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Kinematical transformations of amorphous selenium by DTA measurement

M. MATSUURA
Miyagi Technical College, Natori 981–12, Japan

K. SUZUKI
The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai 980, Japan

The effect of sample preparation procedures on the glass transition and crystallization of amorphous Se has been studied by differential thermal analysis. The glass transition mechanism is essentially identical in the amorphous Se samples prepared by melt-quenching and vapour deposition. In contrast, melt-quenched amorphous Se exhibits a double-step crystallization process, as revealed by an asymmetric DTA peak with a shoulder, while there appears a narrow single peak in the crystallization exothermic curve of vapour-deposited Se. These characteristics in the kinematical transformation of amorphous Se samples are discussed using a disordered chain model in which a statistical occupation of Se atoms at the cis- and trans-site in a molecule is proposed.

1. Introduction

Amorphous selenium (hereafter written as a-Se) is an example of a lone-pair semiconductor [1] where the local change in the atomic structure is brought about by external perturbations which results in the drastic variations in physical and chemical properties. This structure-sensitive character of a-Se originates from the lone-pair 4p-electrons localized on each Se atom.

The structure of a-Se has been determined as a mixture of ring molecules consisting of eight Se atoms and chain molecules connecting successively about 10^2 to 10^4 Se atoms [2]. Recently Misawa and Suzuki [3] have shown that the ring–chain equilibrium in molten selenium can be understood in terms of a disordered chain model [4] as a statistical occupation of Se atoms in cis- and trans-sites in a single molecule. If eight Se atoms are successively located at the cis-site a ring molecule is realized, but chain molecules are otherwise formed. Since the occupation probability for the trans-site is increased at higher temperature, chain molecules become predominant in molten selenium with increasing temperature [3, 4]. Therefore, if the quenching rate from the molten state to the amorphous state is rapid enough, the structure of molten selenium at the holding temperature before quenching may be frozen in melt-quenched a-Se and then the thermal history of a-Se is expected to influence the kinematical process for the glass transition and crystallization of a-Se.

This study is aimed at finding by means of differential thermal analysis (DTA) the differences that occur in the behaviour of the glass transition and crystallization of a-Se prepared by the two different methods of melt-quenching and vapour deposition.

2. Experiment

A-Se was prepared by two methods, i.e. melt-quenching and vapour deposition. Melt-quenched a-Se was made by quenching molten Se of 99.999% purity sealed in an evacuated quartz cylinder with an inner diameter of 8 mm and wall thickness of 0.7 mm, into ice water. Before quenching, the molten Se samples were held at 250 ± 5, 450 ± 5 and 700 ± 5° C for 12 hours.

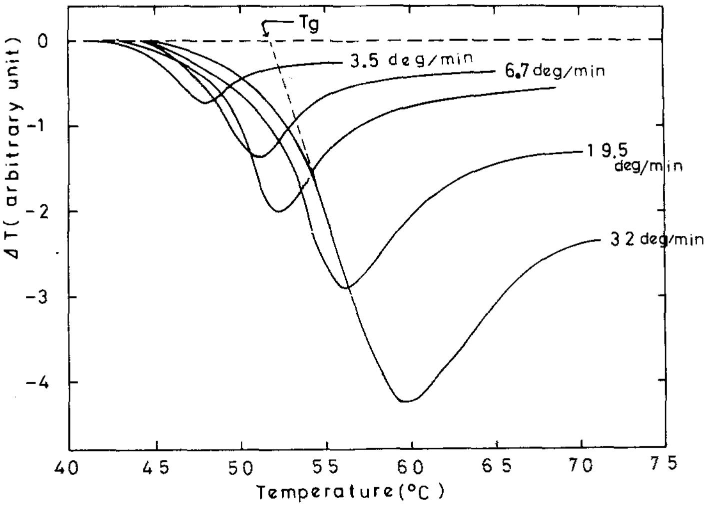

Figure 1 Endothermic curves as a function of heating rate due to the glass transition of amorphous Se melt-quenched from 700° C. The definition of the glass transition temperature (T_g) is shown by a dashed line.

Hereafter these melt-quenched a-Se samples will be referred to as Se_{250}, Se_{450} and Se_{700} respectively.

Vapour-deposited a-Se (hereafter named Se_{vdp}) was prepared by evaporating Se in a vacuum (5×10^{-6} torr) and then depositing it onto the glass substrate which was cooled by liquid nitrogen. The temperature of the molybdenum heater used to evaporate the Se was about 250° C. The vapour deposited a-Se was not a film but fine particles having an irregular form and size distribution of from 10 to 100 μm in length.

