The advantages of methanol-amine solvent mixtures in solution processing of Ge-Sb-S chalcogenide glass thin films – supplementary materials

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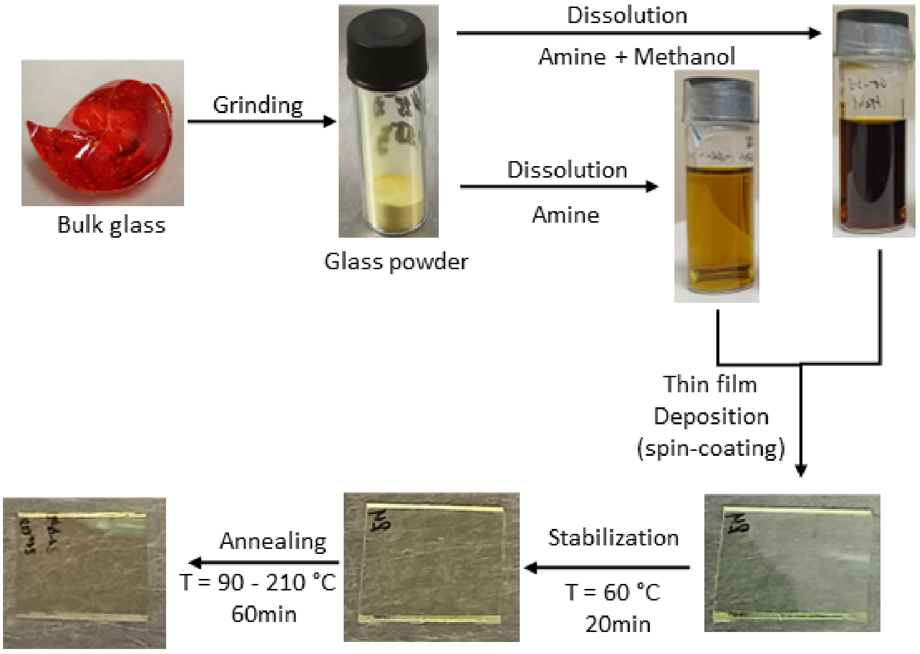
Abstract

We report on the substantial influence of methanol presence on the dissolution mechanism of $Ge_{20}Sb_5S_{75}$ bulk glass with subsequent superior properties of thin films deposited from such solutions. Raman spectroscopy confirmed significant differences in structural features present in glass solutions prepared from pure amines (n-propylamine and n-butylamine) and their mixtures with methanol. The experiments with dissolved elemental sulfur and $Ge_{25}S_{75}$ glass analog proved that both antimony and methanol presence induce further splitting of the $Ge_4S_{10}^{4-}$ cluster structure, which fundamentally affects the properties of deposited thin films. Significant structural and compositional differences were found not only in solutions and as-prepared samples, but also after thin films' thermal treatment (hard baking up to 210°C). The as-prepared thin films deposited from amine-methanol mixtures possessed the exact composition of source bulk glass while thin films of other solvent formulations exhibited sulfur deficiency. The annealing up to 210°C only highlighted this difference. As a result of the different structure of the thin films prepared in this way, the other benefits of methanol addition were found, namely an increase in the refractive index by approx. 0.1 independent of the annealing temperature, or a lower thermally induced thickness contraction (up to 7.5%).

S1: Scheme of thin film samples preparation.

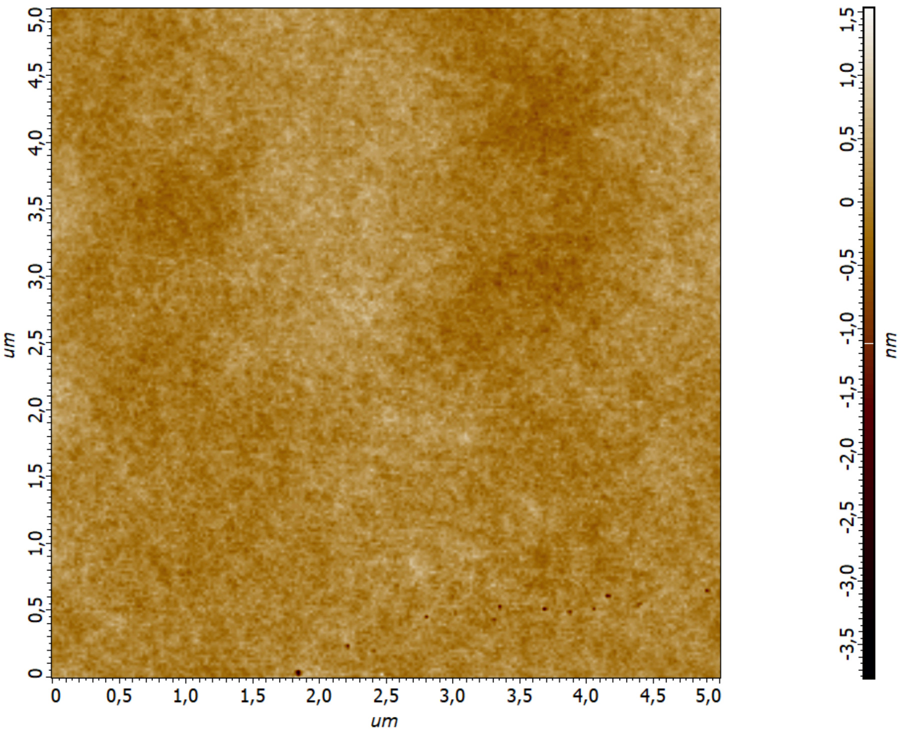


S2: Table of thicknesses evaluated from transmission spectra and measured by AFM at the same samples of $Ge_{20}Sb_5S_{75}$ thin film annealed at 210 °C.

