$Si_2Sb_2Te_5$ phase change material studied by an atomic force microscope nano-tip*

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Abstract: The $Si_2Sb_2Te_5$ phase change material has been studied by applying a nano-tip (30 nm in diameter) on an atomic force microscopy system. Memory switching from a high resistance state to a low resistance state has been achieved, with a resistance change of about 1000 times. In a typical *I–V* curve, the current increases significantly after the voltage exceeds ~4.3 V. The phase transformation of a $Si_2Sb_2Te_5$ film was studied *in situ* by means of *in situ* X-ray diffraction and temperature dependent resistance measurements. The thermal stability of $Si_2Sb_2Te_5$ and $Ge_2Sb_2Te_5$ was characterized and compared as well.

Key words: phase change; electrical probe storage; $Si_2Sb_2Te_5$
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1. Introduction

The phase change random access memory (PCRAM) is considered to be one of the most promising candidates for the next generation of non-volatile semiconductor memories[1, 2]. Although it will be commercialized in the near future, the performance of PCRAM still needs to be improved. Great efforts have been made to develop novel high performance phase change materials. Many kinds of phase change materials have been proposed in the past two decades[3, 4]. In our group, $Si_2Sb_2Te_5$ (SST) phase change material has been studied for PCRAM applications[5], and an SST-based PCRAM array with an electrode contact size of 260 nm in diameter has been fabricated by a standard 0.18-μm CMOS technology[6, 7]. The device shows a more outstanding performance as compared with the conventional $Ge_2Sb_2Te_5$ (GST) based one. RESET and SET times of 10 and 31 ns, respectively, have already been achieved[7]. It is well known that Moore's law will still be valid in the coming decade. According to the references available, the programming power of PCRAM decreases as the contact area shrinks[8], which is accompanied by a reduction in the programming volume. To achieve a lower programming power, the phase change volume in PCRAM cell must be reduced continuously. Hence, the characterization of phase change materials on the nanometer scale is important for both the phase material research and the PCRAM development beyond the 90 nm-CMOS technology. The atomic force microscope (AFM) is a kind of powerful scientific equipment with a nano-sized conductive tip, with which electrical signals can be applied to a film sample. Although GST has been widely studied by AFM[9], no studies of the electrical properties of SST using an AFM system have been reported.

On the other hand, the electrical probe storage memory is currently attracting a great deal of attention since the demonstration of "Millipede" system, in which a thermomechanical probe was used for programming[10]. This technology is considered to be a potential alternative for higher density memories. Recently, an ultra-high-density phase change storage memory has been demonstrated with a density of about 3.3 Tb/inch^2, which is three orders of magnitude denser than currently achievable commercial optical storage technologies[11]. Consequently, the electrical probe storage is another important application area for phase change materials. The study of the electrical properties of SST using an AFM nano-tip is of great significance not only for PCRAM, but also for electrical probe storage applications.

2. Experiments

In this work, firstly, the physical properties of an SST film are studied. Secondly, an electrical probe storage cell based on an SST film is demonstrated by using an AFM system (NT-MDT NTEGRA Prima SPM, Russia). The size of the used AFM tip (DCP11, made by NT-MDT, Russia) has a diameter of about 30 nm. The physical and structural properties of the SST are studied by means of an *in situ* temperature dependent

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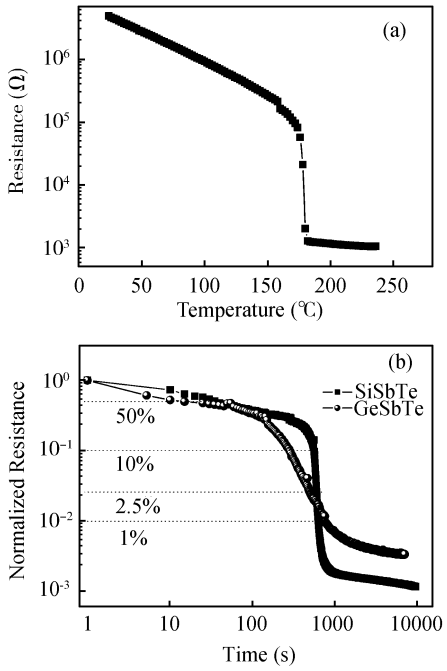

