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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, ΔH_m = 28.55 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-

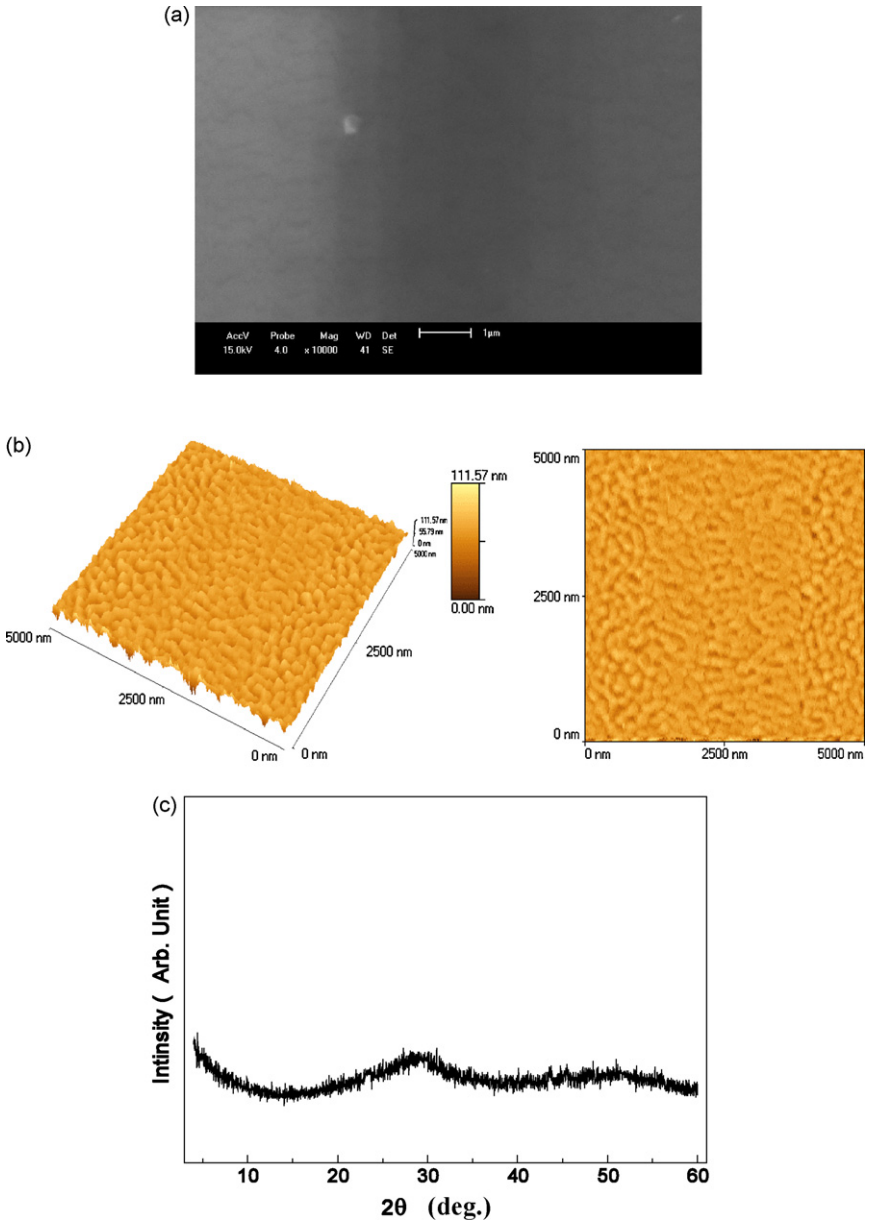

Fig. 1. (a) SEM photograph of a-Se thin film. (b) 3D (left) and 2D (right) 5 μm × 5 μm AFM pictures of the surface of a-Se thin films. (c) XRD pattern of a-Se thin film.