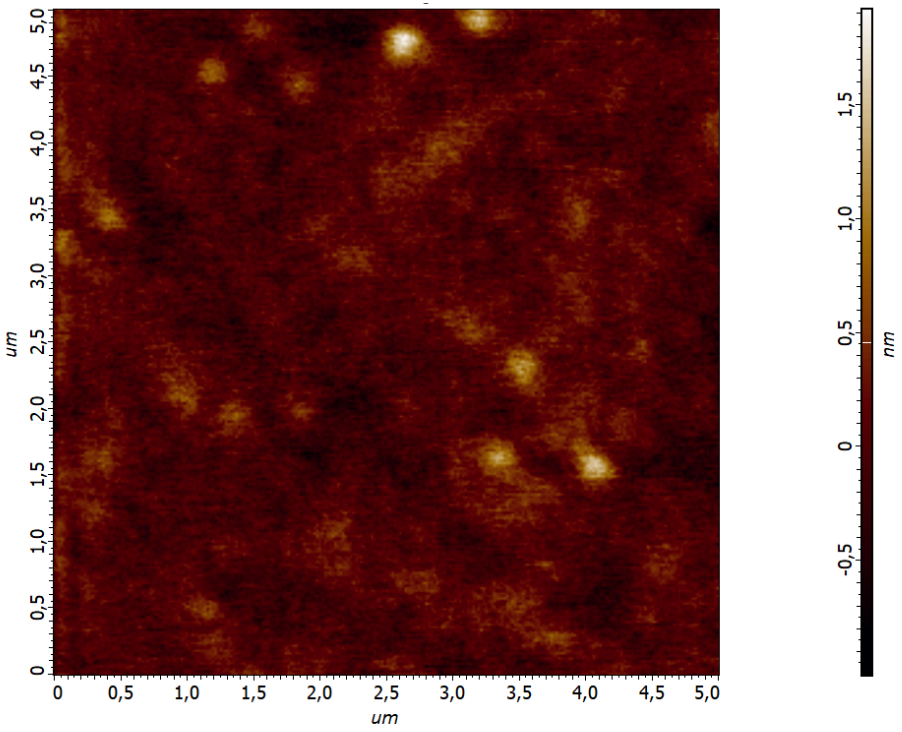
Solution used	**Thickness determined from UV-VIS-NIR transmission spectra (nm)**	**Thickness measured by AFM (nm)**
PA	**258.9**	**257.9**
PA-MetOH	**238.9**	**248.7**
BA	**244.6**	**238.4**
BA-MetOH	**319.2**	**334.3**

S3: AFM scans of as-prepared $Ge_{20}Sb_5S_{75}$ thin films and thin films annealed at 210°C.

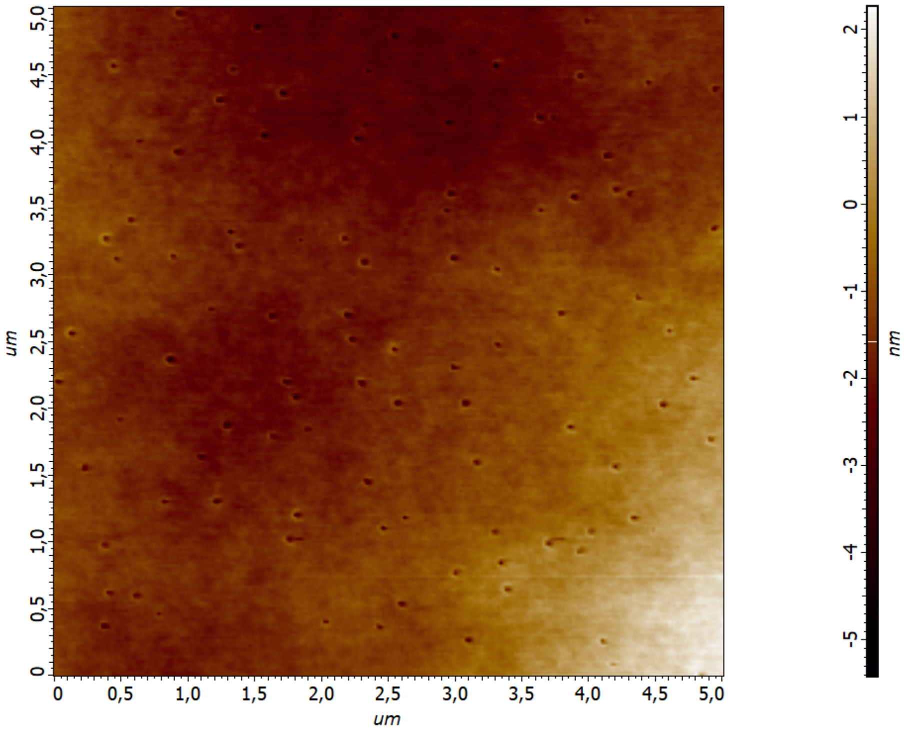
As-prepared thin film from pure PA; RMS = 0.26 ± 0.07 nm



