

CRYSTALLIZATION PROCESS IN AMORPHOUS Sn-Te-Se THIN FILMS

A. BHARGAVA*, JAYA KALLA, B. SUTHAR

*Nanophysics laboratory, Department of Physics, Government Dungar College,
Bikaner-334001, India*

The results obtained for the isothermal crystallization for a-SnTeSe thin films have been used to determine the expressions for the phase transformation rate in a non-isothermal regime. This formalism enables one to determine the apparent energies of the growth rate and nucleation rate using an accepted protocol. The results show that a temperature range exists where the heterogeneous crystallization is preponderant and, for higher temperatures, the crystallization becomes homogenous with crystallites of size greater than the film thickness.

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1. Introduction

The kinetics of first order phase transformations are important in Physics, Chemistry, Ceramics and Materials Science. Common experimental techniques used to study the phase transformation are optical microscopy [1], X-ray diffraction [2], electrical resistivity [3] and thermal analysis [4]. The goals of kinetic studies are to determine the stability of selected phases and to determine the rates at which those phases evolve as a function of temperature. The values for the nucleation and growth rates of the new phase are desired. While the accuracies of the measurements are quite good, the techniques of data analysis are crude. This is particularly true for non-isothermal studies.

Tellurium-selenium-metal films are known as materials for information optical recording [5]. The photoelectrical studies on these films have shown that they are quite stable against ageing. In addition, the films are photosensitive in a wide spectral range and have changes in the reflectivity on crystallization [6].

This paper examines the phase transformation in amorphous Sn-Se-Te thin films so as to modify transformation rates for an isothermal regime to take into account the non-isothermal regime of the DTA technique. This determines the different crystallization regimes obtained from the thermograms for the different heating rates.

2. Theory

2.1 Isothermal crystallization

The crystallized fraction is determined from the extended volume V_e and total volume V_o by [7]

$$x = 1 - \exp\left(-\frac{V_e}{V_o}\right)$$

*Corresponding author: anamib6@gmail.com

The expressions for nucleation rate and growth rate have been described by various authors [8,9]. The variation of V_e/V_0 with time takes into account the thickness e of the film, when the crystallite reaches the surface of the film. The variations of V_e/V_0 versus time have been calculated by Germain et.al.[10] for the different regimes of crystallization.

The crystallized fraction at different times of crystallization can be written in general form as

$$x = 1 - \exp\left[-\sum_n K_n t^n\right]$$

which is a more general form than that proposed by Avrami [7] and Kissinger[11]. Here K is considered to be Arrhenian, i.e. $K_0 \exp(-E/kT)$. Except for the case of surface induced crystallization, with $a_0 \approx e$ the crystallization fraction can be written as either

$$x = 1 - \exp(-K_n t^n)$$

or

$$x = 1 - \exp\left[-K_n \left(t + \frac{a_0}{v}\right)^n\right]$$

Table 1 gives the values of n and K_n for the corresponding crystallization types. Derivation of x with respect to time and elimination of t between x and dx/dt leads to the equation

$$\frac{dx}{dt} = nK_n (1-x) \left[\ln\left(\frac{1}{1-x}\right) \right]^{1-\frac{1}{n}}$$

Table 1 The parameter n and K_n for various crystallization regimes. Here S is the enclosed surface area, v is the growth velocity

n	1	2	3	3	4
K_n	$\frac{\pi P}{e S} a_0^2 v$	$\frac{\pi P}{S} v^2$	$\frac{4 \pi P}{3 e S} v^3$	$\frac{\pi}{3} e N v^2$	$\frac{\pi}{3} N v^3$
Crystallization mode	Epitaxial	Heterogeneous cylindrical growth	Heterogeneous spherical growth	Homogeneous growth ($a_0 > e$)	Homogeneous growth ($a_0 < e$)

2.2 Non-Isothermal Crystallization

Let us suppose that between temperatures T and $T+dT$, the crystallization rate has the value already calculated for the isothermal regime at temperature T . This rate depends upon temperature through the coefficient K_n . Using the approach of Atmani [16] we can define the functions Y_n which are linear in $1/T$ given as

$$Y_n = \ln \frac{dx}{dt} + \ln\left(\frac{1}{1-x}\right) - \frac{n-1}{n} \ln \ln\left(\frac{1}{1-x}\right)$$

and displayed in Table 2.

Table 2 The functions Y_n

Crystallization mode	Y_n
epitaxy	$Y_1 = -\frac{E_v}{kT} + \ln\left(\frac{\pi P}{e S} a_o^2 v_o\right)$
cylindrical heterogeneous growth	$Y_2 = -\frac{E_v}{kT} + \ln 2\left(\pi \frac{P}{S} v_o^2\right)^{1/2}$
spherical heterogeneous growth	$Y_3 = -\frac{E_v}{kT} + \ln 3\left(\frac{4 \pi P}{3 e S} v_o^3\right)^{1/3}$
homogeneous growth with $a_o > e$	$Y_3 = -\frac{E_N + 2E_v}{3kT} + \ln 3\left(\frac{\pi}{3} e N_o v_o^2\right)^{1/3}$
homogeneous growth with $a_o < e$	$Y_4 = -\frac{E_N + 3E_v}{kT} + \ln 4\left(\frac{\pi}{3} N_o v_o^3\right)^{1/4}$

3. Experimental procedure

Amorphous $\text{Sn}_3\text{Te}_{17}\text{Se}_{80}$ bulk samples were prepared from 5N purity Se, Te and 4N purity Sn materials obtained from Aldrich Chemicals Inc. A rocking furnace was used to prepare the samples in a quartz ampoule and subsequently quenched in ice. The samples were confirmed to be amorphous using the x-ray diffraction.

