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Compositional optimization of binary Selenium-Antimony films for low-power electrical and optical storage

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ABSTRACT

Composition dependence of structural, electrical and optical properties of binary Selenium-Antimony films was investigated for electrical and optical nonvolatile memories with low power and high speed. For preferred $Sb_{51}Se_{49}$ and $Sb_{47}Se_{53}$ films, the temperature for 10-year data retention can be up to 125.9 and 141.8 °C. Both amorphous and crystalline resistivities increase with Se content. The resistance ratio between two states maintain almost 3 orders of magnitude. Hall mobility and carrier concentration increases with the decrease in Se content. The microstructure of annealed Sb-Se films exhibits uniform distribution of crystallized phases with orthorhombic Sb_2Se_3 and hexagonal Sb. The high ON/OFF ratios of both refractive index (n) and extinction coefficient (k) between the amorphous and crystalline states alloys Sb-Se film to be favorable for the optical storage in spectral region 1.7–25 μm.

1. Introduction

Phase-change random access memory (PCRAM) is considered to be one of the most feasible candidates for the next-generation nonvolatile memories [1,2]. As the storage media of the PCRAM, phase-change material is quite important and its properties will influence the device's performances directly. The most studied phase change materials are Te-based chalcogenide compounds such as Ge-Sb-Te [3], Ge-Te [4], Si-Sb-Te [5], Ga-Sb-Te [6]. These materials demonstrate a good overall performance in trade-off between fast crystallization speed and high thermal stability. However, there are several issues that need to be solved. Firstly, their relatively low crystallization temperature leads to an unsatisfied thermal stability with low 10-years data-retention temperature [7,8], and thus poses the problem associated with thermal crosstalk of the materials [9]. The low 10-years data-retention temperature cannot meet the demand for the automobile electronics (at least 120 °C). Secondly, high melting temperature and low crystalline resistivity cause a high RESET current [10], which lead to a high power consumption. One of the effective ways to solve these problems is to explore a novel phase change material. In recent years, some non-Te phase change materials have been proposed, such as Si-Sb [11], Sn-Sb [12], Ge-Sb [13], and Ga-Sb [14].

With lower power and higher speed operations, Sb-Se series has been also researched for the application of rewritable optical storage [15–18]. It is known that this material system is a very attractive candidate for PCRAM due to its low melting point and low thermal conductivity [19]. Low melting point is desirable for RESET operation with low power. And low thermal conductivity can inhibit the loss of heat in the device unit, which is helpful to enhance the heating efficiency. However, few studies reported the phase change characteristics of binary Sb-Se for PCRAM. To develop the low-power devices based on Sb-Se materials, it is imperative for us to investigate the electrical and optical properties, thermal stabilities, as well as microstructures. In addition, it is also important to screen the optimum composition for devices. In this work, the structure and the crystallization behavior of Sb-Se thin films are investigated for low-power devices. And the spectral dependence of the optical constants, refractive index (n) and absorption index (k) of amorphous and crystalline Sb-Se films are studied.

2. Experimental

Sb-Se films were deposited on SiO_2/Si (100) and quartz substrates by the magnetron co-sputtering method using a simple substance of Sb and Sb_2Se_3 alloy targets of 50 mm in diameter. The

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background and working pressures were prior to 4.7×10^{-4} Pa and 0.3 Pa, respectively. The Radio Frequency (RF) power on the Sb_2Se_3 target was fixed to be 30 W, while the direct current (dc) power on the Sb target to be 3, 5, 7, 9 and 12 W respectively. And the composition of the as-deposited film was measured by Energy Dispersive Spectroscopy (EDS), so that it can obtain the samples which denoted by $Sb_{47}Se_{53}$, $Sb_{51}Se_{49}$, $Sb_{54}Se_{46}$, $Sb_{57}Se_{43}$ and $Sb_{62}Se_{38}$. The sheet resistance of the as-deposited films as a function of temperature (R-T) was measured by four-point probe method. The electrical properties such as Hall coefficient, Hall mobility and carrier concentration were determined by Hall measurement using Nanometrics Company HP-5500C system. The structures of the as-deposited and annealed thin films were measured by the X-ray diffraction (XRD). The optical transmittance (Top) in the spectral range 400–2500 nm was obtained by a Perkin-Elmer Lambda 950 UV-VIS-NIR spectrophotometer. Raman scattering spectroscopy was employed to study the chemical bonding feature of films. The microstructure of the films was measured by transmission electron microscopy (TEM). The J.A. Woollam Company IR-VASE® Mark II Ellipsometer was used to measure the ellipsometric parameters of films, optical modeling and data analysis are done using the Woollam Company WVASE32™ software package [20].