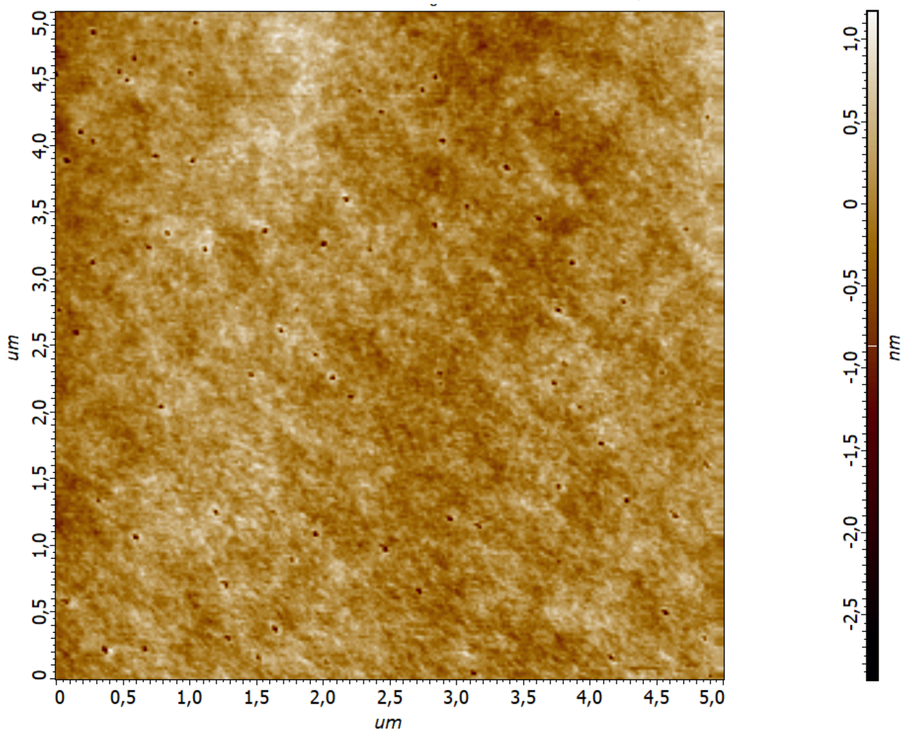
Annealed thin film at 210°C from pure PA; RMS = 0.25 ± 0.08 nm



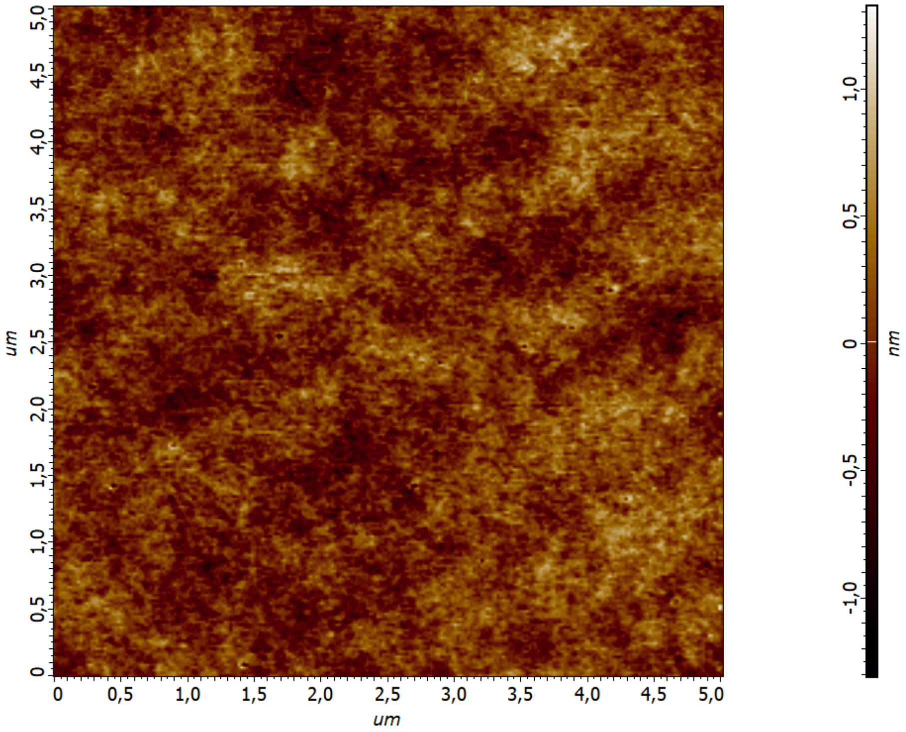
As-prepared thin film from PA-MetOH mixture; RMS = 0.63 ± 0.24 nm



