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Variation of the activation energy of the glass transition in amorphous Se thin film: Isoconversional analysis

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ABSTRACT

The activation energy (E) of the glass transition and the heating-rate dependence of the glass transition temperature (T_g) of amorphous Se thin film were determined using differential scanning calorimetry (DSC) technique. Non-isothermal measurements were performed at different heating rates (12–40 K/min). Variation of the activation energy was confirmed by the application of five isoconversional methods. These methods showed that the glass transition activation energy is not constant but varies with the degree of conversion (α) and hence with temperature (T). The observed temperature dependence of the activation energy is consistent with the free volume model of the glass transition.

1. Introduction

Studying amorphous solids is one of the most active fields of research in the physics of materials science today. One reason for this increase in interest lies in the fact that some amorphous substances show certain unusual switching properties, which could be important in modern technology applications such as switching, electrophotography and memory devices. It is generally agreed that an amorphous solid is a material that has no precise structure, is not periodic, and does not have the long-range order characteristic of crystalline materials. However, it does have a certain local order in its bond with its first neighbors [1–3]. Selenium (Se) exhibits both photovoltaic and photoconductive action. It has been used in photo- and solar-cells as a Se rectifier, and in xerography as a photographic toner [4,5]. The differential scanning calorimetry (DSC) technique is widely used to investigate the glass transformation in glassy materials. The kinetics of the glass transition as studied by the DSC method is important in investigating the nature the glass transformation process. The glass transition temperature, T_g, can be accurately determined by DSC measurements. Moreover, the kinetic aspect of the glass transition is evident from the strong dependence of T_g on the heating rate. This behavior can be used to identify different mechanisms involved in the transition process. One of the key kinetic parameters which can be determined by DSC measurements is the activation energy, E, of the glass transition. It has been assumed by many authors that E is constant during the glass transformation. To test this notion, E was determined from the present measurements using different methods. In particular, the isoconversional methods were used to evaluate the values of E at different stages of the transformation. In this study, the kinetics of the glass transition phenomenon in the amorphous Se thin film is studied using DSC measurements. The objectives of this work are: (1) to investigate the effect of heating rate on the glass transition of the amorphous Se thin film, (2) to investigate the variation of the activation energy of the glass transition and its dependence on extent of conversion and temperature and (3) to use the experimental data to test a number of theoretical models proposed to describe the glass transition.

2. Experimental

The Se powder used in this study was obtained from Sigma–Aldrich Co. with a purity of 99.99%. The films were deposited onto rectangular, optically flat, standard microscope slides acting as substrates with a thickness of 1 mm at room temperature. The slide substrates were ultrasonically cleaned in acetone and rinsed with deionized water. Another group of films were deposited directly onto the lids of the aluminum sample pans via evaporation; the pans have a 5.8-mm diameter. The evaporation was carried out by resistive heating of approximately 20 mg of the Se from a tungsten boat. The boat was heated during the deposition process by passing high current (100 A) under a base vacuum of 7.5×10^{-8} Pa. The

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substrate base was kept under mechanical rotation so that the films were deposited evenly.

Thermal behavior was investigated using a Shimadzu DSC-60 under dry nitrogen supplied at the rate of 35 ml min^{-1}. The accuracy of the thermocouple was ±0.1 K. 1 mg of film was sealed in a standard aluminum pan and heated at different rates, ranging from 12 to 40 K min^{-1}. Since the sample is a uniform thin film, the temperature gradients are kept to a minimum. Temperature and enthalpy measurements were calibrated with indium (Tm = 156.6 °C, $\Delta H_m = 28.55\ \text{J g}^{-1}$) standards supplied by Shimadzu.

The Se structure was examined using a Shimadzu XRD-6000 X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å). The X-ray tube voltage and current were 40 kV and 30 mA, respectively.

The surface microstructure was observed by AFM (Veeco CP-II) in contact mode and Si tips at a scan rate of 1 Hz. The surface microstructure was also imaged by SEM using a Shimadzu Superscan SSX-550. The thin films we analyzed to have a thickness of approximately 840–850 nm.

