



Influence of the vacuum deposition conditions on the microstructure of thin As-S films

J. Dikova,^{a*} K. Starbova,^a E. Michailov,^b ^aCentral Laboratory of Photographic Processes, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria; ^bInstitute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

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The preparation of crystalline As-S films have been studied and some basic experimental conditions for epitaxial growth applied. Films were deposited from As₂S₃ vacuum evaporated from a Ta-crucible on air cleaved NaCl single crystal and Ca-Na silicate glass. It was established that condensation of As₂S₃ on air-cleaved NaCl single crystals at very low deposition rates resulted in thin films with a crystalline microstructure. The composition of the crystalline phase differs from the stoichiometric As/S ratio and strongly depends on the film thickness, deposition rate, type and substrate temperature. From the results obtained the importance is discussed of the vacuum deposition conditions needed to prepare thin films with desired structural characteristics. © 1998 Elsevier Science Ltd. All rights reserved

Introduction

The capability of thin a-As₂S₃ films to change considerably their physical and chemical properties upon actinic radiation has been known for a long time.¹ At present, the nature of these so called 'photostructural' changes remains still obscure, regardless of the numerous experimental studies. Up to now, several models have been proposed, most of them speculative.² Generally, it is believed that the photoinstability is a privilege of the amorphous state only and is due to a rearrangement in the local order of the glassy network.³ This assumption could be verified by following the photoinduced transformations in crystalline films of As₂S₃. However, the latter is known as a very good glass-former and the thin films obtained by thermal evaporation on various substrates are usually amorphous.⁴

It should be reminded here that the epitaxy is a classical method for preparing a large number of vapor deposited films in a relatively perfect crystalline form.⁵ As known, this method requires specific vacuum condensation conditions which provide oriented growth of the thin films on single crystalline substrates.

It is the aim of the present paper to study the possibilities for obtaining crystalline As₂S₃ films by applying some basic experimental conditions for the epitaxial growth.

Experimental

The experiments were performed with thin films obtained by vacuum condensation of high purity As₂S₃ in a standard high-

vacuum unit maintaining 5.10⁻⁴ Pa residual pressure. A resistively heated Ta crucible with a special design was used as an evaporation source.⁶ It allowed the sublimation and evaporation of As₂S₃ without local overheating, thus preventing undesirable effects of thermal decomposition. The substrates represented air-cleaved NaCl single crystals. Pre-cleaned Ca-Na silicate glass plates were also used for comparison. The temperature of the substrates was varied between 25° and 65°C with a step of 10°C. The deposition rate was kept always low and was changed between 0.005 and 0.05 nm/s.

Conventional electron-microscope preparation techniques were applied for studying the film micromorphology. The direct TEM imaging, electron diffraction and the inspection of the replicas from the free surface of the specimen were performed by using a transmission electron microscope JEM 100 B(JEOL). The surface microstructure was investigated in a scanning electron microscope Philips 515. XRD and EDS analysis were performed for studying the structure and composition of the films.

Results and discussion

Figure 1 presents a series of electron micrographs of Pt/C replicas from the surface of As-S films with thickness 5(a), 10 nm (b), 50 nm (c) and 100 nm (d), vapor deposited at 0.02 nm/s on air-cleaved NaCl single crystals. As can be seen the samples are structurally inhomogeneous and two morphologically different phases are formed during the film growth. A grain-like structure prevails in the thinner samples, which are amorphous as confirmed by electron diffraction patterns. Simultaneously, a phase with crystalline-like habit is observed at every stage of the film

*To whom all correspondence should be addressed.

