

An Interrelation between Electrical Conductivity, Crystallization Process and Meyer-Neldel Relation in a-SeTeSn Films

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Abstract

Electrical conductance is measured in amorphous SeTeSn films to investigate the crystallization mechanism in the system. The crystallization is found to occur at the sample-substrate interface. Using the conductance dependence on time, the crystallization growth velocity is determined. The Arrhenian temperature dependence of crystallization velocity estimates the activation energy. The Meyer-Neldel relation (MNR) has been observed in amorphous SeTe films through a correlation between pre-exponential of growth velocity and activation energy. The presence of localized states in the gap in amorphous chalcogenides suggests that the crystallization is controlled by viscosity in the films.

Keywords: Amorphous Chalcogenide, electrical conductivity, crystallization, Meyer-Neldel rule

1. INTRODUCTION

Crystallization in amorphous chalcogenide binary and ternary alloys has been studied using various techniques such as Differential Scanning Calorimetry (DSC) [1], Differential Thermal Analysis (DTA) [2-3], Electron Microscopy [4-5] etc. The measurement of the crystallization velocity v_c in thin films is difficult using above techniques. The electrical conductivity has been previously used to determine the crystallization process in amorphous bulk alloys and films [6-7]. Since in chalcogenides, the conductivity of the amorphous state is lower than that of crystallized state, the electrical measurements are expected to be very sensitive to the phase changes in thin films in comparison with other conventional methods such as DSC or DTA [8]. This paper describes an attempt to deduce from the crystallization

kinetics, the growth rate and activation energy when the crystallization is induced at the sample-substrate interface.

2. EXPERIMENTAL DETAILS

The $(\text{Se}_{100-x}\text{Te}_x)_{97}\text{Sn}_3$ films were prepared by vacuum evaporation technique onto degassed glass substrates held at room temperature. The Te content of the prepared samples was 0, 10, 20 and 30 at.% of Se. The thickness was kept constant and was measured to be 750nm. The X-ray diffraction pattern showed that the samples were amorphous in nature. Before evaporation of the thin films, Indium electrodes of about 1mm thickness were deposited on the glass substrates. The contacts were found to be ohmic in the present voltage range of measurements.

The electrical measurements were made by applying a voltage to the samples. The sample current was measured by measuring the potential drops across a resistance connected in series with the sample using a digital microvoltmeter (Systronics). The samples were annealed at various temperatures (333K - 348K), which were chosen to observe crystallization in appropriate crystallization velocities. A vacuum of 5×10^{-3} Torr was maintained during the entire procedure.

3. RESULTS AND DISCUSSION

3.1 Crystallization Kinetics in Amorphous Chalcogenide Films

When nuclei covers a surface of radius r and when r is large compared to the thickness of the layer, e , then the crystallization occurs similar to an epitaxial growth, the crystalline phase reaching the opposite surface of the layer at a time $t = e/v_c$ (v_c is the growth rate) [9]. This is referred to as Surface Induced Crystallization (SIC). Such crystallization is actually polycrystalline. It has been shown that at any given time t , the conductance of the layer can be written as

$$\Sigma(t) = \Sigma(a) \left\{ 1 + \left[\frac{\sigma_m}{\sigma_a} - 1 \right] \frac{v_c t}{e} \right\} \quad (1)$$

where σ_m is the conductivity of the partially crystallized layer during the annealing process and σ_a is the conductivity of the amorphous layer [10]. The crystallization velocity was obtained through the measurements of τ (time at which the linearity of $\Sigma(t)/\Sigma(a)$ curve breaks off).

The conductance variation during the isothermal annealing of amorphous films of Se:Te (Te = 0-30 at.% of Se) is shown in Fig.1. The crystallization time τ was obtained at each annealing temperature and corresponding growth rates v_c were calculated.

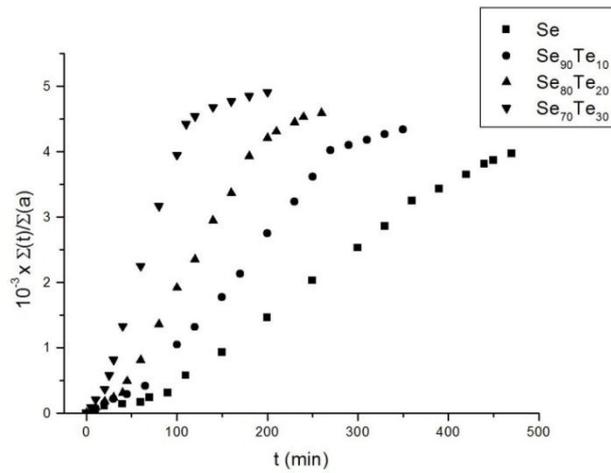


Figure 1: Variation of the conductance ratio as a function of annealing time for a-Se:Te:Sn films at annealing temperature of 333K.

3.2 Crystallization Process in Amorphous Se:Te Thin Films

The crystallization process was seen to occur in three stages. During the first stage ($0 < t < t_0$), conductance increases quadratically with time as the fit of the data has predicted. It has been shown that the crystallization in a-Se:Te:Sn films occur in a two-dimensional way at the interface [5]. According to Landauer [8], the above two-dimensional crystallization leads to a quadratic variation of conductance with time.