3. Results and discussion

The deposited Se thin films are formed of heterogeneous clusters embedded in glassy matrix, as shown from Fig. 1(a), indicating the amorphous state of the film. In addition, the surface morphology obtained by AFM confirms the amorphous state of the as-deposited Se films as shown in Fig. 1(b). It is clear that the film has very smooth surface with tiny grains of about 40 nm in size and very low roughness (∼1.9 nm). The amorphous character of the deposited films was confirmed by the absence of crystallinity peaks in the XRD pattern as shown in Fig. 1(c). XRD patterns do not exhibit any difference among all deposited Se films with different thicknesses, i.e. all deposited films are amorphous.

A typical DSC curve of the crystallization process of the amorphous Se thin film obtained at heating rate 40 K/min is shown in Fig. 2. The DSC thermogram is characterized by two temperatures. The glass transition temperature, T_g, as defined by the endothermic change in the DSC trace, marks a transformation from amorphous solid phase to supercooled liquid state. The heating-

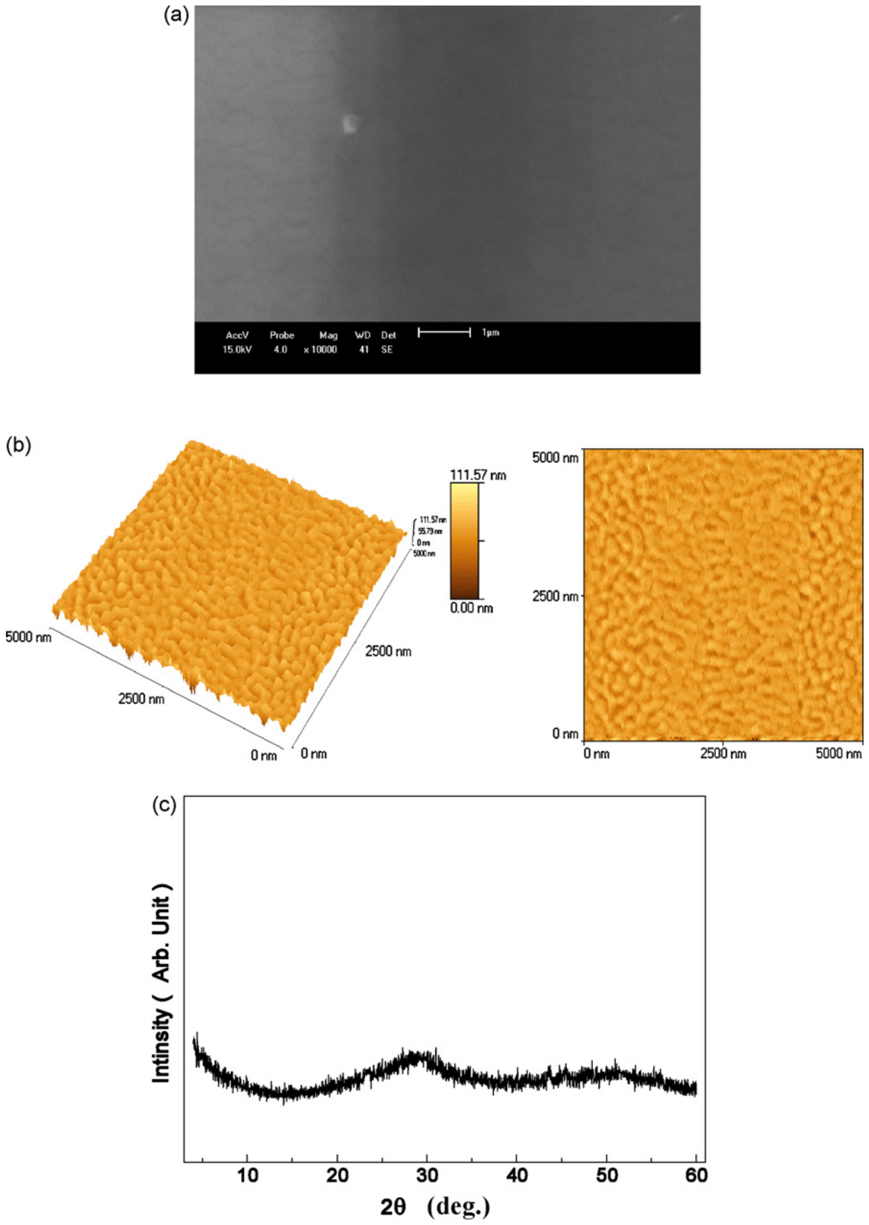

Fig. 1. (a) SEM photograph of a-Se thin film. (b) 3D (left) and 2D (right) 5 μm × 5 μm AFM pictures of the surface of a-Se thin films. (c) XRD pattern of a-Se thin film.

