Thin Solid Films 517 (2009) 6137–6141

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Isoconversional kinetic analysis of the crystallization phases of amorphous selenium thin films

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ARTICLE INFO

Article history:
Received 6 May 2008
Received in revised form 3 March 2009
Accepted 18 May 2009
Available online 23 May 2009

Keywords:
Crystallization kinetics
DSC
Thermal analysis
Annealing effect
Model-free
Selenium

ABSTRACT

The crystallization kinetics of Se thin films were determined under nonisothermal conditions using a differential scanning calorimetry (DSC) technique. The development of crystal phases by thermal treatment of the film at various temperatures was analyzed by X-ray diffraction. Microstructures were identified by studying the morphology of the films using scanning electron microscopy and atomic force microscopy. This study reveals the simultaneous presence of distinct hexagonal and monoclinic phases; the DSC crystallization curve is formed by overlapping the exothermic crystallization curves of both phases. Two isoconversional methods, the Kissinger–Akahira–Sunose and Vyazovkin methods, were used to determine the variation of the activation energy for crystallization with temperature. The results show that the crystallization activation energy decreases with the extent of crystallization or temperature, which suggests that the examined phases follow multi-step kinetics.

1. Introduction

Selenium exists in one of four major structures: amorphous, trigonal (hexagonal), and α- or β-monoclinic. The most stable crystal form is the trigonal (hexagonal) Se, consisting of helical Se_n chains. Both monoclinic α and β Se consist of Se_8 rings. Se atoms in the same chain or ring are covalently bound, and the chains or rings are bonded to each other by van der Waals forces [1,2].

Several thermal and structural tests have been performed on amorphous Se created by various deposition techniques [1–8]. Industrial processes often depend on the kinetic behaviour of systems undergoing phase transformation in nonisothermal conditions. The kinetic model equation, combined with the Arrhenius approach for the temperature dependent reaction rate constant ($\beta = \mathrm{d}T/\mathrm{d}t$), can generally be described by [2]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{\mathrm{d}\alpha}{\mathrm{d}t}\left(\frac{1}{\beta}\right) = \frac{A}{\beta}exp\left(-\frac{E}{RT}\right)f(\alpha), \tag{1}$$

where t is time, T is temperature, α is the conversion fraction that represents the volume of the crystallized fraction, A (s^{-1}) is the pre-exponential (frequency) factor, β (K min^{-1}) is the reaction rate constant, E (kJ mol^{-1}) is the activation energy, R is the universal gas constant, and $f(\alpha)$ is the reaction model.

An isoconversion method is a reliable way of obtaining reliable and consistent kinetic information for both nonisothermal and isothermal processes. Two methods have been the most popular for analyzing the crystallization kinetics of the Se films: the Kissinger–Akahira–Sunose (KAS) method [9–11], and a method developed by Vyazovkin [12–14]. The KAS method takes the form:

$$\ln\left(\frac{\beta_i}{T_{\alpha i}^2}\right) = C_{\mathrm{K}}(\alpha) - \frac{E_\alpha}{RT_{\alpha i}}, \tag{2}$$

where the subscript i denotes different heating rates and the parameter $C_{\mathrm{K}}(\alpha)$ is defined as:

$$C_{\mathrm{K}}(\alpha) = \ln\left[\left|\frac{\mathrm{d}f(\alpha)}{\mathrm{d}\alpha}\right|\frac{AR}{E_\alpha}\right].$$

For each degree of the crystallized volume fraction α, a corresponding $T_{\alpha i}$ and heating rate are used to plot $\ln(\beta_i/T_{\alpha i}^2)$ against $1/T_{\alpha i}$. The activation energy E_α is then determined from the regression slope.

Another way of extracting the same information is by using the advanced isoconversional method developed by Vyazovkin. For a set of n experiments carried out at different heating rates, the activation energy can be determined at any particular value of α by finding the value of E_α that minimizes the objective function Ω, where:

$$\Omega = \sum_{i=1}^{n}\sum_{j \neq i}^{n} \frac{I(E_\alpha, T_{\alpha i})\beta_j}{I\left(E_\alpha, T_{\alpha j}\right)\beta_i}, \tag{3}$$

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doi:10.1016/j.tsf.2009.05.034

and

$$I(E_\alpha, T_{\alpha i}) = \int_0^{T_{\alpha i}} \exp\left(\frac{-E_\alpha}{RT}\right) \mathrm{d}T. \qquad (4)$$

The temperature integral I is evaluated using an approximation suggested by Gorbachev [15]:

$$\int_0^T \exp\left(\frac{-E}{RT}\right) \mathrm{d}T = \frac{RT^2}{E}\left(\frac{1}{1+\frac{2RT}{E}}\right)\exp\left(\frac{-E}{RT}\right). \qquad (5)$$

This paper studies the crystallization kinetics of a system that exhibits a single, well-defined broad peak, which was formed by the overlapping of two exothermic crystallization curves. The activation energies for the crystallization of Se thin films were calculated by nonisothermal techniques. The effect of annealing the Se films was investigated by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

2. Experimentation

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 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 2 to 99 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 (T_m = 156.6 °C, ΔH_m = 28.55 J g^{-1}) standard supplied by Shimadzu.