Fig. 1. (a) Electrical resistance of the SST film as a function of temperature, with a heating rate of 15 °C/min; (b) Normalized resistance of GST and SST as a function of time when the baking temperature is 160 °C.

resistance measurement and *in situ* X-ray diffraction (XRD). Time-resolved XRD, with which the structural transformation during the annealing process could be followed *in situ*, is an important tool for the research of phase change materials[12]. In addition, the dependencies of the adhesion strength between the GST/SST and the TiN electrode were studied by applying nano-scratch testing on a Nano Indenter® system[13, 14]. In the experiments, the surfaces of these films are scratched by a Berkovich diamond-tip and tested via the LFM (lateral force measurement) groupware of the MTS Nano Indenter® system. Additionally, the tip radius of the curvature is less than 50 nm. The vertical load increases linearly in the range of 500 μm from 100 μN to 100 mN, and the horizontal movement of the tip has a velocity of 10 μm/s. This article describes the critical load for the vertical load.

An SST film with a thickness of about 100 nm was deposited on TiN (40 nm)/Ti (100 nm)/Si and SiO_2/Si substrates by co-sputtering Si, Sb, and Te targets. The background pressure and the Ar gas pressure were 1×10^{-4} and 0.21 Pa, respectively. The composition of the SST film was determined by means of energy dispersive spectroscopy (EDS). According to the EDS results, the as-deposited film has a composition of Si : Sb : Te = 2 : 2 : 5 (atomic ratio).

3. Results and discussion

The resistivity as a function of the temperature for the SST film is shown in Fig. 1(a). The heating rate in the test was fixed at 15 °C/min. As shown in the figure, the resistance of the SST decreases with increasing temperature, with a steep drop around the crystallization temperature. The crystallization temperature (T_c) is identified as the temperature at which the derivative of the resistance with respect to the temperature (dR/dT) reaches the minimum value. According to the measurement, T_c is about 175 °C for SST. The data retention of the SST film was characterized by an evaluation of the time-dependent resistance change under a constant temperature baking at 160 °C. The SST films for the measurement were pre-coated with a 5 nm-thick SiO_2 layer to avoid the films from oxidating and evaporating during the baking process. The normalized resistance as a function of time is shown in Fig. 1(b)[15]. As shown in the figure, the retention time of SST is about two times longer than that of GST, when the 10% resistance drop criterion is applied. (The retention of the SST and the GST will be similar if a 1% criterion is used.) However, it is well known that the resistance contrast between the high-resistance-state and the low-resistance-state is only about two orders of magnitude in the applications of PCRAM[16]. Hence, the 10% resistance drop criterion would be more suitable for the PCRAM and electrical probe storage applications.

Table 1. Adhesion strength between the GST/SST film and the TiN electrode measured by the nano-scratching method.

Film	As-deposited	250 °C
$Si_2Sb_2Te_5$	93.8 ± 2.6	22.0 ± 3.6
$Ge_2Sb_2Te_5$	25.0 ± 3.6	8.0 ±0.1

The adhesion strength between the SST/GST and the TiN electrode was determined by applying a Nano Indenter® system. The critical load determined by the system is shown in Table 1. According to the table, the critical loads for the amorphous SST and GST samples are about 93.8 and 25.0 mN, respectively. In contrast, for the polycrystalline samples, the values are 22.0 and 8.0 mN for GST and SST, respectively. Obviously, the adhesion strength between the SST and the TiN electrode is higher than that between the GST and the TiN. Besides, the experiment also implies that the adhesion strength value between the phase change material and the electrode decreases when the phase change material (both GST and SST) crystallizes. The adhesion strength between the phase change materials and the electrodes is extremely important for electrical probe storage applications. A higher adhesion strength will lead to more reliable performance. Compared with GST, amorphous SST is a better candidate due to its higher adhesion strength to the TiN electrode.

