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J.J. Gervacio-Arciniega, E. Prokhorov, G. Trapaga

Electrical Properties of Policristalline $Ge_2Sb_2Te_5$ Thin Films

Cinvestav del IPN, Querétaro, Libramirnto Norponiente 2000, Juriquilla, 76230, México,
+(52) 442 2119900, prokhorov@qro.cinvestav.mx

The aim of this article is to study the properties of the crystalline face centered cubic (fcc) $Ge_2Sb_2Te_5$ phase as a function of annealing temperature. The electrical properties of the crystalline phase have been investigated using two independent methods, the impedance and the Hall measurements, and the results are interpreted in terms of structural parameters obtained from x-ray diffraction.

The results obtained have shown the polycrystalline nature of the crystalline film and that the transport properties have a strong dependence on the annealing temperature. The presences of high resistivity grain boundaries are responsible for the appearance of potential barriers. The mobility is limited by scattering of charge carriers at the grain boundaries and can be described by a conduction model that includes thermionic emission over the potential barriers. Additionally, the ferroelectric properties in the $Ge_2Sb_2Te_5$ fcc phase have been observed by direct impedance measurements.

Key words: $Ge_2Sb_2Te_5$, impedance, Hall, grain boundaries, thermionic emission.

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Introduction

Phase-change memory technology is based on the high speed reversible amorphous-to-crystalline transformation of a thin film material and employs the difference in optical or electrical properties between both states. In these technologies the most commonly employed materials have stoichiometric compositions of $Ge_2Sb_2Te_5$. It is known that upon annealing, amorphous phase of this material first undergo the amorphous-to-crystalline (fcc) transition in the range of 403-433 K and at higher temperatures (at about 493 K) the crystal (fcc)-to-crystal hexagonal transition. In the actual phase change device, only the fcc phases occurs during the fast transition to the crystalline state, probably because the heating time during the laser or electrical pulse is too short to form the stable hexagonal structure [1].

It is necessary to note that in contrast to the optical phase-change recordings nonvolatile electrical data storage has not appeared in the market yet. This related that the electronic properties of $Ge_2Sb_2Te_5$ films remain to be studied. It has been established that polycrystalline $Ge_2Sb_2Te_5$ films in the fcc phase have a p-type conductivity [2], but the transport and electrical properties of this phase are not yet well known. For example, for the $Ge_2Sb_2Te_5$ in cubic phase, the room temperature resistivity reports varies in wide range ($2x10^{-2}$ Ω-cm [3], $1\text{-}3x10^{-3}$ Ω-cm [2] and $2\text{-}7x10^{-4}$ Ω-cm [4]).

The aim of this article is to study the properties of the crystalline face centered cubic (fcc) $Ge_2Sb_2Te_5$ phase as a function of annealing temperature.

I. Experimental details

$Ge_2Sb_2Te_5$ ($Ge_{22}Sb_{22}Te_{56}$) thin films with thickness about 200 nm were prepared by vacuum evaporation of the bulk alloy onto unheated glass substrates. The as-deposited films were confirmed to be amorphous by X-ray diffraction. The film composition was determined by energy dispersive spectroscopy. It was found that deviation from the target composition was not larger than 2 % for every element.

The electrical properties, in the frequency range of 40 Hz–300 kHz, of the films deposited on the glass substrate were obtained from impedance measurements (Agilent Precision Impedance Analyzer 4294A) using the four collinear probe array. Hall measurements were carried out on squared shaped samples using a modified Escopia HMS-3000 Van der Paul Hall measurement System.

The sample was heated using a resistive heater. The measurements on the polycrystalline fcc films were carried out on the samples annealed for 10 minutes at a temperature above the amorphous-fcc transition, but lower than the needed to induce the fcc-hexagonal transition. The resistivity of samples obtained by two independent methods (4 probe impedance and Van der Paul measurements) was similar, with a difference no larger than 17 %.

