On the surface crystallization process in Ge-Ga-Se chalcogenide glasses

H. Klym[1*], I. Karbovnyk[1,2], O. Shpotyuk[3], L. Calvez[4]

[1]Lviv Polytechnic National University, 12, Bandery Str., Lviv, 79013, Ukraine
*E-mail: halyna.i.klym@lpnu.ua; klymha@yahoo.com
[2]Department of Electronics and Computer Technologies, Ivan Franko National University of Lviv, 107, Tarnavskogo Str., Lviv, 79000, Ukraine
[3]Vlokh Institute of Physical Optics, 23, Dragomanova Str., Lviv, 79005, Ukraine
[4]Equipe Verres et et Céramiques, UMR-CNRS 6226, Institute des Sciences chimiques de Rennes, Université de Rennes 1, 35042 Rennes Cedex, France

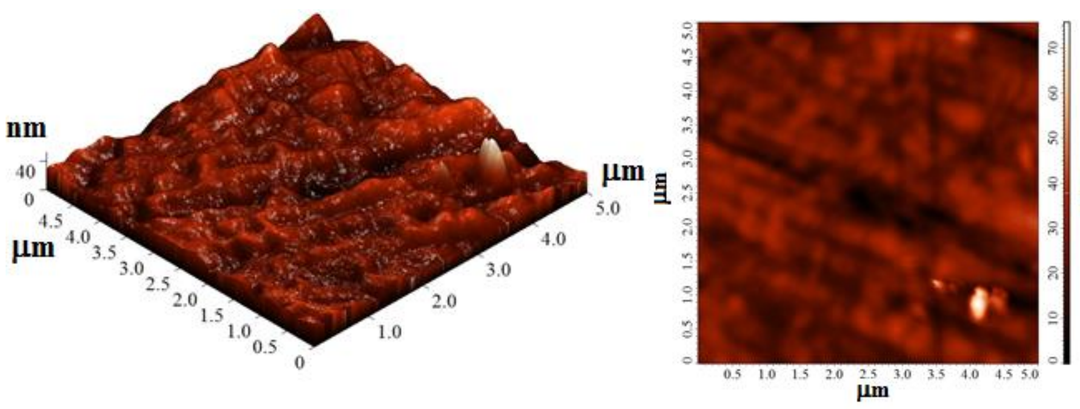
Introduction

The Ge-Ga-Se chalcogenide glasses (ChG) are known for their wide application in optoelectronic systems and IR photonics [1-5]. The crystallization processes in such materials as glass and glass-ceramics can refine their thermal and exploitation properties. In such cases transmission often decreases because the growth of crystals is not controlled, this makes the materials non-transparent. In this work, we analyze crystallization processes on the surface of $80GeSe_2$-$20Ga_2Se_3$ ChG caused by thermal treatment for 25 and 80 h using atomic force microscopy (AFM) probes