During the second stage ($t_0 < t < \tau$), the conductance varies linearly and the data is fitted to Eq.(1). The crystallization is completed at $t = \tau$, the growth of the crystallized area towards the free surface becomes dominant during second stage. The linear time dependence of the conductance up to a time τ was found to occur in all the samples. The process is termed Surface Induced Crystallization (SIC). Since the second term in the square brackets of eq.(1) is much larger than the first term, the conductance varies linearly with time, until $t = t_0 + \tau$, at which SIC is completed ($\tau = e/v_c$). The crystallization velocity obtained using the above relation for $(\text{Se}_{80}\text{Te}_{20})_{97}\text{Sn}_3$ film as a function of temperature is shown in Fig.2. The behavior for all compositions is the same. Similar behavior was also observed in bulk glasses [6].

Finally, the conductance saturates for $t > \tau$. The saturation of the conductance relation after time τ results from the crystallization of the rest of the amorphous domains in the thin films. This occurs as all the nucleation sites were exhausted and the growth of the crystallites stops, i.e., site saturation [10].

The crystallization velocity obtained in the experiment was found to decrease continuously with increasing Te concentration at each of the annealing temperatures. As is evident from Fig. 2, the crystallization velocities show a thermally activation behaviour with an Arrhenian dependence for each of the composition given by

$$v_c = v_{c0} \exp(-E_c/kT) \quad (2)$$

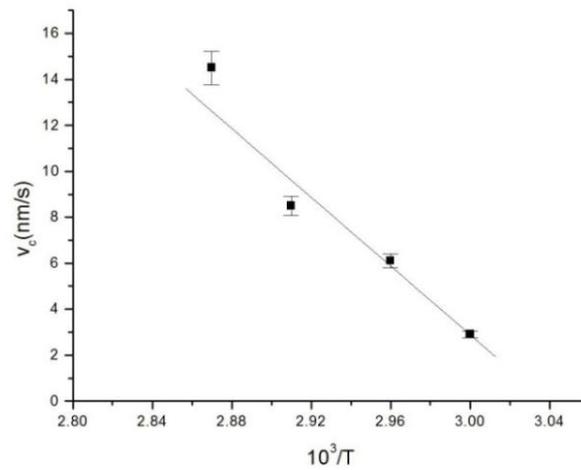


Figure 2: Crystallization velocity as a function of temperature for a-(Se₈₀Te₂₀)₉₇Sn₃ films.

Fig.3 shows the dependence of the activation energy E_c of crystallization on the Te content. The pre-exponential of crystallization velocity also show same type of behaviour. In the range $x = 0$ to 20 at.% in the studied films, both E_c and v_{co} decrease monotonically. The Te induced retardation was also observed in the melt quenched bulk glasses studied by us [6] and others [12]. With a further increase in Te, these quantities go through a minimum at 20 at.% Te. A similar compositional dependence of the activation energy of crystallization has been reported in melt quenched Se:Te bulk glasses by Ganaie et.al. [13].

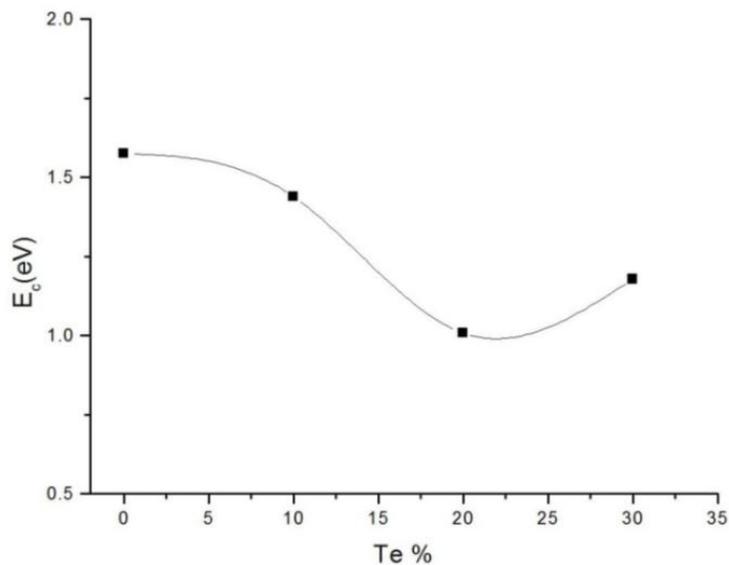


Figure 3: The activation energy of crystallization as a function of Te content in films.

The minimum in E_c can be understood as follows. The cis- (ring segment) and trans- (helical chain segment) configurations in amorphous Se differ only in the placement of the 5th neighbour atom for molecular bondings[14]. The placement of the likely atom depends on the competition between the intra-chain and inter-chain forces. The intra-chain force decreases and the inter-chain force increases with the addition of Te atoms to a-Se. The minimum activation energy at the particular Te concentration is therefore, likely to be attributed to such an intermediate range structural modification. The increase of glass transition temperature with Te concentration also indicates a more rigid network [15].