Before DTA measurement all of the a-Se was annealed for 3 hours at $60 \pm 2°$ C, which was above the glass transition temperature (T_g) and well below the crystallization temperature (T_c) of a-Se and then cooled at a rate of $0.42°\,\mathrm{C\,min^{-1}}$ to room temperature. This treatment means that all of a-Se samples have the same thermal history over the temperature range related to the glass transition. Therefore, only the effect of the holding temperature of molten Se before quenching upon the glass transition behaviour of a-Se is then observed by DTA measurement. A micro-DTA apparatus of a Shimazu MD-20H model was used for the DTA measurements which were carried out using a 15 mg sample under 1 atm N_2 gas at various heating rates from 4 to $33°\,\mathrm{C\,min^{-1}}$.

3. Experimental results

3.1. Glass transition

The endotherm due to the glass transition occurred in all a-Se samples over a temperature range of 43 to 52° C depending on heating rates. For higher heating rates, the endothermic peak due to the glass transition shifts towards a higher temperature region and the area under the peak becomes larger. Figs. 1 and 2 show the effect of

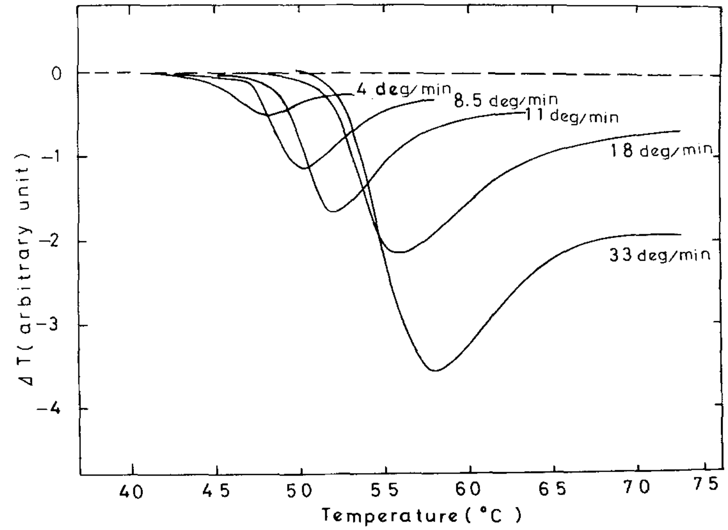

Figure 2 Endothermic curves as a function of heating rate due to the glass transition of amorphous Se deposited from vapour.

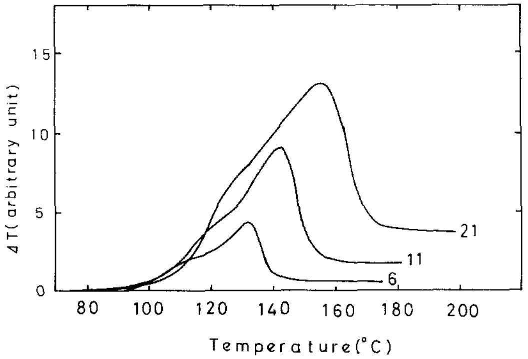

Figure 3 Exothermic curves as a function of heating rate due to the crystallization of amorphous Se melt-quenched from 250° C.

the heating rate on the DTA endothermic peak due to the glass transition of Se_{700} and Se_{vdp}. The definition of T_g is shown in Fig. 1. The other a-Se samples showed identical behaviour about the glass transition endotherm.

3.2. Crystallization

Following the glass transition endotherm, the exotherm due to the crystallization of a-Se begins at temperatures in the range of 80 to 100° C. Unlike the glass transition, the features of the exothermic peak due to crystallization varies remarkably depending on the thermal history of a-Se samples. Figs. 3, 4 and 5 show the exothermic peaks due to crystallization for three samples of Se_{250}, Se_{700} and Se_{vdp}, respectively. Se_{450} displayed similar features to Se_{700} and is therefore not shown.

The crystallization peaks show a pronounced asymmetry in Se_{250} and slight asymmetry in Se_{700}. The exothermic curve, of Se_{vdp}, however, shows sharp and symmetric peaks, and the peak temperatures are lower than those of the melt-quenched a-Se samples by about 25° C. For the melt-quenched a-Se samples, the peak temperature depends little on the holding temperature of molten Se before quenching. This fact suggests that the crystallization rate of Se_{vdp} is higher than those of the melt-quenched a-Se samples. The change in heating rate affects the peak temperature of the crystallization but not the peak shape. The larger the heating rate, the higher is the peak temperature of crystallization. The temperature at which the crystallization begins depends little on the preparation method, thermal history and heating rate for all of the a-Se samples.

