

# Crystallization in Se-Te thin films

Jiri Málek<sup>1\*</sup>, Jaroslav Barták<sup>1</sup>, Hiroyo Segawa<sup>2</sup>, Yoko Yamabe-Mitarai<sup>2</sup>

<sup>1</sup>Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic

<sup>2</sup> National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044 Japan

\*corresponding author: [jiri.malek@upce.cz](mailto:jiri.malek@upce.cz)

## ABSTRACT

Crystallization process in  $\text{Se}_{100-x}\text{Te}_x$  thin films ( $x = 10, 20$ ) was studied by direct observation of crystal growth by using scanning electron microscopy (SEM) and in-situ X-ray diffraction (XRD). The experimental data were analyzed and described by 2D surface-nucleated model and conventional Johnson-Mehl-Avrami model.

## 1. INTRODUCTION

Chalcogenide phase change materials can be rapidly switched between amorphous and crystalline state that exhibit a significant difference of optical and electrical properties. A detailed understanding of crystallization process is of great importance [1,2]. Several methods of analysis should be applied to elucidate the mechanism of this process, separate nucleation and growth phases, as well as distinguish the bulk and surface crystallization. Some additional properties such as shear viscosity and heat capacity of supercooled liquid are needed as well. It is also convenient to select such a composition that can be prepared in the form of bulk material, powder fractions with defined particle size distribution as well as thin films. Recently, a detailed study of bulk and surface crystallization in Se-Te system has been published [3]. The crystal growth in the same system was studied by d.c. electrical conductivity and IR microscopy [4]. In present paper, the crystallization process in Se-Te thin films is studied by direct observation of crystal growth using SEM and in-situ XRD. It is demonstrated that the crystal growth kinetics can be described by standard kinetic models that provides the description and prediction of the crystallization behavior and related material properties under various experimental conditions. Such description can be useful for finding and optimization of new hi-tech materials.

## 2. EXPERIMENTS

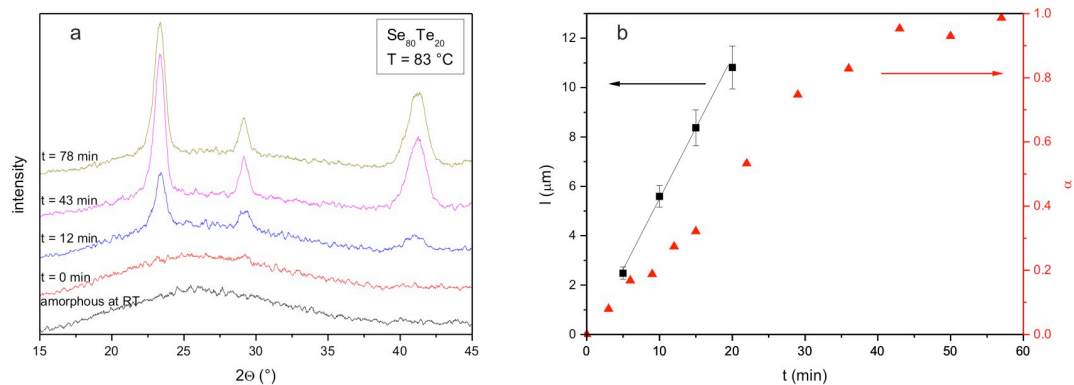
Bulk glasses of chosen compositions ( $\text{Se}_{90}\text{Te}_{10}$ ,  $\text{Se}_{80}\text{Te}_{20}$ ) were prepared from pure elements (5N, Sigma Aldrich) by conventional melt-quench technique (synthesis at 450 °C for 24 hrs, quenching in flow of air). As prepared bulk glasses were used as a starting material for preparation of thin films of the same composition. Thin films were prepared by thermal evaporation in vacuum ( $2 \cdot 10^{-4}$  Pa) on microscopy glass substrates (deposition rate was 1-2 nm/s). Final thickness of prepared films was 1  $\mu\text{m}$ . The composition of prepared films was determined by energy dispersive X-ray (EDX) microanalyser and correlated well with bulk composition.

The isothermal crystallization was studied by in-situ X-ray diffraction (XRD) (Rigaku TTR-III, CuK $\alpha$  radiation – 50 kV, 300 mA, parallel plate method) with Pt-heater. Samples were heated at chosen temperatures in the range from 65 to 90 °C. During the isothermal heating, the XRD scans were taken over scattering angles,  $2\theta$  from 15° to 45° at the scanning speed 15°/min.

Microscopy measurements of crystal growth were performed by using field emission electron microscope (SEM) JEOL JSM-6500 F. The samples of  $\text{Se}_{100-x}\text{Te}_x$  thin films were previously heat-treated in a computer-controlled furnace for various times at temperatures where the optimum crystal growth rates are observed. All heat-treated samples were extensively examined, and the sizes of the well-developed crystals grown in thin films were measured and recorded.