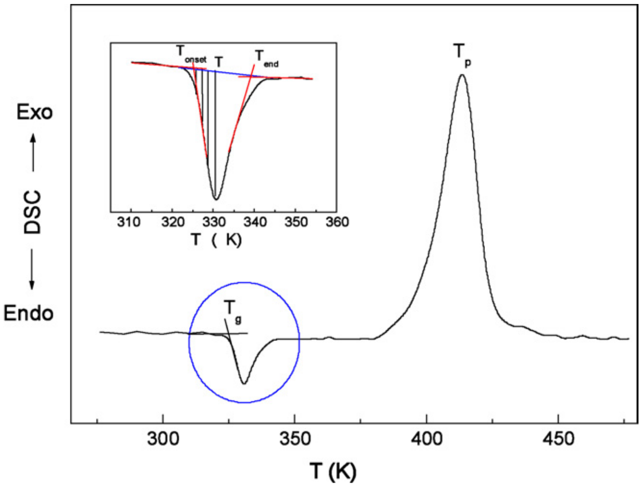

Fig. 2. DSC curve of the a-Se thin film at heating rate 40 K/min. The inset illustrates the determination of extent of conversion (α) using partial area method.

rate dependence of the glass transition temperature T_g can be used to determine the activation energy of the transition from glassy to supercooled liquid state [6,7]. In this work, the extrapolated onset of the endothermic trace was used to define T_g. The exothermic peak temperature T_p is used to identify the crystallization process. Both T_p and T_g shift to higher temperatures with increasing heating rate. The heating-rate dependence of T_g is clearly indicated in Fig. 3. The kinetic aspect of the glass transition is evident from the pronounced shift in T_g.

It has been widely observed that the dependence of the T_g on the heating-rate β follows Lasocka's relationship [8]:

$$T_g = a + b\,\ln\beta \tag{1}$$

where a and b are constants for a given glass composition. In order to see if Eq. (1) describes the heating-rate dependence of T_g, the T_g is plotted against $\ln\beta$ as shown in Fig. 4. As evident from this figure, the present data can be fitted to Eq. (1) for the whole range of β (with correlation coefficient = 0.992). The least square fit to Eq. (1) gives $a = 307.2 \pm 0.9$ K and $b = 5.2 \pm 0.3$ min. As pointed out by Mehta et al. [9], the value of b is sensitive to the cooling rate of the melt. This behavior indicates that the physical significance of b is related to the nature of the structural relaxation within the glass transition region.

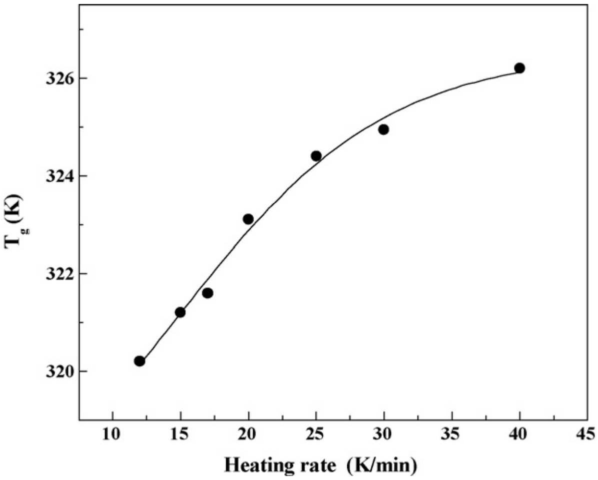

Fig. 3. The heating-rate dependence of the glass transition temperature T_g.