3.3 Meyer-Neldel Relation

Fig. 4 shows the plot of the pre-exponential factor v_{co} versus the activation energy E_c of the crystallization velocity in thin films. There is a very good correlation between the v_{co} and E_c , often referred to as the Meyer-Neldel relation [16] and is described as

$$\ln v_{co} = \ln v_{coo} + E_c / E_{co} \tag{3}$$

where v_{coo} is a constant with a value of about $1.8 \cdot 10^{-3}$ nm/s and $E_{co} \sim 0.0483$ eV as deduced from Fig.4.

Although the Meyer-Neldel relation has been observed in various physical systems, there is still no satisfactory uniform explanation for its occurrence. Assuming that the crystallization velocity in amorphous materials is inversely proportional to the viscosity of the melt η [12], which has a Vogel-Tammann-Fulcher type of behaviour [17], i.e., $\eta = \eta_0 \exp (E_0 / k (T-T_0))$, where η_0 , E_0 and T_0 are constants, then the crystallization velocity becomes

$$v_c = c \eta_0 - 1 \exp (- E_0 / k (T - T_0)) \tag{4}$$

This equation is almost indistinguishable from eqn. (2) in a narrow range of temperature except for the vicinity of T_0 . Moreover, if we try to fit the Arrhenian dependence of v_c in a temperature range T_1 to T_2 , we obtain [5]

$$\ln v_{co} = \ln c \eta_0 - 1 + E_c / E_{co} \tag{5}$$

where

$$E_{co} = kT_0 \frac{(y_1 y_2 + y_2 y_3 - y_3 y_1)}{y_2^2 - y_2 y_3 + y_3 y_4} \tag{6}$$

$y_1 = a - b$, $y_2 = \ln(a/b)$, $y_3 = \ln\{(a - 1)/(b - 1)\}$, $y_4 = (1/b)-(1/a)$, $a = T_2 / T_0$; $b = T_1 / T_0$.

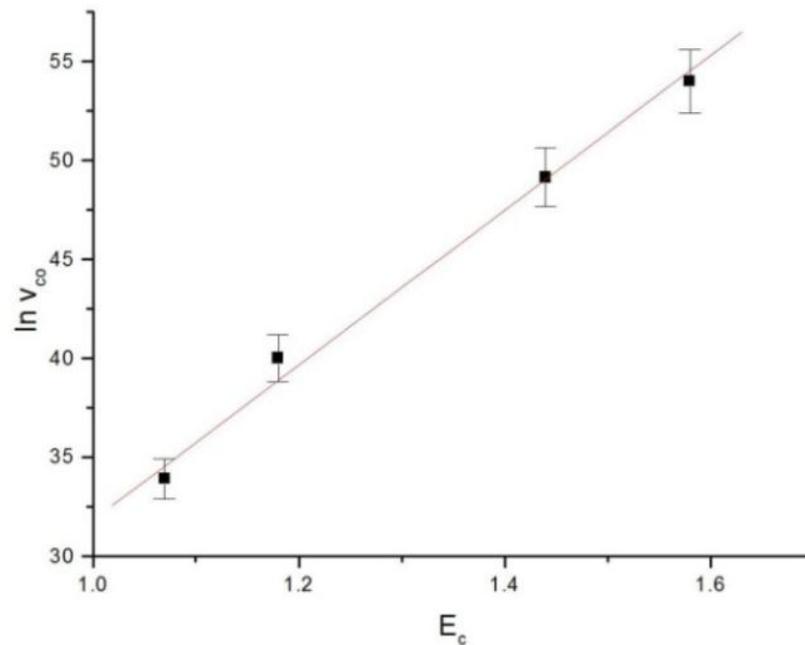


Figure 4 The Meyer-Neldel relation in a-Se:Te:Sn films

The estimated E_{co} value of 0.0325eV obtained using $T_1 = 330K$, $T_2 = 360K$ and $T_0 = 303K$ using eq. (9). This is an indication that the crystallization velocity in amorphous chalcogenide films is controlled by the viscosity of the melt. The variation in Vicker's hardness in chalcogenides around crystallization temperatures also allows us to correlate our results with viscosity [18]. The increase in glass transition temperature with Te concentration is also a good indicator of the increase in viscosity with Te [19]. This occurs as a result of the increase in the localized states in the gap reducing mobility and increasing the viscosity.

4. CONCLUSIONS

The conductance measurements carried out on SeTeSn amorphous films between the glass transition and crystallization temperatures provides information about the crystallization mechanism in thin films. During the early times, the crystallization is due to nucleation and conductance varies quadratically with time. When the nucleation is completed, the conductance varies linearly and the process occurs as a result of growth of crystallites towards the surface. The addition of Te reduces the growth and activation energy show a minimum at $x = 0.6$. Meyer Neldel relation is found to be obeyed in the present case through pre-exponential of velocity and activation energy. This can be assigned to an increase in localized states resulting in increase in viscosity of the specimen around Te 60 at% Se.

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