## 3. RESULTS AND DISCUSSION

The isothermal crystallization in  $\text{Se}_{100-x}\text{Te}_x$  thin films ( $x = 10, 20$ ) was studied by direct observation of crystal growth using SEM and by in-situ XRD. The time-resolved XRD patterns for  $\text{Se}_{80}\text{Te}_{20}$  thin film heated at 83 °C are shown in Fig. 1a. During the crystallization three peaks in XRD patterns were formed (at  $2\theta = 23^\circ, 29^\circ$  and  $41^\circ$ ), and their intensity increased with the increasing crystal fraction, the similar behavior was observed also for the  $\text{Se}_{90}\text{Te}_{10}$  composition. The crystallization fraction,  $\alpha$ , was calculated using a simple formula:  $\alpha = \Sigma I / \Sigma I_{cr}$ , where  $I$  is integrated intensity of diffraction peaks and the  $I_{cr}$  is the same of the fully crystallized sample. The time dependence of the transformed crystal fraction is shown in Fig. 1b for the  $\text{Te}_{20}\text{Se}_{80}$  at 83°C. The transformation mechanism from amorphous to crystal state (for XRD data) can be described by the Johnson-



**Fig.1** a) Time evolving XRD patterns of Se<sub>80</sub>Te<sub>20</sub> thin film preheated at 83 °C, b) Time dependence of crystal length evaluated from SEM measurements and crystallization fraction evaluated from XRD measurements for Se<sub>80</sub>Te<sub>20</sub> thin film preheated at 83 °C.

Mehl-Avrami (JMA) equation:  $\alpha = 1 - \exp[-(kt)^n]$ , where  $k$  is temperature dependent rate constant,  $t$  is time and  $n$  is Avrami exponent. The linearised JMA plot was used to determine Avrami coefficient and the rate constant from the experimental XRD data. The activation energies of crystallization were calculated in assumption of simple exponential temperature dependence of rate constant  $k$ . The kinetic analysis showed that the mechanism is changing during the crystallization process which is indicated by the variation of Avrami exponent from the value of 1 to 1.8. The crystal growth in Se<sub>100-x</sub>Te<sub>x</sub> thin films was also observed using SEM. It seems that the crystals start to grow from randomly distributed nuclei. The crystals grow spherulitically and their size changes linearly with time as is shown in Fig. 1b for the Se<sub>80</sub>Te<sub>20</sub> composition preheated at 83°C. This type of behavior is typical for crystal growth controlled by interface kinetics. The crystal growth can be described by 2D surface-nucleated model which is operative in this particular case and the calculated temperature dependence of crystal growth rate is in good agreement with the experimental data. Activation energies of crystal growth for both compositions (for SEM data) were calculated from the simple exponential temperature dependence of crystal growth rate. The activation energy of crystal growth seems to be close to activation energy of crystallization calculated from kinetic analysis of the XRD data.

#### 4. CONCLUSION

The crystallization in Se<sub>100-x</sub>Te<sub>x</sub> thin films ( $x = 10, 20$ ) was studied by using in-situ XRD. Applying of JMA model on the measured data it was found that the crystallization mechanism is changing during the crystallization process which is indicated by variation of the Avrami exponent. From the temperature dependence of rate constant calculated from JMA model, the activation energies of crystallization were found. The activation energies of crystallization observed from the XRD experiments are close to those obtained from the direct observation of crystal growth in thin films of the same compositions by using SEM.

*Authors would like to acknowledge financial support from Ministry of Education Youth and Sport (project "Team CMV" CZ.1.072.3.00/09.104) and Czech Science Foundation (project No. P106/11/1152).*

#### REFERENCES

1. S. Raoux, W. Welnic, D. Ielmini: "Phase Change Materials and Their Application to Nonvolatile Memories" Chem. Rev. 110 (2010) 240.
2. M. Wuttig, N. Yamada: "Phase-change materials for rewriteable data storage" Nature Materials 6 (2007) 824.
3. R. Svoboda, J. Málek: "Extended study of crystallization kinetics for Se-Te glasses" J. Therm. Anal. Calorim., (2012), doi 10.1007/s10973-012-2347-x.
4. J. Barták, R. Svoboda, J. Málek: "Electrical conductivity and crystallization kinetics in Te-Se glassy systems" J. Appl. Phys. 111 (2012) 094908, doi 10.1063/1.4712625

#### Biography

Jiri MALEK received his Ph.D. degree in Chemistry at the Inst. Chem. Technol., Pardubice in 1986. He is currently professor of Physical Chemistry at University of Pardubice. His research interest cover kinetics of nucleation-growth processes, structural relaxation in non-crystalline materials and viscosity behavior of highly supercooled liquids. He is a member of Engineering Academy and R&D Council of the Czech government.