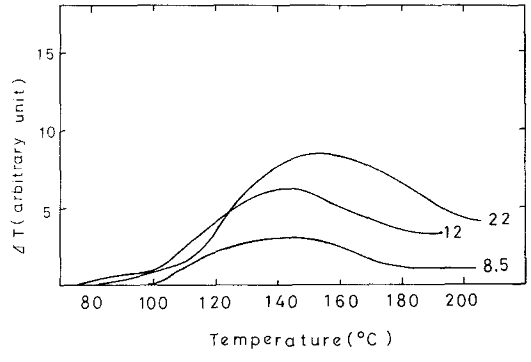

Figure 4 Exothermic curves as a function of heating rate due to the crystallization of amorphous Se melt-quenched from 700° C.

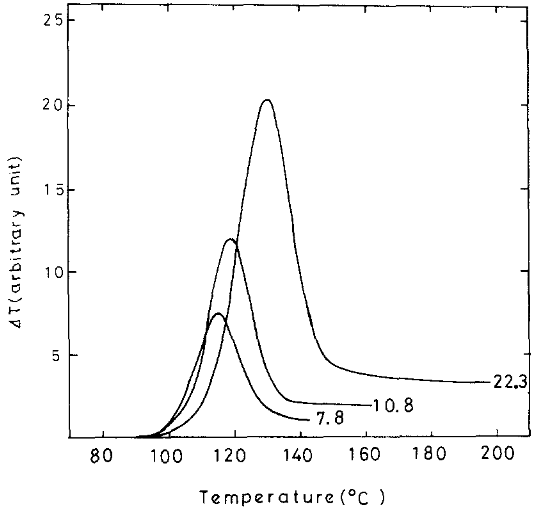

Figure 5 Exothermic curves as a function of heating rate due to the crystallization of amorphous Se deposited from vapour.

4. Discussion

Theories on the effect of heating or cooling rate on the glass transition temperature have been proposed by McMillan [5] and Moynihan *et al.* [6]. The relationship between the glass transition temperature (T_g) and heating rate (q) has been derived by Moynihan *et al.* [6] as follows

$$d \ln |q|/d(1/T_g) = -\Delta h/R \qquad (1)$$

where Δh is the activation enthalpy for the relaxation time controlling the structural enthalpy. If T_g is defined as the onset temperature of the endotherm of the DTA curves, as shown in Fig. 1, the relationship between $\ln q$ and $1/T_g$ is that shown in Fig. 6.

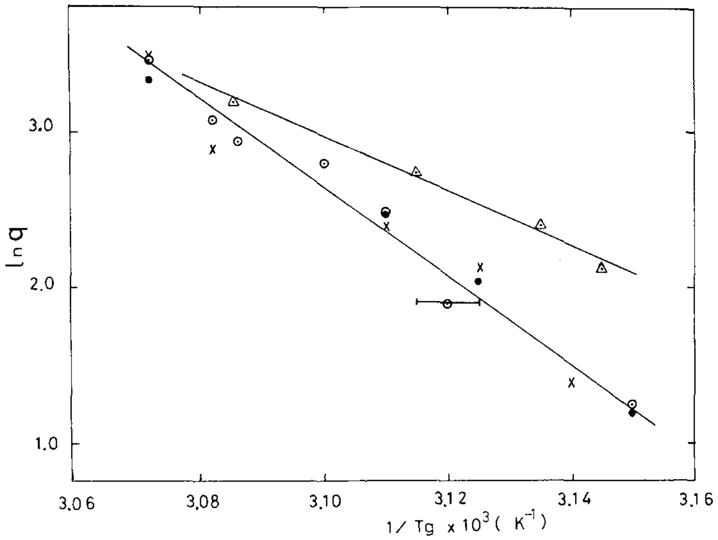

Figure 6 Relationships between glass transition temperature (T_g) and heating rate (q): △, Se_{250} ; ×, Se_{vdp}; ⊙, Se_{700} ; •, Se_{450} .

The results for Se_{vdp}, Se_{700} and Se_{450} but not Se_{250} approximate to an identical straight line. The activation enthalpy Δh was estimated from the slope of the lines in Fig. 6 according to Equation 1. Their values are 37 ± 5 kcal mol^{-1} for Se_{250} and 57 ± 5 kcal mol^{-1} for Se_{vdp}, Se_{700} and Se_{450}. These magnitudes of Δh are smaller than those obtained from the stress relaxation by Eisenberg and Tobolsky [7]: 50 kcal mol^{-1} and 65 kcal mol^{-1} for the melt-quenched at 270 and 500° C, respectively. Though the absolute values of Δh in this work are different those of Eisenberg and Tobolsky, both works agree about the tendency that the lower the holding temperature of molten Se before quenching, the smaller the value of Δh becomes. In contrast, Wolpert *et al.* [8] have reported that the influence due to the thermal history appears on T_g only when the holding temperature of molten Se before quenching attains 900° C, but their experimental results indicate clearly that the plot of $\ln q$ versus $1/T_g$ for Se_{235} differs from the other melt-quenched a-Se samples.