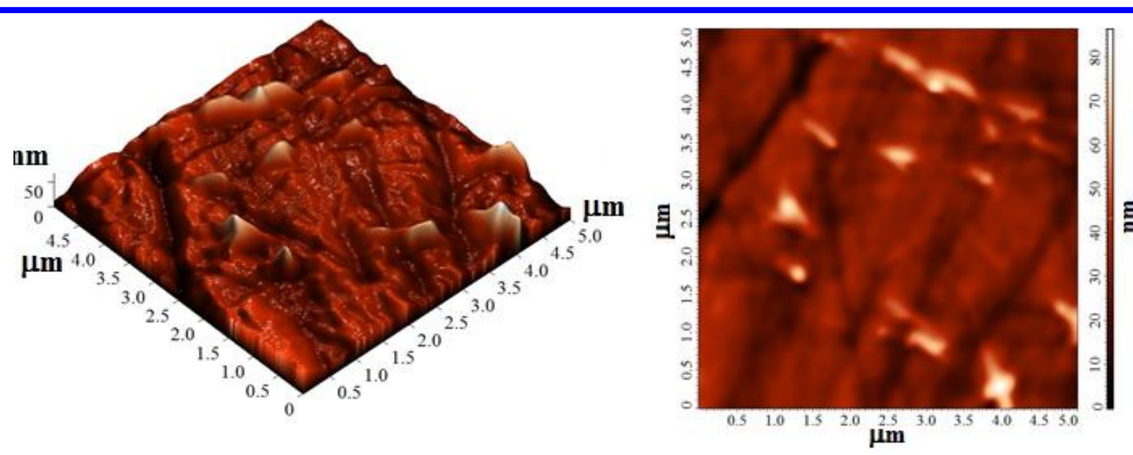
Experimental

Investigated $80GeSe_2$-$20Ga_2Se_3$ ChG were obtained from Ge, Ga and Se high pure materials, as it was described elsewhere [7,9]. The crystallization of the $80GeSe_2$-$20Ga_2Se_3$ glasses were performed at 380 oC (*Tg* + 10 °C). This temperature is optimal for control crystallization of typical Ge-Ga-Se ChG. Morphology of the surface in non-crystallizes and crystallized for 25 h and 80 h $80GeSe_2$-$20Ga_2Se_3$ ChG was investigated by Solver P47-PRO AFM. The images were analyzed by Image Analysis program (NT-MDT).

Results and discussion



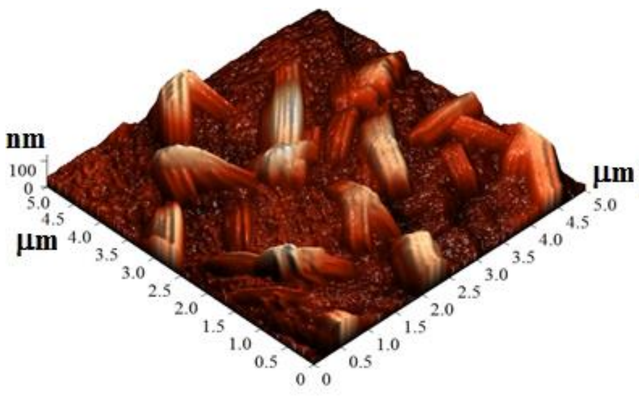
AFM images of base $80GeSe_2$-$20Ga_2Se_3$ glass

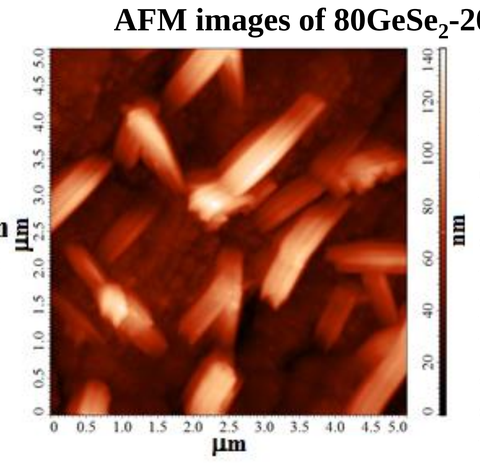


AFM images of $80GeSe_2$-$20Ga_2Se_3$ glass annealed for 25 h

Surface of base $80GeSe_2$-$20Ga_2Se_3$ glass (0 h) is mostly morphologically uniform. At various cycles of potential scan, the surface irregularities and individual appearances appear. It can be caused by hitting under scanning probe microparticles from air since microscope stand is pleased not in a vacuum chamber. The elemental analysis of surface testifies stoichiometric composition of $Ge_{23,5}Ga_{11,8}Se_{64,7}$ glass.

However, the thermal annealing of glasses for slight duration (25 h) causes obvious changes in the surface morphology.