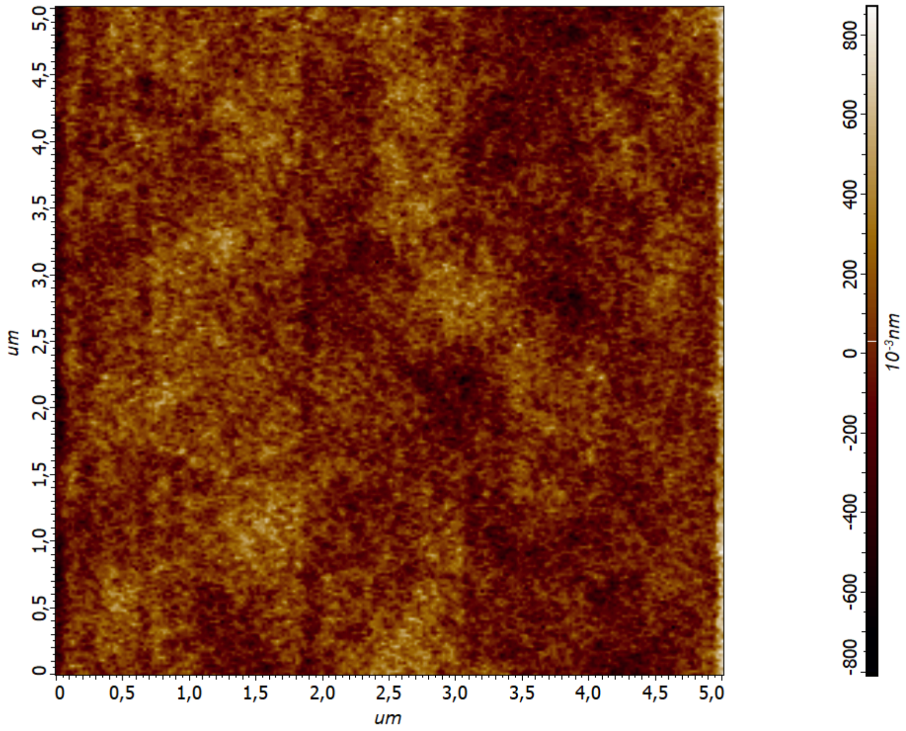
Annealed thin film at 210°C from PA-MetOH mixture; RMS = 0.34 ± 0.04 nm



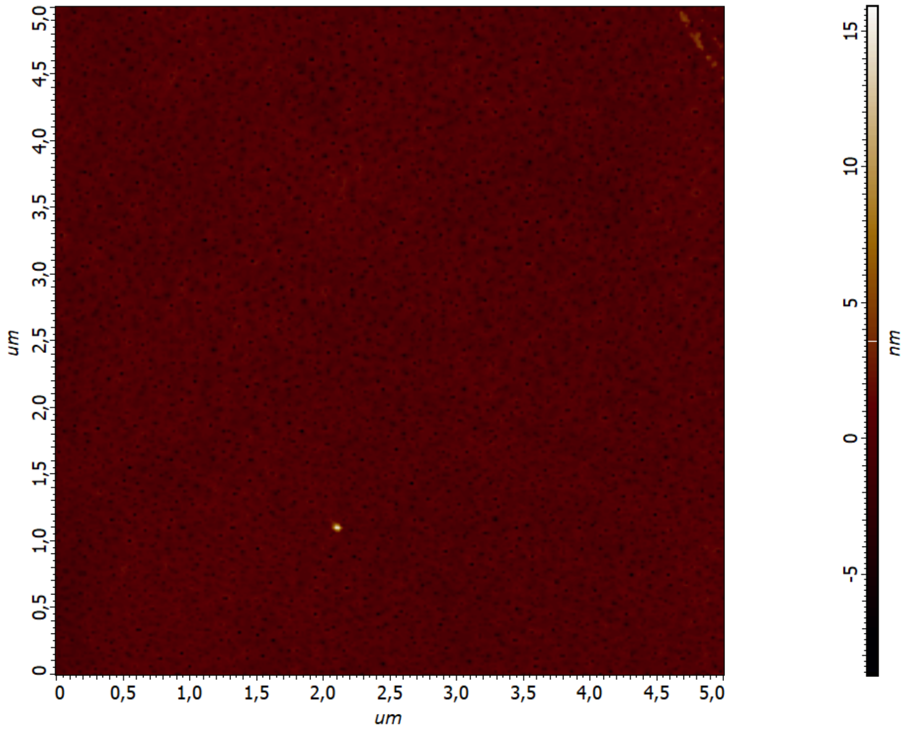
As-prepared thin film from pure BA; RMS = 0.26 ± 0.01 nm



