doping ions though OIDD.