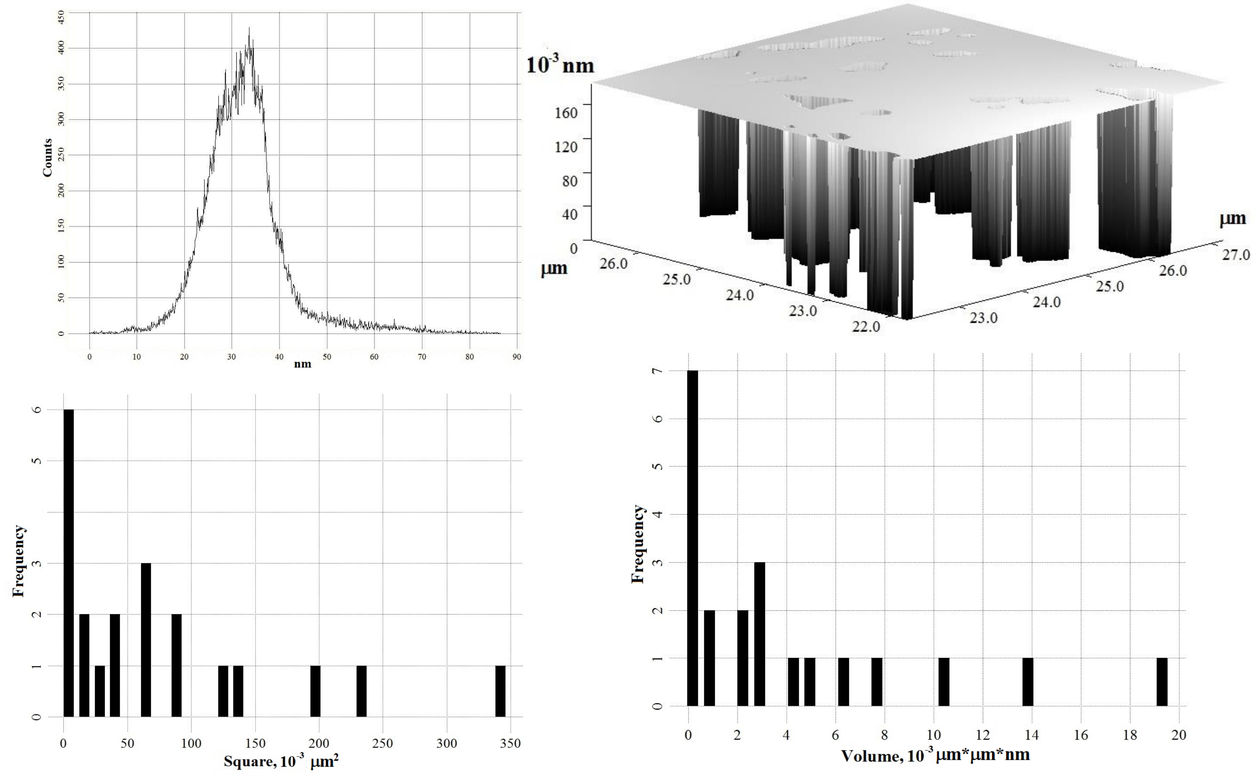
AFM images of $80GeSe_2$-$20Ga_2Se_3$ glass annealed for 80 h

After analyzing the images, we can conclude that thermal annealing at 380 oC for small durations leads to internal transformation of free volume in the $80GeSe_2$-$20Ga_2Se_3$ glass due to formation of addition crystalline phase on the surface. With growing treatment time to 80 h, the wire-like crystallites of $GeSe_2$ phase with size of 1-3 μm are formed on the surface of glasses.