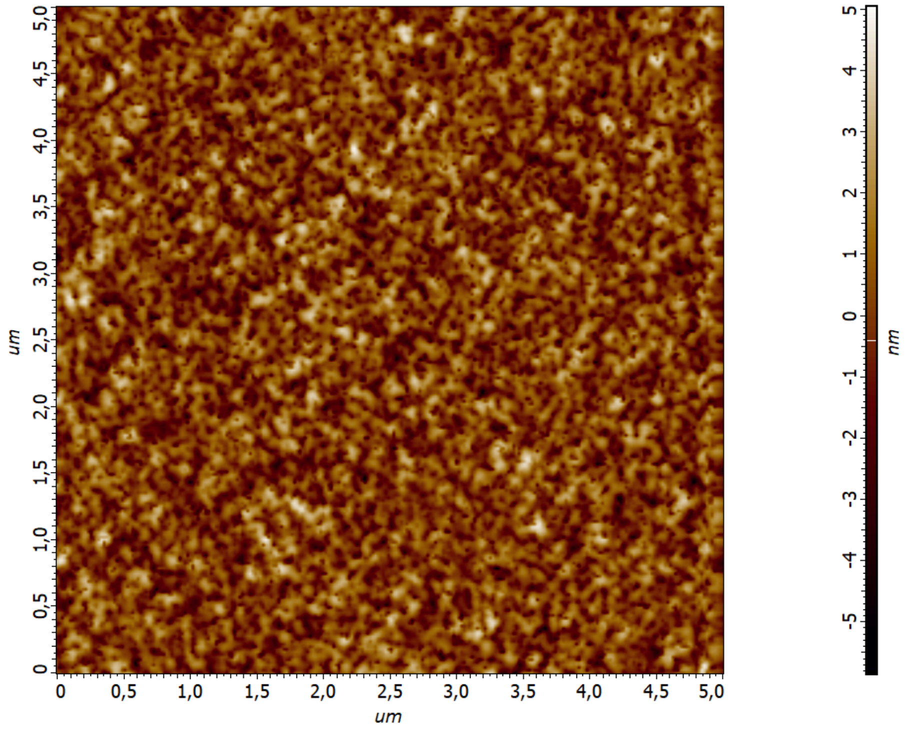
Annealed thin film at 210°C from pure BA; RMS = 0.34 ± 0.04 nm



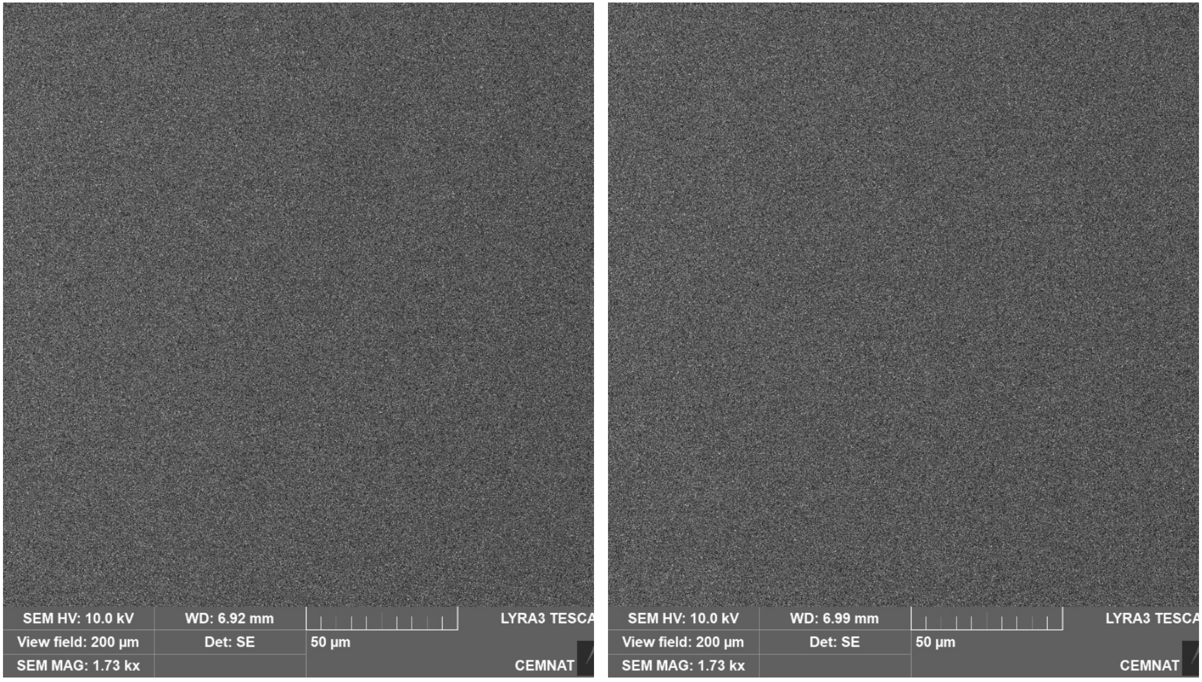
As-prepared thin film from BA-MetOH mixture; RMS = 0.95 ± 0.02 nm