In situ XRD was employed to study the structural properties of the SST film during the heating process. The SST film was heated in the *in situ* XRD setup at a rate of 20 °C/min, and the diffracted peak intensities were recorded with the linear detector over a 2θ range of 10°–60°. According to the XRD patterns shown in Fig. 2, the SST film changes from an amorphous structure to a polycrystalline structure when the temperature exceeds ~200 °C. As shown in Fig. 2, the polycrystalline structure at 200 °C is a face-centered cubic one. The film will change to the hexagonal state when the temperature is higher than 250 °C according to the XRD results.

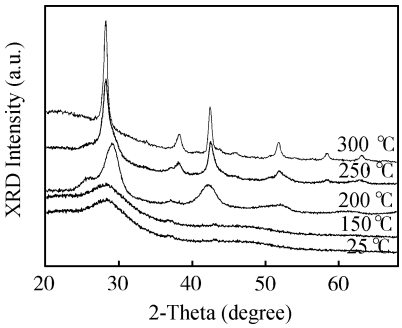

Fig. 2. *In situ* XRD patterns of SST during the heating process.

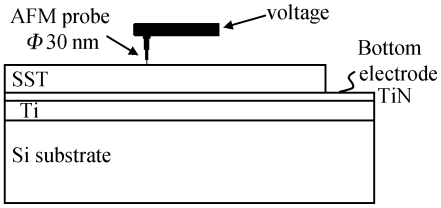

Fig. 3. Schematic of the SST based electrical probe storage system.

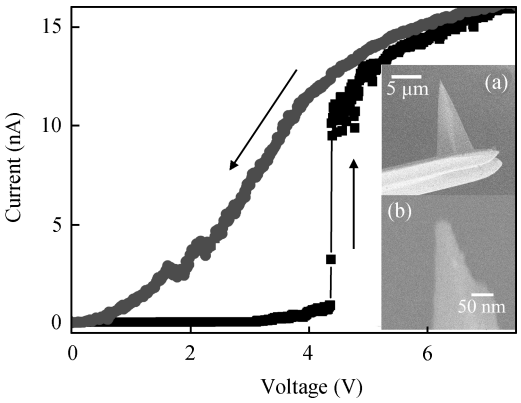

Fig. 4. Typical *I–V* curve of the electrical probe storage cell based on SST. Inset figures (a) and (b) are the SEM images of the AFM tip.

The schematic of the electrical probe storage system using an SST phase change media is shown in Fig. 3. As mentioned above, the thicknesses of the SST, TiN, and Ti layers are 100, 40, and 100 nm, respectively. The AFM tip employed in the demonstration has a diameter of 30 nm. The inset figures in Fig. 4 show the scanning electron microscopy images of the AFM tip used in the experiment. An *I–V* characterization is carried out on the AFM system. As shown in Fig. 4, the current increases significantly when the applied voltage exceeds ~4.3 V. The resistance contrast between the high-resistance-state and the low-resistance-state is about 1000 times (both values are read at 3 V), which is large enough for electrical probe storage applications. However, the current is small, as shown in Fig. 4. Several reasons are proposed for the small current value (in range of nA). (1) The AFM tip is coated with a doped diamond layer with a conductivity of about 1 Ω·cm. (2) The AFM tip has a small size, leading to a high resistance according to the formula: $R = \rho l/s$, where R is the resistance, ρ the resistivity of the film, l the film thickness, and s the contact area. (3) The SST film in this demonstration is relatively thick, compared with the diameter of the AFM tip. However, the current value is similar to the available reference[17]. Switching from the low-resistance state to the high-resistance state is important for the storage application. However, it is difficult to apply an electrical pulse to the film sample through the nano-tip in our AFM system, making the switching impossible at present. Further work is still under way. A detailed study of the electrical probe storage on the SST will be carried out, including an optimization of the films thickness, the conductivity of the AFM tip, the coating dielectric material, and so on.

4. Conclusions

In this work, we have studied the physical properties of SST by means of *in situ* temperature dependent resistance and XRD measurements. A prototype electrical probe storage cell based on SST phase change material was demonstrated using an AFM system. The switching from the high-resistance-state to the low-resistance-state has been achieved with a resistance contrast of about 1000 times.

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