The exothermic curves for the crystallization of Se_{250}, Se_{700} and Se_{vdp} samples with similar heating rates are compared in Fig. 7. a-Se_{250} and Se_{700} samples show asymmetric exothermic peaks and have a shoulder on each peak on the low temperature side as indicated by an arrow in the figure. The temperature at the shoulder is consistent with the peak temperature of the Se_{vdp} sample. This fact suggests that the crystallization of the melt-quenched a-Se takes place in the same manner as Se_{vdp} at the first step and then follows an additional crystallization process.

This double-step mechanism for the crystallization process of a Se may be interpreted in terms of cis- and trans-site occupation of Se atoms

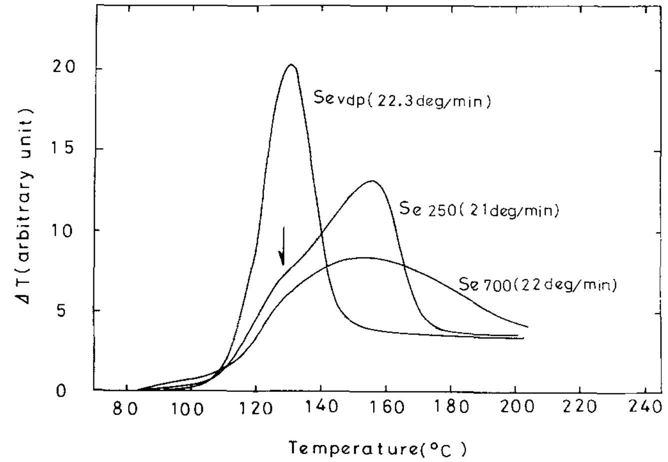

Figure 7 Comparison of exothermic curves with similar heating rates due to crystallization of Se_{vdp}, Se_{700} and Se_{250}.

in a-Se. Since the potential energy of the trans-site is less than the cis-site in molten Se [3], the occupation probability for the trans-site in a-Se must become higher with increasing holding temperature. Therefore Se$_{\mathrm{vdp}}$ can be regarded as the sample quenched rapidly from a very high holding temperature. If Se$_{\mathrm{vdp}}$ consists almost entirely of Se atoms located at the trans-site and the melt-quenched a-Se samples include both the cis- and trans-sites for Se atoms, the exothermic peaks in Se$_{250}$ and Se$_{700}$ at higher temperatures result from the transition of Se atoms from the cis-site to the stable crystalline site. Such a double step for the crystallization process has been reported from DSC measurements by Kawarada and Nishina [9], though they have found it only at holding temperatures higher than 625° C.

The activation energy of the crystallization for a-Se samples having different thermal histories was estimated using the equation derived by Kissinger [10]

$$\frac{\mathrm{d}[\ln\,(q/T_{\mathrm{m}}^2)]}{\mathrm{d}(1/T_{\mathrm{m}})} = -E/R \qquad (2)$$

where T_{m} is the maximum or shoulder peak temperature, q the heating rate and E the activation energy for the crystallization. Fig. 8 shows the linear relationships between $\ln(q/T_{\mathrm{m}}^2)$ and $1/T_{\mathrm{m}}$ for Se$_{\mathrm{vdp}}$, Se$_{700}$ and Se$_{250}$. The plots for Se$_{\mathrm{vdp}}$ and the shoulder peak of Se$_{250}$ are in a good agreement. The magnitude of E was estimated from the slopes of the straight lines in Fig. 8, i.e. 20 ± 2 kcal mol^{-1} for Se$_{\mathrm{vdp}}$, Se$_{700}$ and the shoulder peak of Se$_{250}$ and 16 ± 2 kcal mol^{-1} for the main peak of Se$_{250}$. For Se$_{700}$ the apparent maximums found without a strict definition were used to plot the relationship of Equation 2, because the exothermic peaks for Se$_{700}$ were too broad, as shown in Fig. 4, to separate the shoulder from the main peak. These values are smaller than the values of 26 kcal mol^{-1} obtained from X-ray diffraction by Mamedov and Nurieva [11] and 25 kcal mol^{-1} from dilatometric study by Janjua *et al.* [12]. One of the reasons for the lower values of the activation energy in this work is because Equation 2 is not always rigorous as T_{m} does not necessarily correspond to the temperature of the maximum reaction rate as indicated by Reed *et al.* [13]. An alternative reason may be based on the size difference between a-Se samples used in the measurements, i.e. 0.1 to 0.5 mm in diameter for Se$_{250}$, Se$_{450}$ and Se$_{700}$, and 0.01 to 0.1 mm in length for Se$_{\mathrm{vdp}}$ used in this work in contrast to the large bulk samples used in the other works described above. The smaller the sample size, the more easily the heat of the crystallization can be released. Therefore, the activation energy of the crystallization is smaller in this work than in the other works.