II. Results and discussion

Fig. 1 shows the DC surface resistance as a function of temperature, obtained from 4-probe impedance

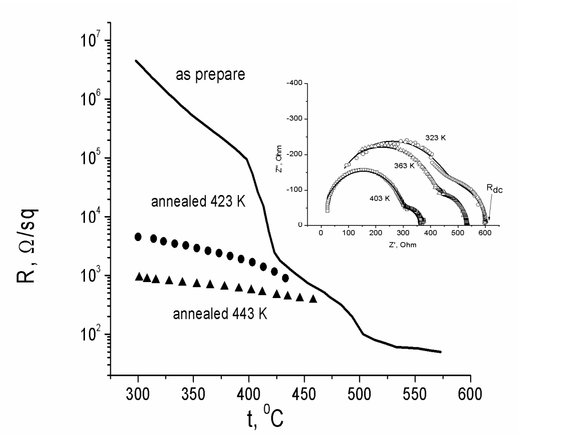

Fig. 1. Surface DC resistance versus temperature obtained from four-probe impedance measurements (continuous line). The points represent the resistance obtained on the fcc polycrystalline sample previously annealed at 423 K and 443 K during 10 min. Insert shows impedance spectra obtained in fcc crystalline films at the temperature indicated on the graph.

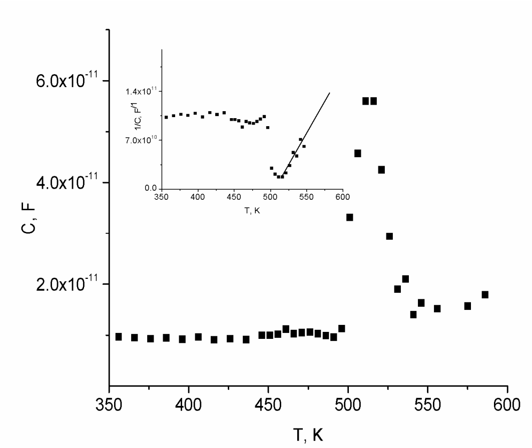

Fig. 2. Volume fraction of grain boundaries x_{gb} calculated from brick model for films previously annealed at 423 K and 443 K. Insert shows the equivalent circuit used to fit the impedance measurements.

measurements (as interception with Z' axis as shown on insert of Fig.1) on as-prepared $Ge_2Sb_2Te_5$ films (continues line). This dependence demonstrate abrupt decreasing in resistance at the temperature about 403 and 493 K which corresponding to amorphous-fcc and fcc-hexagonal transitions (confirm by X-ray measurements). The points represent the resistance obtained on the fcc polycrystalline sample previously annealed at 423 K during 10 min and 443 K (lower than the needed to induce the fcc-hexagonal transition). Insert of Fig. 1 shows typical impedance spectra for $Ge_2Sb_2Te_5$ films measured using 4-probe impedance techniques in samples previously annealed at 443 K during 10 min. The spectra were measured at the temperatures indicated in the graph and consisted of two well define semicircles. Insert in Fig. 2 shows the equivalent circuit (consisting of two RC circuit connected in series) used to fit the electrical response of the fcc polycrystalline films using the brick layer model. This model assumes cubic shaped grains separated by flat grain boundaries. The R_gC_g and $R_{gb}C_{gb}$ circuits are associated with the grains and the grain boundaries respectively. The frequency response using the proposed equivalent circuit has been fitted to the experimental 4-probe impedance spectra with help of the commercial program ZView. The results from the fittings are shown with the continuous lines on the insert of Fig. 1.

The brick layer model establishes the following relation between capacitances, dielectric constants of the grain ε_g, dielectric constant of grain boundaries ε_{gb} and the volume fraction of the grain boundaries x_{gb} [5]:

$$x_{gb} = 3\frac{C_g}{C_{gb}} \bullet \frac{\varepsilon_{gb}}{\varepsilon_g}$$

This relation establishes a correlation between microstructure and electrical properties. From electrical impedance measurements the volume fraction of grain boundaries are usually estimated by assuming $\varepsilon_g = \varepsilon_{gb}$ [5]. The volume fraction of grain boundaries x_{gb} calculated for the film is shown in Fig. 2. The graph shows, that an increase in the annealing temperature results in a reduction in the volume fraction of grain boundaries.