Annealed thin film at 210°C from BA-MetOH mixture; RMS = 1.30 ± 0.24 nm

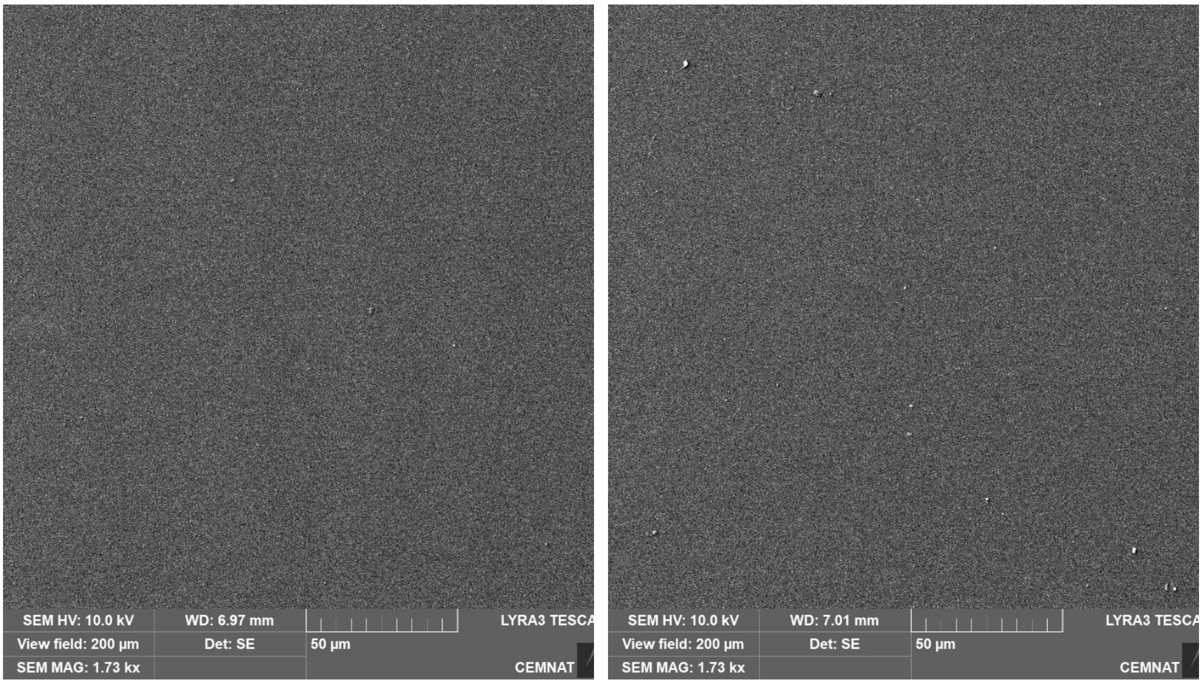


S4: FE-SEM scans of as-prepared $Ge_{20}Sb_5S_{75}$ thin films and thin films annealed at 210 °C.



As-prepared thin film from pure PA

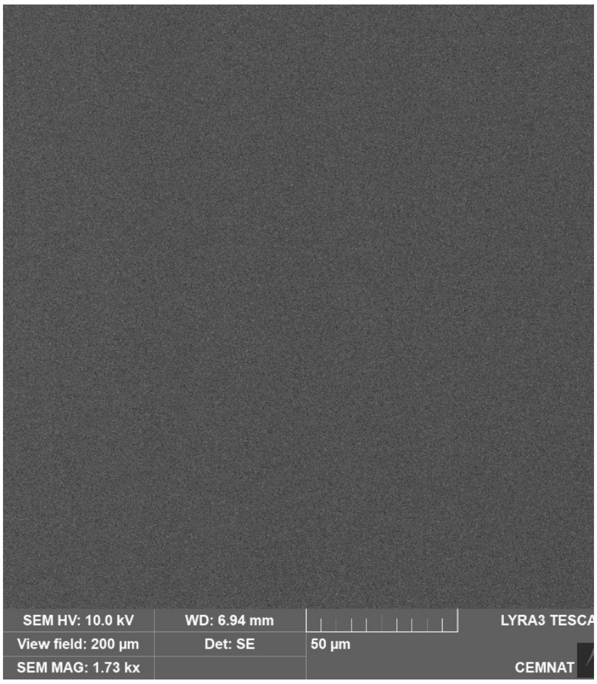
Annealed thin film at 210°C from pure PA