5. Conclusions

A kinematical study on the glass transition and crystallization process was carried out using DTA measurements on a-Se samples which were prepared by melt-quenching and vapour deposition methods. The overall behaviour of the endotherms due to the glass transition seem to be similar in

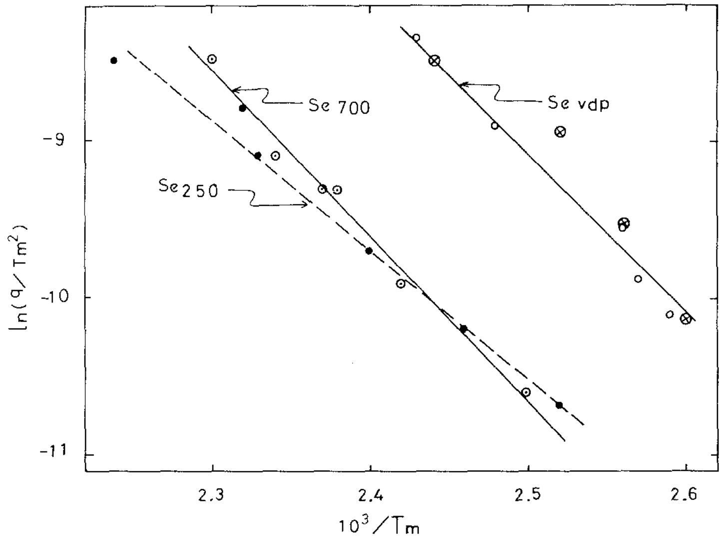

Figure 8 Plot of $\ln(q/T_{\mathrm{m}}^2)$ versus $1/T_{\mathrm{m}}$. ○, Se$_{\mathrm{vdp}}$; ●, Se$_{250}$; ⊙, Se$_{700}$; ⊕, shoulder peak temperature in Se$_{250}$.

the a-Se samples prepared by the two methods. However, the activation enthalpy for the glass transition of the a-Se sample melt-quenched from near the melting point is smaller in value than that for the samples quenched from temperatures far from melting point. The vapour-deposited a-Se sample shows, interestingly, the same behaviour of the glass transition with the a-Se samples melt-quenched from high temperatures.

The exotherm due to the crystallization of vapour-deposited a-Se sample had sharp and symmetrical peak corresponding to a single-step process, while melt-quenched a-Se samples show a broad and asymmetrical peak with a shoulder in the region of 20 to 25° C below the main peak temperature which indicates a double-step process. The magnitude of the activation energy for the crystallization of the vapour-deposited a-Se sample is quite close to the value obtained from the shoulder in the exothermic peak due to the crystallization of the melt-quenched a-Se sample, which is smaller than the value obtained from the main peak in the crystallization exotherm of the melt-quenched a-Se sample.

These experimental results can qualitatively be understood in terms of the disordered chain model [3, 4] which proposes that Se atoms occupy statistically the cis- and trans-sites in a single molecule. The fraction of Se atoms located at the cis-site, which is the more stable conformation energetically, is increased in a-Se with decrease of holding temperature in the molten state. On the other hand, the occupation probability for the trans-site rises in both the a-Se samples vapour-deposited and melt-quenched from higher temperatures. In the a-Se sample quenched from near the melting point, therefore, ring molecules are much predominant and the activation enthalpy for the glass transition becomes small because of the high mobility of ring molecules. The first step is the transition of Se atoms from the trans-site to the trigonal crystalline site which occurs in the crystallization process, and is followed by the second process of the transition from the cis-site to the trigonal crystalline site. The crystallization is a single-step process in the vapour-deposited a-Se sample which has only trans-sites, because the vapour deposition corresponds to melt-quenching from very high temperatures.

Further experimental work on the atomic scale structures and calorimetry especially with constant heating rates [14] are needed to obtain more detailed and definite conclusions about the kinematical process of the glass transition and crystallization of a-Se prepared by various methods.

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