The presence of high resistivity grain boundaries (as have been determined from 4-probe impedance measurements) has a strong influence on the current transport in the polycrystalline films. The grain boundaries formed by disordered atoms contain change trapping centers, which lead to an inter-grain band bending and potential barriers [6]. A conduction model proposing a thermionic emission over the potential barriers formed at the grain boundaries have been applied to polycrystalline materials [6, 7].

According to ref. [7] for polycrystalline films, if the transport mechanism is dominated by the thermionic emission, the conductivity σ can be expressed as:

$$\sigma = Lq^2 p(\frac{1}{2\pi m^* kT})^{1/2} exp(-\frac{E_\sigma}{kT}),$$

where L, q, p, m^*, k and E_σ are, respectively, the average grain size, the electron charge, the carrier concentration, the effective mass, the Boltzmann constant and the activation energy of conductivity.

In the case of the thermionic emission across the grain boundaries the Hall mobility μ in polycrystalline films may be expressed as [8]:

$$\mu = \mu_0 \, exp(-\frac{E_\mu}{kT}) = Lq(\frac{1}{2\pi m^* kT})^{1/2} exp(-\frac{E_\mu}{kT}),$$

where E_μ is the barrier height across the grain boundary.

According to these equations the plots $ln(\sigma T^{1/2})$ and $ln(\mu T^{1/2})$ versus T^{-1} for polycrystalline samples must show a linear dependence in which the slope determines the activation energy and potential barrier height across the grain boundary. Fig. 3 shows the corresponding experimental values of the $ln(\sigma T^{1/2})$ and $ln(\mu T^{1/2})$ as a function of $1000/T$, which are linear in the measured

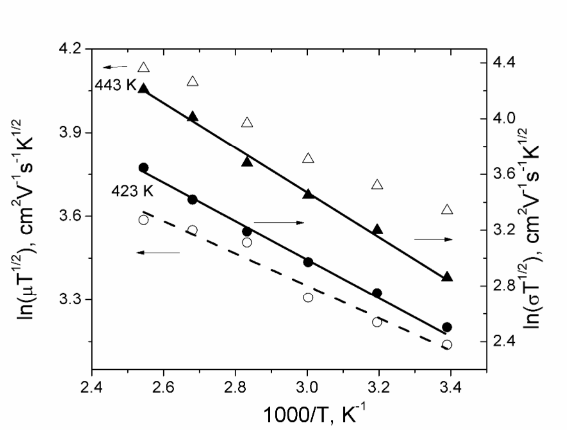

Fig. 3. Experimental dependencies of the $ln(\sigma T^{1/2})$ (a) and $ln(\mu T^{1/2})$ (b) as a function of *1000/T* obtained on the samples annealed to the temperature indicated on the graph.

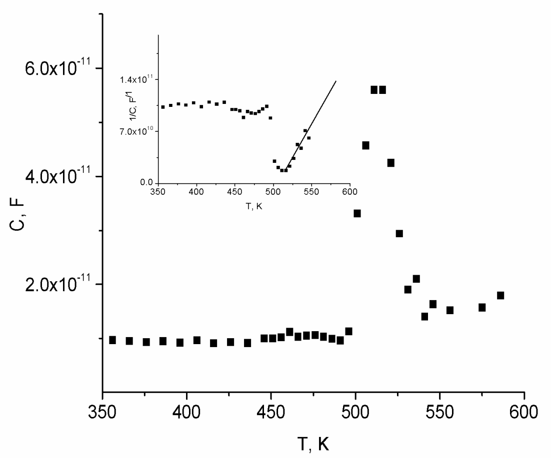

Fig. 4. Temperature dependencies of capacitance obtained in $Ge_2Sb_2Te_5$ films during fcc-hexagonal transition. Insert shows the reciprocal capacitances as a function of temperature.

temperature range for samples annealed at 423 K and 443 K with an activation energy of conductivity of 115 and 136 meV and potential barrier height at the grain boundaries equal to 50 and 54 meV respectively.