3. Results and discussion

Fig. 1(a) shows the temperature dependence of the sheet resistance at a heating rate of 50 °C/min with the increasing temperature, a continuous decrease in resistance is observed for all the films due to the heat active carrier for hopping conduction [21]. Then, an abrupt drop in resistance appears when the temperature reaches their respective crystallization temperature (T_c), suggesting that phase transition from amorphous to crystalline phase occurs, as shown in Fig. 1(a). The obtained T_c increases with increasing Se concentration, being 210 ± 2, 225 ± 2, 230 ± 2, 239 ± 2 and 241 ± 2 °C for $Sb_{62}Se_{38}$, $Sb_{57}Se_{43}$, $Sb_{54}Se_{46}$, $Sb_{51}Se_{49}$ and $Sb_{47}Se_{53}$ films, respectively, given in Table 1. In addition, the amorphous and crystalline resistivities increase with increasing Se content, which is conducive to low power consumption. It is also shown that the resistance ratio between the two states maintain at least 3 orders of magnitude, which provides large margin of sensing window for memory [22]. The sheet resistance curve shift toward higher value with increasing Se content. In order to investigate the role of Se on the resistivity of the Sb-Se films, the electrical properties such as Hall coefficient, Hall mobility and carrier concentration are measured. Electrical properties of Sb-Se films annealed at 300 °C are listed in Table 2. Hall coefficients of all films are positive value, which indicate the Sb-Se films belong to p-type conduction. As the Se content increases in the Sb-Se films from 38% to 53%, Hall mobility and carrier concentration decrease from 3.54 cm^2/Vs and 1.14×10^{21} to 0.42 cm^2/Vs and 1.05×10^{20} per cm^3, respectively. These results imply Se prevents electrical defects when it is introduced in Sb-Se films. Thus, sheet resistance curve shift to higher value.

Table 1
The crystallization temperature (T_c), data retention temperature for 10 years ($T_{10\text{-}years}$) and Optical band gap of as-deposited and annealed (at 300 °C) Sb-Se films.

Composition	T_c (°C)	$T_{10\text{-}years}$ (°C)	Optical band gap (eV)	
			As-dep.	300 °C
$Sb_{47}Se_{53}$	241 ± 2	141.8 ± 0.1	0.919	0.645
$Sb_{51}Se_{49}$	239 ± 2	125.9 ± 0.1	0.799	0.501
$Sb_{54}Se_{46}$	230 ± 2	118.2 ± 0.1	0.731	0.431
$Sb_{57}Se_{43}$	225 ± 2	115.6 ± 0.1	0.593	0.321
$Sb_{62}Se_{38}$	210 ± 2	97.8 ± 0.1	0.535	0.282

The thermal stability of the film can be estimated by data retention which is judged by the time-dependent isothermal change in resistance. It is measured by fitting the data with Arrhenius equation $t = \tau \cdot \exp(E_\alpha/K_BT)$ [23], where t, τ, E_α and K_B are the time to failure, a proportional time constant, activation energy for crystallization, and the Boltzmann constant, respectively. The time to failure is defined as the time which the film resistance reaches half of its initial value at the specific temperature. The Arrhenius plot of thermal stability for the as-deposited amorphous Sb-Se films is shown in Fig. 1(b). The data retention temperature for 10 years of the amorphous $Sb_{62}Se_{38}$, $Sb_{57}Se_{43}$, $Sb_{54}Se_{46}$, $Sb_{51}Se_{49}$ and $Sb_{47}Se_{53}$ films are estimated to be about 97.8 ± 0.1, 115.6 ± 0.1, 118.2 ± 0.1, 125.9 ± 0.1 and 141.8 ± 0.1 °C, respectively (see Table 1), suggesting the significant improvement in thermal stability of the Sb-Se film by the Se addition. Therefore, PCRAM based on Sb-Se could store the information longer with increasing Se content.

The crystal structure of $Sb_{54}Se_{46}$ film is measured by the x-ray diffraction (XRD), as shown in Fig. 2(a). There are no crystallization peaks for the as-deposited film, suggesting its nature of the amorphous state [24]. The characteristics diffraction peaks of $Sb_{54}Se_{46}$ appear as the annealing temperature increased to 250 °C. It indicates that the T_c of the $Sb_{54}Se_{46}$ film is below 250 °C, which is

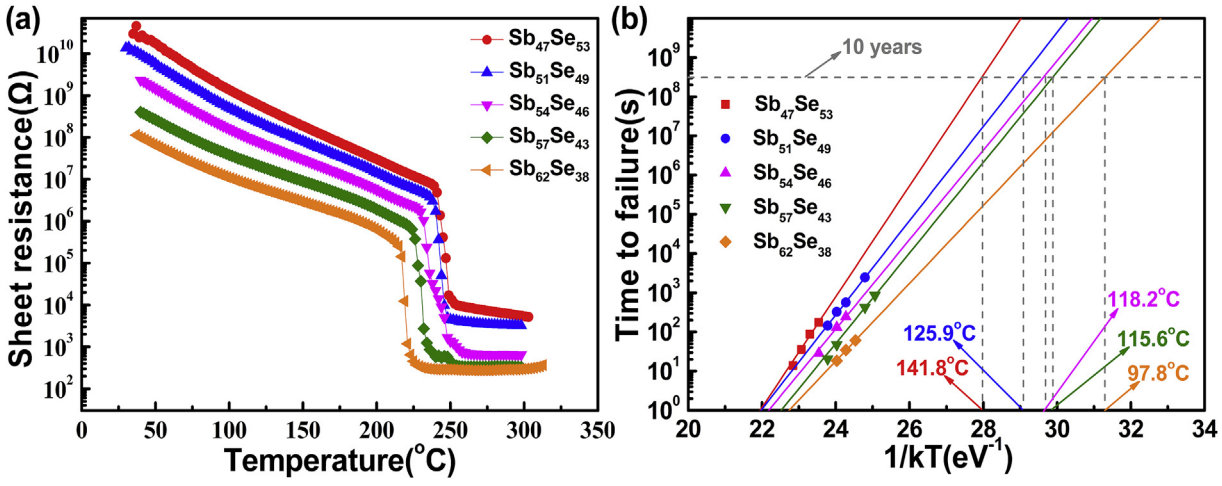

Fig. 1. (a) Sheet resistance as a function of temperature. (b) The Arrhenius extrapolation of 10-years data retention for Sb-Se films.