The films were prepared by thermal evaporation of the bulk material on aluminum substrates in a high vacuum system (Hind High Vacuum). This ensures a good thermal contact in the Differential Thermal Analyzer. The evaporation source was maintained at a temperature of 500K, whereas the substrates were held at room temperature. It is well known that the film stoichiometry, uniformity, microstructure and the level of light elements contamination would have a great effect on the material crystallization process. Sn, Te and Se are all very sensitive to oxygen and moisture. Therefore, care was taken to prepare about eighty films simultaneously and the films were stored in vacuum to avoid ambient effects. The DTA measurements were done in the Perkins-Elmer analyzer.

For different heating rates r_1, r_2 etc, it was assumed that homogeneous crystallization with $a_o > e$ becomes preponderant in different temperature domains. It is then possible to calculate the values of Y_2 for the different domains and show it to be a linear function of $1/T$. Since Y_2 does not depend on the heating rate, therefore we had taken samples in such a way that E, a_o and P/S remains same. Conversely, we can plot Y_2 with different domains. Then the values of the slope and of the ordinate at the origin enable us to determine the crystallization parameters.

Thermograms were determined for heating rates in the range 0.1 to 0.8 Ks^{-1} . It was observed that the shape of the peak depends on the heating rate $r = dT/dt$, the maximum shifting to higher temperature as r increases. The values of x and dx/dt were determined using the method of Borchard[12]. The proportionality coefficient was obtained by the normalization condition. The Y_n functions were calculated using a MATLAB program. By plotting Y_n versus $1/T$, we determine the temperature range for which n (2 or 3) becomes preponderant.

4. Results and discussion

Fig. 1 shows the Y_2 values for different heating rates. As expected, it was found that higher the heating rate, higher is the temperature range. Using the expression deduced in Table 3, the

slope of the common straight line is equal to $-E/k$, which leads to a value of $E = 0.54\text{eV}$. This value of growth energy is different from the value obtained by Mahajan et.al. [13].

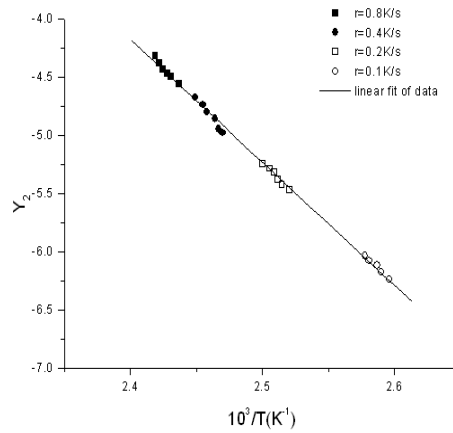


Fig. 1. Variation of Y_2 function with temperature for different heating rates r .

In the present work the $n=1$ regime is not preponderant in the experimental temperature range. For $n=3$ (Figure 2), there is in fact a straight line. But to which of the two regimes, heterogeneous (slope $-E_v/k$) or homogeneous (slope $-(E_N+2E_v)/3k$), does this curve correspond to needs to be examined. The experimental value of the slope corresponds to an activation energy of about 0.88eV , which is different from the value found above. Therefore, we assign this value to $-(E_N+2E_v)/3k$ with $E_N=1.56\text{eV}$ and the homogeneous crystallization with $a_o > e$ preponderant. Unfortunately, the values of the ordinate at the origin deduced from figures do not permit an estimation of the parameters v_o , N_o and P/S . Further, there are clearly two domains for the heating rates which suggest that at the beginning of the crystallization process, the crystallization is heterogeneous and then the homogeneous crystallization becomes dominant process.

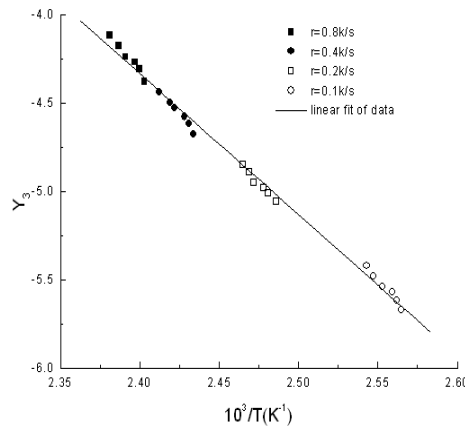


Fig. 2. Variation of Y_3 function with temperature for different heating rates r .

