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Electrical and crystallization properties of indium doped Ge-Sb-Se films

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ABSTRACT

Rapid advances in information technology rely on large capacity, high speed, and thermally stable phase-change nonvolatile materials. This work is investigating the capacitance-voltage characteristics of multinary chalcogenides ($Ge_{15}Sb_{80}Se_5$ and $Ge_{15}Sb_{70}Se_{10}In_5$) to study their electrical properties and their reliant on frequency, bias voltage, and temperature. The results show different capacitance behavior for the two films, $Ge_{15}Sb_{80}Se_5$ and $Ge_{15}Sb_{70}Se_{10}In_5$. Adding indium to Ge-Sb-Se alloy improved its thermal stability by increasing the crystallization temperature by almost 20 K, and shows a fast crystallization process. The results illustrate that the capacitance of $Ge_{15}Sb_{70}Se_{10}In_5$ film has a nonlinear-temperature behavior and becomes negative at high temperatures. The negative capacitance could be attributed to a significant increase in the conductivity of the film due to temperature and applied bias voltage. Moreover, during the phase change, the amorphous-crystalline interfaces might behave as a junction with a potential barrier where charge carriers accumulate. The nonlinearity in the capacitance and conductance is attributed to the nucleation-growth mechanism when the temperature becomes close to the amorphous–crystalline transition temperature (T_c).

1. Introduction

In the field of glass science, it is known that the physical structures of chalcogenide glasses can be tuned by adjusting their chemical compositions. At present, multinary chalcogen-based materials are being researched in the context of next-generation non-volatile memory devices [1]. These chalcogenide materials exhibit fast transitions between amorphous (glassy) and crystalline phases when suitable electrical or thermal energy is applied. However, the physical mechanisms of the phase-change processes in multinary chalcogenides are the subject of some discussion, mainly because of incomplete understanding of the correlations among the structural properties of the glassy phase. Because of the unsteadiness of the amorphous state and the slow polycrystalline conversion, investigations seeking a rapid-crystallization material have recently been conducted.

In our earlier work, we investigated the crystallization characteristics of amorphous $In_{0.3}Ge_{15}Sb_{58}$ thin films [2]. To achieve phase changes in chalcogenide materials, the composition can be tuned using additives such as Se. Assimilation of Se into Ge/Sb atoms has been shown to yield improved phase-change/switching behavior, and the resultant material is a promising candidate for electrical memory switching applications [3]. The effect of Sb variation on the optical properties of the Ge-Sb-Se thin films has also been studied [4]. Doping has been found to be an effective method of tailoring the properties of alloys applied in phase-change memory devices and many more dopants remain available, such as As [5], Al [6], Ga [7], In Refs. [8–10], and Si [11]. However, there is limited knowledge on the effects of some dopants. For example, the effects of doping chalcogenide materials such as Sb–Se with an In dopant has not been clarified because of the phase segregation problem [8]. This problem arises during sample preparation in vacuum, regardless of whether the sample is in bulk or thin-film form, because of its volatile nature. The effects on the phase change properties of doping Ge, Sb, and Se with In are also of interest. Moreover, along with the crystallization properties, the dependence of the capacitance (C) on the frequency at various temperatures is of great importance, as this behavior provides information on the amorphous-crystalline phase transition. The variation of the capacitance-voltage (C–V) can be tuned by adjusting factors such as the frequency and temperature [12].

The present article attempts to elucidate the phase-change

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behavior mechanism in Ge-Sb-Se and In-doped Ge-Sb-Se thin films. Furthermore, the effects of an applied electric field (bias *V*), temperature, and frequency on the *C* variation characteristics of $Ge_{15}Sb_{80}Se_5$ and $Ge_{15}Sb_{70}Se_{10}In_5$ thin films are systematically studied and presented.

2. Experimental procedure

Bulk $Ge_{15}Sb_{80}Se_5$ and $Ge_{15}Sb_{70}Se_{10}In_5$ were prepared by melting pure (99.999%, Sigma Aldrich) Ge, Sb, Se, and In elements at a stoichiometric ratio in a quartz ampoule of 10 mm in diameter and at a vacuum of 10^{-3} Torr. The ampoule was kept in a horizontal furnace at 1050 °C for 24 h with 10-rpm rotation so that a homogeneous mixture was obtained. After 24 h, the melt was quenched in an ice-water bath. The obtained material was used to prepare thin films using a vacuum evaporation technique (Torr International) under a pressure of 10^{-6} Torr. $Ge_{15}Sb_{80}Se_5$ and $Ge_{15}Sb_{70}Se_{10}In_5$ thin films with thicknesses of 115 and 110 nm, respectively, were prepared on glass substrates. For *C*–*V* analysis, gold Au were deposited to form a co-planar electrodes of 1 mm distance separation using a suitable mask. A schematic diagram of the preparation technique is available in the literature [13].

Using a scanning electron microscope (SEM; JEOL JSM – 6010) with an energy-dispersive X-ray spectroscope (EDX) attachment, the surface structures and elemental compositions of the prepared films were analyzed. For each sample, the film structure was detected by an X-ray diffractometer (XRD; Shimadzu 6100), equipped with Ni-filtered Cu Kα radiation. The ultraviolet–visible (UV–vis) transmittance spectra were recorded using a spectrophotometer (Jasco-670) with a wavelength range of 300–2600 nm.

The *C*–*V* measurements were performed using a Keithley 590 CV meter at two different frequencies: 100 KHz and 1 MHz. The measurements were performed for a *V* sweep from −20 to +20 V at different temperatures, while the temperature was adjusted in the range of 300–500 K at a heating rate of 5 K/min using a Lakeshore 335 temperature controller. The samples were heated inside a Janis ST-100H cryostat under a vacuum of 10^{-3} Torr. Note that short coaxial cables were used in this measurement to minimize the inductive interference of the environment, which may affect measurements, especially at high frequencies. Lab View software was used for data acquisition. To check the reproducibility, measurements were performed at different positions on the thin films.