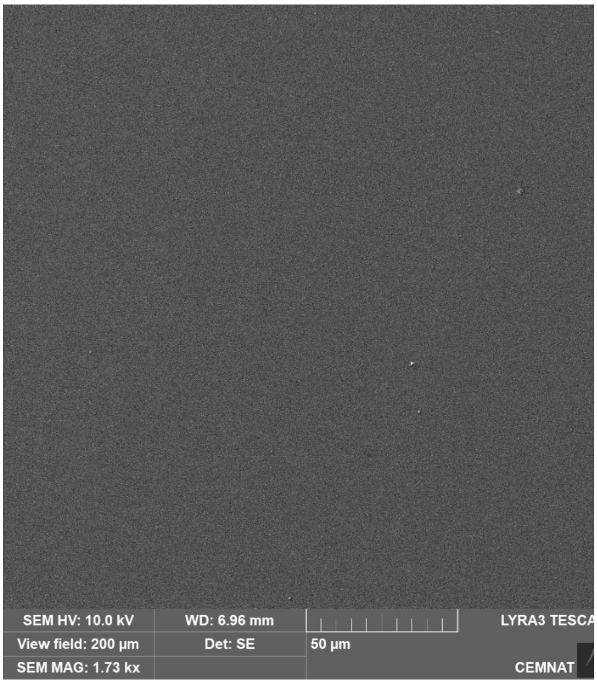
As-prepared thin film from PA-MetOH mixture

Annealed thin film at 210°C from PA-MetOH mixture

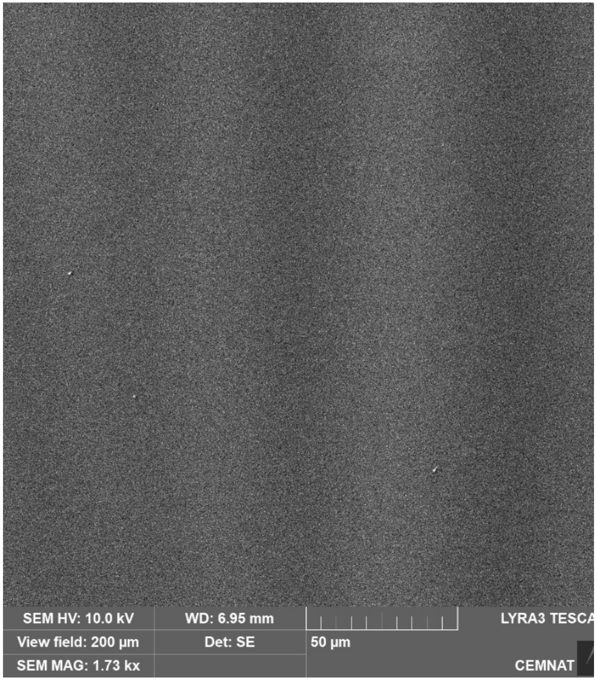
As-prepared thin film from pure PA with MetOH addition



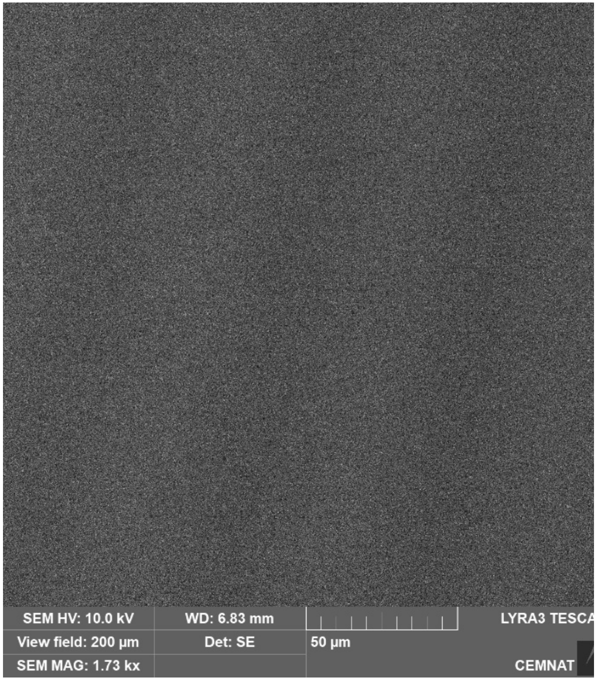
Annealed thin film at 210°C from pure PA with MetOH addition