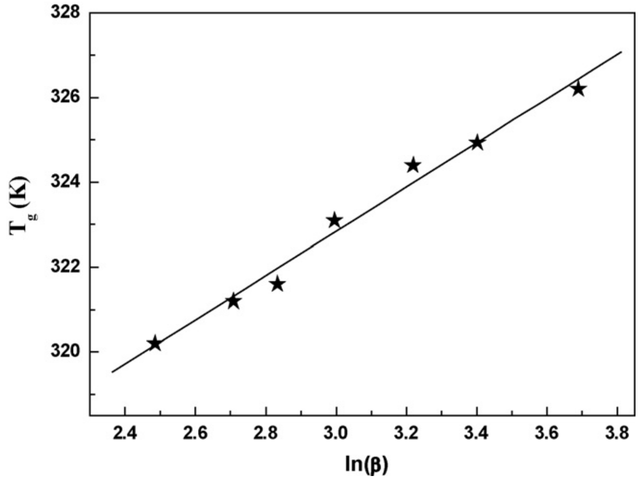

Fig. 4. The glass transition temperature T_g is plotted against $\ln\beta$.

Based on structural relaxation models, the heating and cooling rate dependence of the glass transition temperature was investigated by many authors [6,10–13]. Moynihan et al. [6] have shown that the dependence of the glass transition temperature T_g on heating-rate β is given to a high degree of approximation by:

$$\frac{d\,\ln\beta}{d(1/T_g)} = -\frac{E}{R} \tag{2}$$

where E is the activation energy for the structural relaxation associated with the glass transition and R is the gas constant. According to this model, a plot of $\ln(\beta)$ versus $1/T_g$ gives a straight line. The activation energy for the glass transition can be determined from the slope. In Fig. 5, $\ln(\beta)$ was plotted against $1/T_g$. From the slope of the straight line, it is possible to derive the value of the activation energy for the glass transition, yielding $E = 163.6 \pm 9$ kJ/mol.

On the basis of the free volume model of glass transition, Ruitenberg [14] showed that the well-known Kissinger method for determining the activation energy for crystallization process can also be used to determine the glass activation energy. According to the Kissinger method, the glass activation energy can be obtained using the following equation:

$$\frac{d\,\ln(\beta/T_g^2)}{d(1/T_g)} = -\frac{E}{R} \tag{3}$$

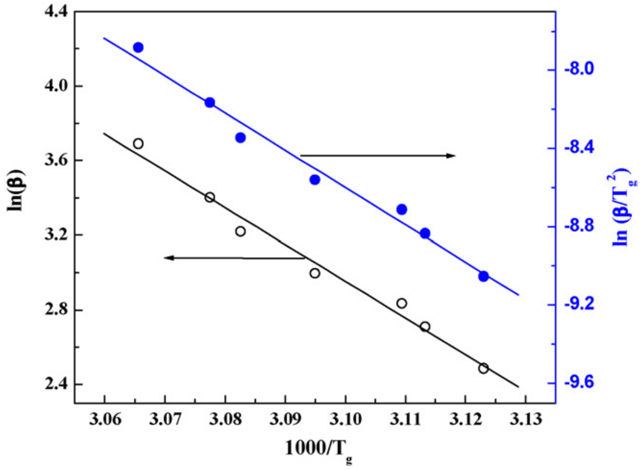

Fig. 5. $\ln(\beta/T_g^2)$ versus $1/T_g$ plot (●) and $\ln(\beta)$ versus $1/T_g$ plot (○) for the a-Se thin film.

A straight line is obtained by plotting $\ln(\beta/T_g^2)$ versus $1/T_g$, as shown in Fig. 5. From the slope of the straight line, the calculated value of E is equal to 159.3 ± 9 kJ/mol.

It is worth mentioning that although Moynihan and Kissinger equations are based on different theoretical models, they both led to similar values of the activation energies.

The variation of E throughout the transformation has been widely observed by many workers. This variation can be investigated using the advanced isoconversional method. The variation of the activation energy throughout the glass transition region can also be revealed using the isoconversional methods. The isoconversional methods were used to investigate the variation of the effective activation energy with extent of transformation and hence with temperature. The extent of conversion α used in the isoconversional analysis was determined using the partial area method: the value of α at temperature T is defined as $\alpha = A_T/A$, where A is the area under the curve of the endotherm between the temperatures $T_{g,\text{onset}}$ and $T_{g,\text{end}}$ (see the inset of Fig. 2). A_T is the area between $T_{g,\text{onset}}$ and T. Using this method, we obtain α versus T at different heating rates as shown in Fig. 6.