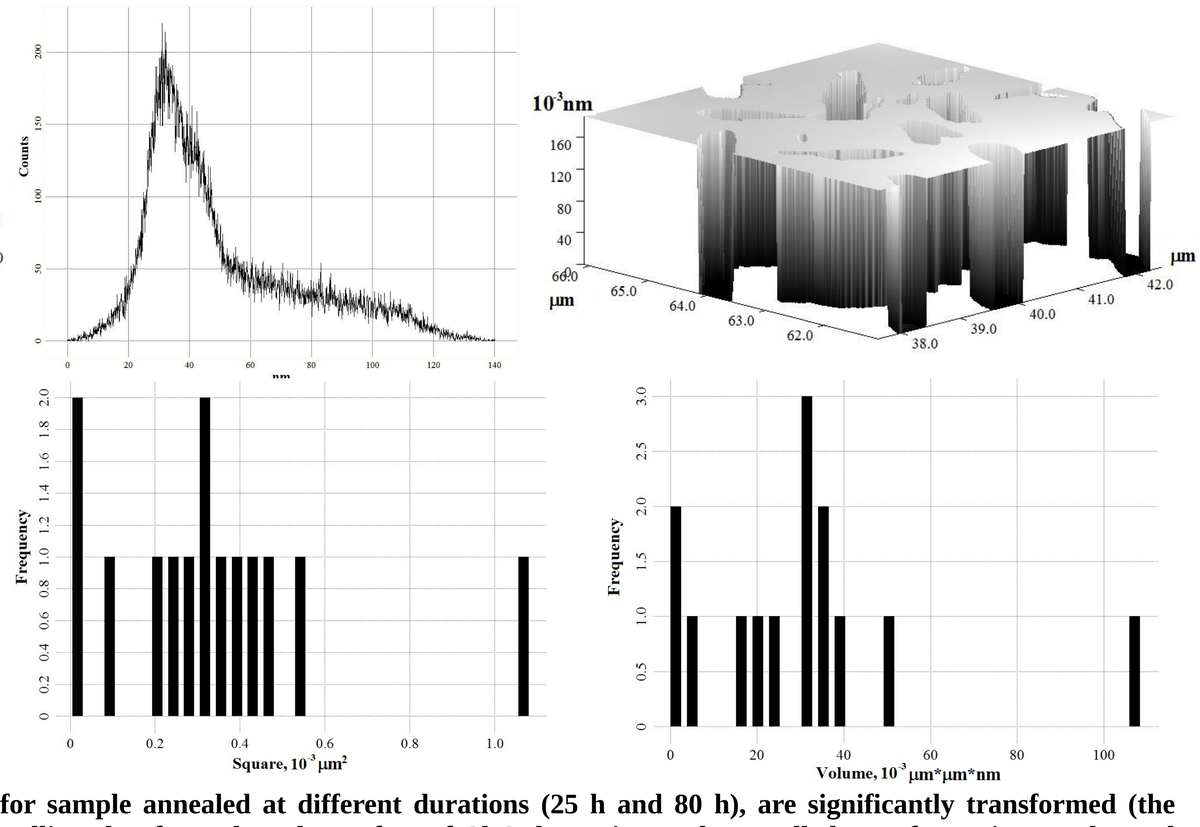
However, after annealing of glasses for longer time (80 h), the significant changes in the morphology of their surface are observed. Crystallites in the form of wires with a clear cut are already clearly formed and unevenly distributed over the glass surface. Their shape and size allows visually to assert that the detected surface phenomenon is the formation of $GeSe_2$ crystallites.

Dimensional distribution of nanocrystals on the surface of the Ge-Ga-Se glasses

Histogram of size distribution of $GeSe_2$ nanocrystals on the surface of ChG annealed for 25 h



Histogram of size distribution of $GeSe_2$ nanocrystals on the surface of ChG annealed for 80 h



The histograms, which reflect the area occupied by crystallites and the volume of the glass surface for sample annealed at different durations (25 h and 80 h), are significantly transformed (the parameters change in order). Particularly clearly these changes are reflected in the volume of $GeSe_2$ crystallites that formed on the surface of ChG due to internal controlled transformations at thermal treatment at 380 °C for 80 h.

Conclusion

Surface crystallization processes in the $80GeSe_2$-$20Ga_2Se_3$ chalcogenide glasses annealed at 380 oC for 25 h and 80 h were studied using atomic force microscopy method. It is shown that crystallites of $GeSe_2$ phase are formed in the crystallized glasses on the surface. It is established that with prolongation of the thermal annealing of $80GeSe_2$-$20Ga_2Se_3$ glasses, additional crystallization of $GeSe_2$ phase occurs on the surface, contributing redistribution of their internal free volume. Optimal conditions for crystallization of ChG were selected.