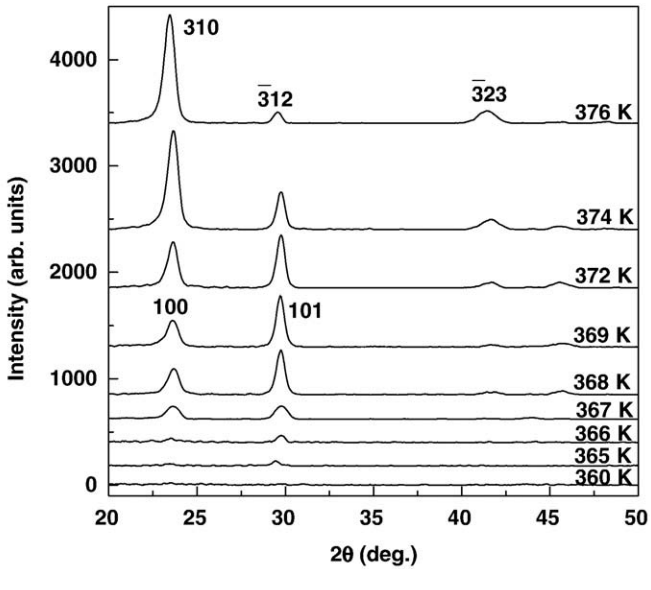

Fig. 1. The XRD patterns of the annealed Se thin films at different annealing temperatures, T_a.

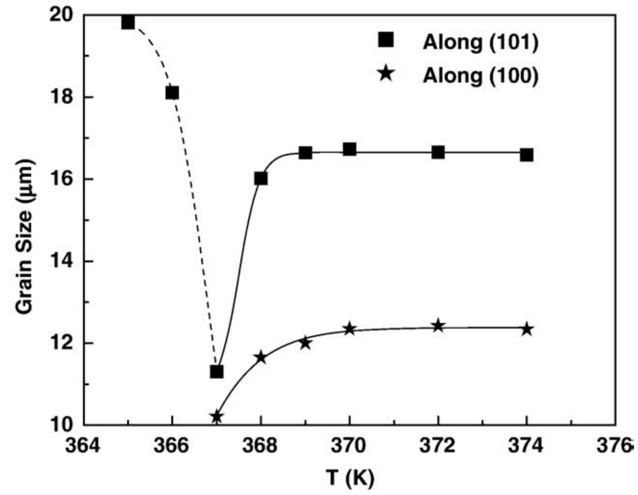

Fig. 2. The estimated crystal size along (101) and (100) as a function of annealing temperature.

The Se structure was examined using a Shimadzu XRD-6000 X-ray diffractometer using CuK$_\alpha$ radiation (λ = 1.5418 A°). The X-ray tube voltage and current were 40 kV and 30 mA, respectively. The scan range was 4–60° (2θ) and the scan speed was 2°/min.

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, and the operating voltage was 15 kV. The analyzed thin films have a thickness of approximately 848 nm. The films were subjected to temperature dependent annealing (T_a) for temperatures between 360 and 380 K for 15 min under a base vacuum of 2×10^{-8} Pa.

The purity of deposited films was checked using the energy dispersive X-ray spectrometer (EDX) accompanying the SEM. Oxygen or other impurity was not detected in the films within the sensitivity of the EDX technique.

3. Results and discussion

The types of Se samples we use have already been investigated by another research group, but they treated the DSC crystallization peaks as corresponding to a single crystallization process [8]. However, the activation energy of crystallization for amorphous Se bulk has been studied by several workers, but agreement has not yet been reached. Pang et al. [16] have reported that the crystallization of amorphous Se prepared by rapid quenching takes place in three separate stages and that the activation energies of the crystallization processes are 52.9, 65.9, and 84.8 kJ mol^{-1}, respectively. Kotkata [17] has reported a value of 96.5 kJ mol^{-1} for quenched samples of Se. Zhang et al. [18] have reported that the crystallization of amorphous Se occurs in a single step and the corresponding activation energy is 54.5 kJ mol^{-1}. Fan et al. [19] have reported that the activation energy for the crystallization of amorphous Se samples prepared by ambient-temperature milling is 83.2 kJ mol^{-1}. Holubova et al. [20] have reported that the activation energy of isothermal crystallization of amorphous Se prepared by the melt–quench technique is 83 kJ mol^{-1}. Joraid [8] studied the crystallization kinetics of Se thin films under nonisothermal conditions and reported that the activation energy varies with temperature, and gave values in the range 83–55 kJ mol^{-1} for results obtained using the KAS method. More recently, Joraid et al. [2] have studied the variation of the activation energies of crystallization, $E_\alpha(T)$, of Se bulk samples and these were found to be strongly temperature dependent. The KAS and Vyazovkin methods gave identical values, and the range of $E_\alpha(T)$ was found to vary in the range 110.4–44.2 kJ mol^{-1}.

However, when a DSC peak in glass is a result of multiple phenomena, the overlapping region between the DSC crystallization