As can be observed, the room temperature resistivity values of fcc $Ge_2Sb_2Te_5$ films, properties of grains and grain boundaries are strongly depend on the thermal history of the film. For example, surface resistance at room temperature for the film annealed to the temperature of 150 °C changes from 4500 to 960 Ohm in the film annealed at 170 °C and decreases to 360 Ohm in the films annealed at 195 °C. This effect is responsible for the dispersion in resistivity for fcc phases reported in the literature [2-4].

According to the literature the fcc $Ge_2Sb_2Te_5$ has NaCl type structure [1]. In this structure, the 4(a) site is fully occupied by Te atoms, whereas the 4(b) site is randomly occupied by Ge and Sb atoms and vacancies. The vacancies play an important role in the stability of crystalline phase and act as holes, so that the electrical conductivity of fcc phase is p-type [2]. Our Hall measurements confirm that fcc crystalline films have p-type conductivity. With increasing annealing temperature there is also an increase in grains size and carrier concentration, due probably to the growth in the number of vacancies on the 4(b) sites of the NaCl-type structure, which leads to the appearance of the dependencies of resistivity on the annealing temperature.

Additional, impedance measurements allowed investigating not only resistance changes during fcc-hexagonal transition (Fig. 1) but change the value of capacitance and dielectric constant. From impedance measurements in planar configuration it is difficult to calculate the dielectric constant, but in ref. [8] was shown that for this geometry, the capacitance is proportional to the dielectric constant.

The temperature dependence of capacitance shows an abrupt change (about 4-6 times) with a maximum at the temperature T_c= 515 K which corresponds to the end of the fcc-hexagonal transition (Fig. 4). Additionally, the reciprocal capacitance as a function of temperature above T_c demonstrates the typical Curie-Weiss dependence (inset in Fig. 4). This behavior is characteristic of ferroelectric materials and T_c is related to the ferroelectric–paraelectric transition [9]. Results obtained confirm the model in refs. [10, 11] which proposed that the fcc $Ge_2Sb_2Te_5$ is a distorted rocksalt-like structure. Ge and Sb atoms deviate from the ideal rocksalt positions not in a random way but in a strongly correlated manner with respect to the neighboring Te atoms. The off-center location of Ge atoms means that there is a net dipole moment and suggests that fcc phase of the $Ge_2Sb_2Te_5$ is a ferroelectric material [11].

Conclusion

Properties of fcc $Ge_2Sb_2Te_5$ phase strongly depend on the annealing temperature. The presences of high resistivity grain boundaries are responsible for the appearance of potential barriers and conduction can be described by a conduction model which includes thermionic emission over the potential barriers. Additionally, the ferroelectric properties in $Ge_2Sb_2Te_5$ fcc phases has been observed by direct impedance measurements.

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J.J. Gervacio-Arciniega, E. Prokhorov, G. Trapaga

Електричні властивості полікристалічних тонких плівок $Ge_2Sb_2Te_5$

Cinvestav del IPN, Querétaro, Libramirnto Norponiente 2000, Juriquilla, 76230, México,
+(52) 442 2119900, prokhorov@qro.cinvestav.mx

Метою цієї статті є вивчення властивостей кристалічної fcc фази $Ge_2Sb_2Te_5$ в залежності від температури відпалу. Електричні властивості кристалічної фази досліджено двома незалежними методами: імпедансним та холівськими вимірюваннями.

Отримані результати показали полікристалічну природу кристалічної плівки та сильну залежність властивостей переносу від температури відпалу. Наявність високоомних меж зерен приводить до появи потенціальних бар'єрів. Рухливість обмежена розсіюванням носіїв заряду на межах зерен та може бути описаною моделлю провідності, що включає термоіонну емісію над потенціальними бар'єрами. Крім того, фероелектричні властивості fcc фази $Ge_2Sb_2Te_5$ спостерігалися прямими вимірюваннями імпедансу.