Using the experimental data shown in Fig. 6, five isoconversional methods are used to investigate this variation.

(I) On the basis of the Kissinger–Akahira–Sunose method [15–17] (or the generalized Kissinger method as it is sometimes called), the E_α can be determined for each α using the following expression:

$$\ln\left(\frac{\beta_i}{T_{\alpha_i}^2}\right) = C_K(\alpha) - \frac{E_\alpha}{RT_{\alpha_i}} \tag{4}$$

(II) The Flynn–Wall–Ozawa (FWO) method, suggested independently by Flynn and Wall [18] and Ozawa [19]. This method is given by:

$$\ln\beta_i = C_W(\alpha) - 1.0518\frac{E_\alpha}{RT_{\alpha_i}}, \tag{5}$$

(III) The Tang method. A more precise formula for the temperature integral has been suggested by Tang et al. [20], which can be put in the form:

$$\ln\left(\frac{\beta_i}{T_{\alpha_i}^{1.894661}}\right) = C_T(\alpha) - 1.00145033\frac{E_\alpha}{RT_{\alpha_i}} \tag{6}$$

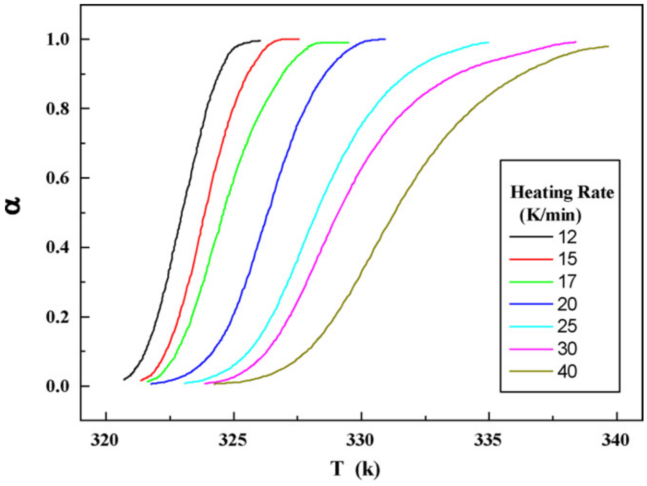

Fig. 6. Degree of transformation α as a function of temperature at different heating rates.

(IV) The Starink method [21,22], another new method, which is given by:

$$\ln\left(\frac{\beta_i}{T_{\alpha_i}^{1.92}}\right) = C_S(\alpha) - 1.0008\frac{E_\alpha}{RT_{\alpha_i}} \tag{7}$$

(V) The fifth approach of extracting the same information is by using the isoconversional method developed by Vyazovkin [23]. For a set of n experiments carried out at different heating rates, the glass activation energy can be determined at any particular value of α by finding the value of E_α which minimizes the objective function Ω, where

$$\Omega = \sum_{i=1}^{n}\sum_{j \neq i}^{n} \frac{I(E_\alpha, T_{\alpha_i})\beta_j}{I(E_\alpha, T_{\alpha_j})\beta_i}, \tag{8}$$

and

$$I(E_\alpha, T_{\alpha_i}) = \int_0^{T_{\alpha_i}} \exp\left(\frac{-E_\alpha}{RT}\right) dT. \tag{9}$$

The temperature integral, I, was evaluated using an approximation suggested by Gorbachev [24]:

$$\int_0^T \exp\left(\frac{-E}{RT}\right) dT = \frac{RT^2}{E}\left(\frac{1}{1+(2RT/E)}\right)\exp\left(\frac{-E}{RT}\right). \tag{10}$$

Fig. 7 shows the variation of the activation energy, E, as a function of the degree of conversion α according to the above five isoconversional methods. The temperature dependence of E can be extracted from Fig. 7 by replacing α with an average T using α versus T curve for the heating rate 20 K/min (from Fig. 6) (shown in Fig. 7 as a solid line) [25]. As indicated in Fig. 8, the five methods show a gradual decrease in E as the temperature increases. All methods show a similar variation of E as a function of α. This close agreement between all isoconversional methods was also reported by Joraid et al. [26], Jankovic et al. [27] and Abu-sehly et al. [28,29]. It is possible that the use of a similar numerical evaluation of an integral equation (like Eq. (10)) in the above isoconversional methods give similar values of E. A decrease of the activation energy with temperature was first reported in polymers by Vyazovkin et al. [7,30].