To determine the apparent activation energy of crystallization ΔH , assuming that all the maxima of the thermograms corresponds to the same crystallization type, the temperature T_p corresponding to this maximum is linked to the heating rate r [14]

$$\ln \frac{r}{T_p^2} = -\frac{\Delta H}{nkT_p} + \text{const.}$$

The curve $\ln(r/T_p^2)=f(1/T_p)$ (Figure 3) leads to a value of $\Delta H/n=1.12\text{eV}$ which is close to the value determined above for $(E_N+2E_v)/3k$. In addition, we can also plot $\ln(r/T_p)$ as a function of $1/T_p$ [15] i.e.

$$\ln \frac{r}{T_p} = \frac{1}{n} \left[-\frac{\Delta H}{kT_p} + \ln K_o \right]$$

so that the slope of the straight leads to $\Delta H/n \approx 1.09\text{eV}$ (Fig. 4).

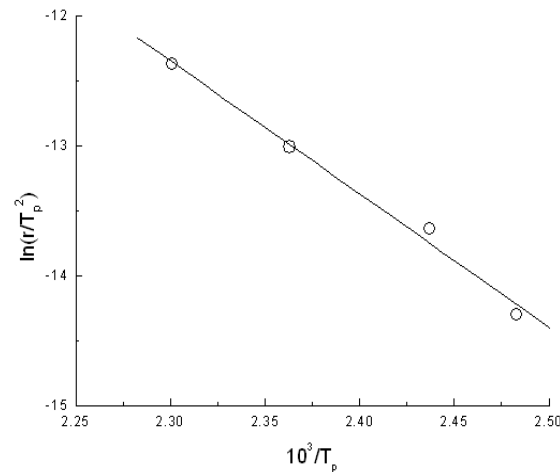


Fig. 3. $\ln(r/T_p^2) = f(1/T)$

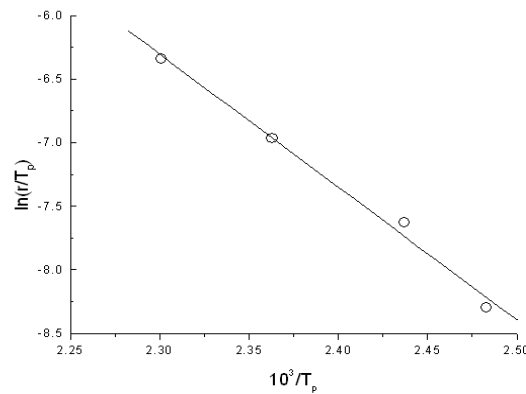


Fig. 4. $\ln(r/T_p) = f(1/T)$

5. Conclusions

We have tried to estimate the non-isothermal kinetic parameters in the temperature range studied for different heating rates. The study shows that in the non-isothermal crystallization, a temperature exists where the heterogeneous crystallization is preponderant, then as the temperature increases the homogeneous crystallization becomes a dominant process, especially when the crystallization rate is maximum. The apparent activation energy E_N is about 1.12eV while that of growth rate E_v is 0.54eV.

References

- [1] A.K.Vashnaya , J. Non-Cryst. Solids **273**, 1 (2000).
- [2] M.Belhadji, N.Ziam and M.Mustafa, Chinese J. Phys. **43**, 95 (2005).
- [3] A.Bhargava, A.Williamson, Y.K.Vijay, I. P.Jain, J. Non-Cryst. Solids **192&193**, 494 (1995).
- [4] M.Saxena, P.K.Bhatnagar, Bull. Mater. Sc. **2695**, 547 (2003).
- [5] P.Upadhyay and A.Bhargava, Solid State Physics (India) **53**, 615 (2008).
- [6] I. Georgieva, D.Nnasheva, D. Dimitrov, V.Kozhukharov, J.Non-Cryst. Solids **160**, 105 (1993).
- [7] J.W.Christian, Theory of Transformation in Metals and Alloys (2nd Ed., Pergamon Press, Oxford , 1975) Ch. 10.
- [8] K.Zellama, P.Germain, S.Squelard, J.C.Bourgoin and P.A.Thomas, J. Appl. Phys. **50**, 6995 (1979).
- [9] P.Germain, K.Zellama, S.Squelard, J.C.Bourgoin and A.J.Gheorghiu, J. Appl. Phys. **50**, 6986 (1979).
- [10] A.Bhargava, Ph.D.Thesis (University of Rajasthan, Jaipur, India, 1997) Ch. 3.
- [11] H.E.Kissinger, J. Res. Nat. Bur. Standards **57**, 217 (1956).
- [12] H.J.Borchard, J.Inorg. Nuclear Chem. **12**, 252 (1960).
- [13] N.B.Mahajan, Kedar Singh and N.S.Saxena, Phys. Stat. Solidi(a) **195**, 305 (2003).
- [14] D.W.Henderson, J.Non-Cryst. Solids **30**, 301 (1979).
- [15] H.Yinnon and D.R.Uhlmann, J.Non-Cryst. Solids **54**, 253 (1982).
- [16] H.Atmani, Phy. Stat. Sol.(a) **88**, 113 (1985).