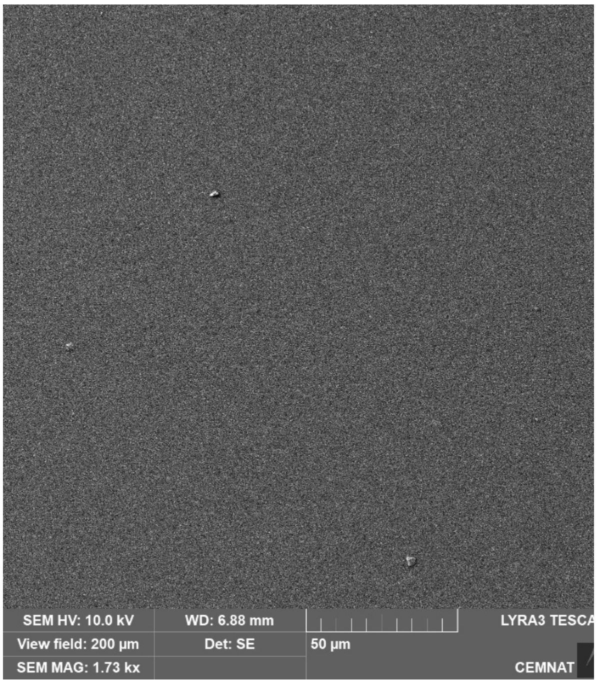
As-prepared thin film from pure BA



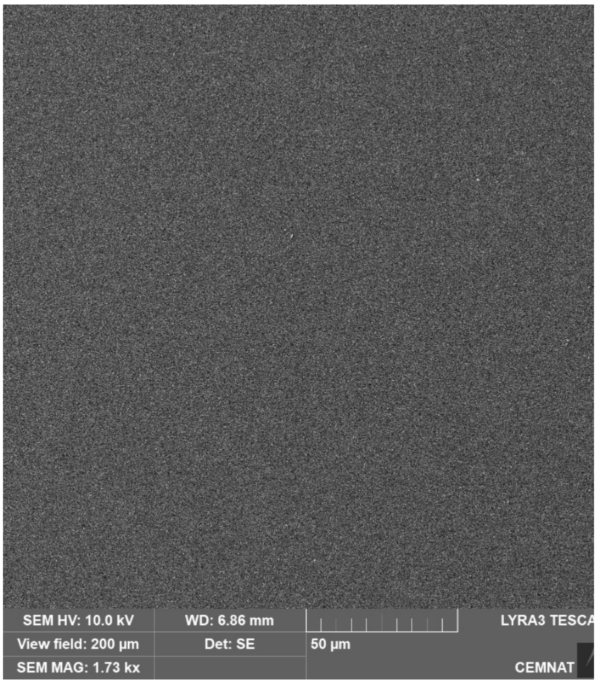
Annealed thin film at 210°C from pure BA



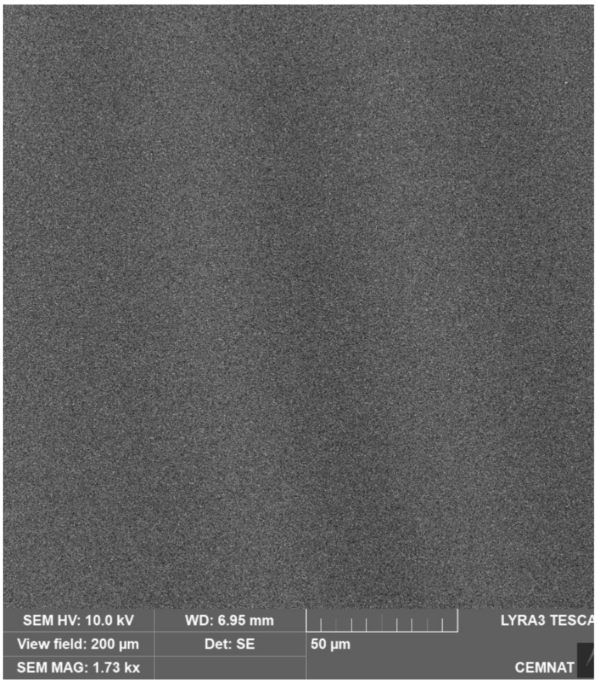
As-prepared thin film from BA-MetOH mixture



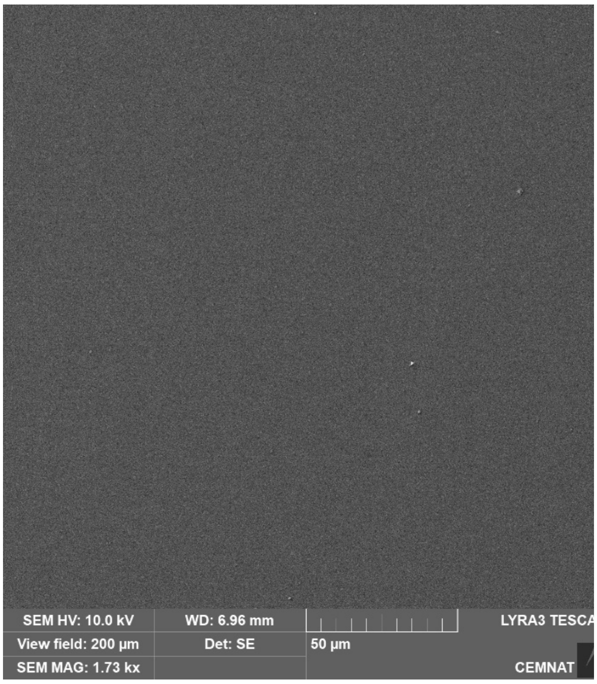
Annealed thin film at 210°C from BA-MetOH mixture



As-prepared thin film from pure BA with MetOH addition



Annealed thin film at 210°C from pure BA with MetOH addition



S5: Transmission spectra of as-prepared $Ge_{20}Sb_5S_{75}$ thin films and thin films annealed at 210 °C.