It is worth noting that the value of E obtained from Moynihan method ($E = 163.6$ kJ/mol) is very closed to the value determined from isoconversional method at $\alpha = 0.1$ (see Fig. 7). This may be due to the fact that in Moynihan method E was obtained from the

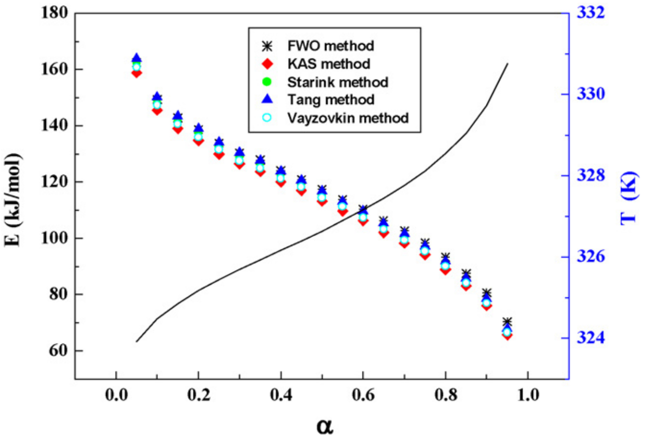

Fig. 7. The effective activation energy as a function of α as determined using different isoconversional methods. Solid line represents $\alpha(T)$ curve corresponding to the average heating rate 20 K/min.

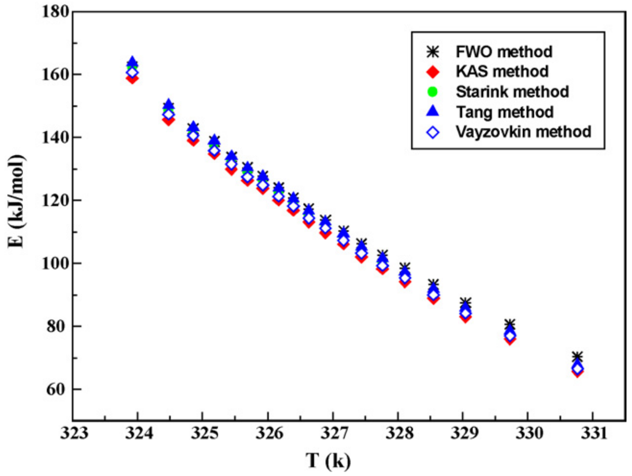

Fig. 8. Variation of the glass activation energy with temperature at different isoconversional methods.

heating-rate dependence of onset T_g which correspond to the early conversion of glass transition, i.e. small α.

The observed decrease of the activation energy with increasing temperature is consistent with prediction of the free volume model of the glass transition. According to this model, the activation energy of the process E depends on the amount of the free volume in the sample. More free volume is related to lower activation energy. The amount of the free volume is assumed to vary linearly with temperature according to the following equation [31,32]:

$$f = f_0 + a(T - T_0) \tag{11}$$

where f is the free volume fraction, f_0 is a free volume fraction at a reference temperature T_0 and a is a constant.

4. Conclusions

Thin films of amorphous Se were prepared by thermal evaporation technique, the films' structure was investigated by XRD, SEM and AFM. The heating-rate dependence of the glass transition temperature in amorphous Se thin films was carried out using DSC technique. It was shown in this work that the transition process cannot be described in terms of single activation energy. Five different isoconversional methods were used to calculate the effective activation energy of the glass transition in amorphous Se thin films. The activation energy was found to vary with extent of conversion (and with temperature). The observed temperature dependence of the activation energy is consistent with the free volume model of the glass transition.

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