3. Results

The *C* variations of the $Ge_{15}Sb_{80}Se_5$ and $Ge_{15}Sb_{70}Se_{10}In_5$ thin films as functions of temperature are shown in Figs. 1 and 2, respectively, for frequencies of both 100 KHz and 1 MHz. The C(V) measurements have been done under a sweep of voltages from −20 to +20 V. From Fig. 1, the *C* values of the $Ge_{15}Sb_{80}Se_5$ film at 300 K were 86 and 75 pF for frequencies of 100 KHz and 1 MHz, respectively. When the temperature was raised beyond 300 K, the *C* decreased slowly until 450 K; then, a sudden drop in *C* was observed. This abrupt drop in *C* around 450 K pinpoints the amorphous-crystalline transition temperature (T_C) for $Ge_{15}Sb_{80}Se_5$ thin films. In Fig. 2, for the low-temperature range (300–460 K) and the $Ge_{15}Sb_{70}Se_{10}In_5$ film, *C* remained constant. The *C* value was 103 pF under 100-KHz frequency. As the temperature increased, *C* dropped suddenly to a value of 15 pF at 470 K and reached a negative value of −5 pF when the temperature reached 500 K. Under the high frequency of 1 MHz, the film *C* was constant at low temperatures. A sudden change in *C* was again observed at high temperatures close to T_C (470 K) but no negative value was obtained. The observed drop in the capacitance is less than that at 100 kHz, and the capacitance does not show negative values.

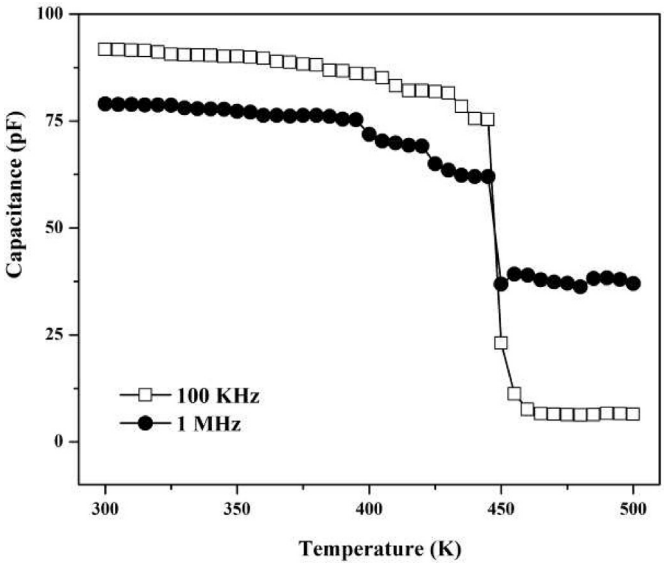

Fig. 1. Variation of capacitance with different temperatures (300–500 K) for a frequency of 100 KHz and 1 MHz of $Ge_{15}Sb_{80}Se_5$ thin films.

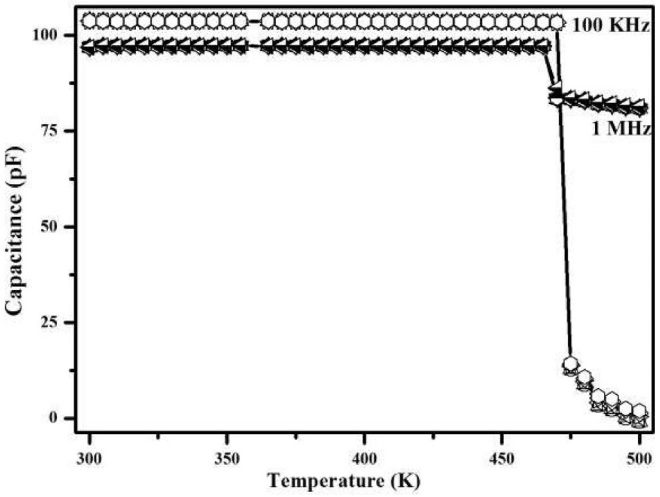

Fig. 2. Variation of capacitance with different temperatures (300–500 K) for a frequency of 100 KHz and 1 MHz of $Ge_{15}Sb_{70}Se_{10}In_5$ thin films.

As apparent from Fig. 2, at low temperatures, the *C* measured for the $Ge_{15}Sb_{70}Se_{10}In_5$ film was field independent, as there was no variation in *C* when the applied *V* was varied in the range of −20 to +20 V. At temperatures above 470 K, the *C* became field dependent, with greater variation in *C* being observed at low frequency and high temperature. The rapid fall in *C* at 470 K indicates the T_C for $Ge_{15}Sb_{70}Se_{10}In_5$ thin films. Note that the transition process occurred relatively quickly compared to that for the $Ge_{15}Sb_{80}Se_5$ thin films. Further, several phase-change memory materials such as Ge-Te-Zn [14], Ge-Te-Ga [15], and $Ge_2Sb_2Te_5$ [16], with better crystallization temperatures, have potential applications as phase-change memory alloys. Fig. 3 shows the variation of *C* with applied *V* at temperatures above 470 K, where a nonlinear behavior was observed. The nonlinearity in the *C*–*V* measurements at high temperatures is obvious, and more prominent at low frequency (100 kHz), for which the *C* values vary by approximately 2 pF. For the high frequency (1 MHz), the *C* variation is very small and the trend is approximately linear.