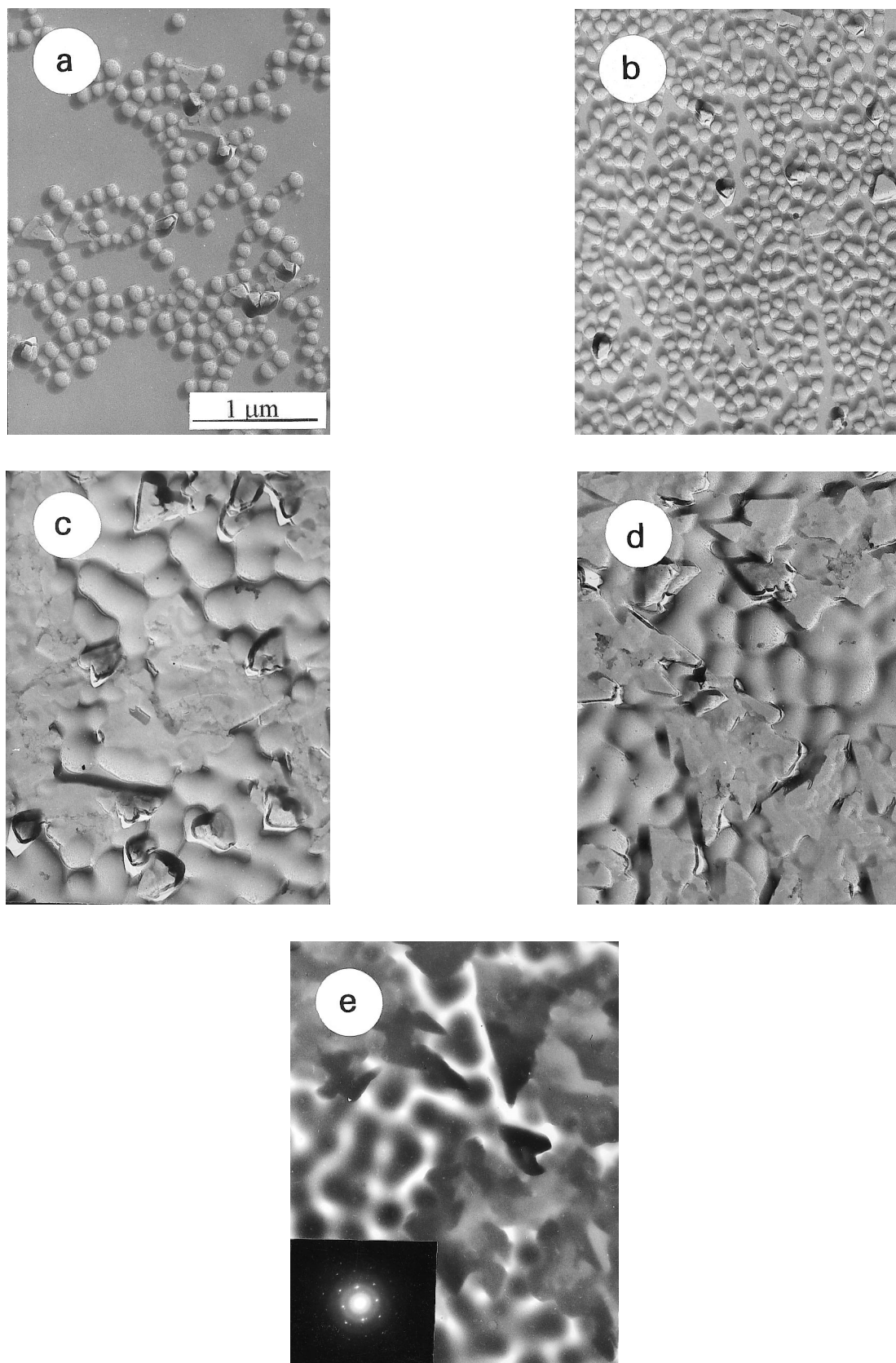


Figure 1. Transmission electron micrographs of Pt/C replicas of As-S films grown on air-cleaved NaCl single crystal: 5 nm (a), 10 nm (b), 50 nm (c) and 100 nm (d) thick; (e) direct electron image and SAD pattern of 100 nm thick As-S film. Deposition rate 0,02 nm/s.

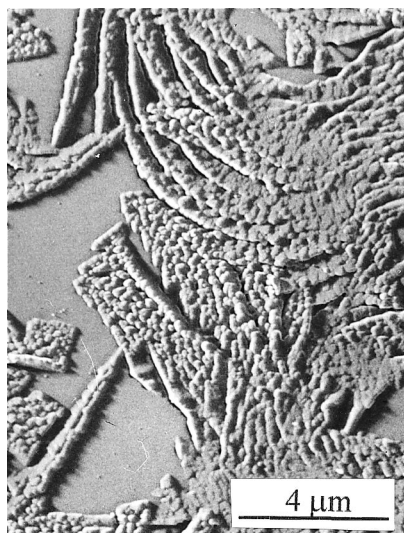


Figure 2. Scanning electron micrograph of the top surface of 1000 nm thick As-S film grown on air-cleaved NaCl surface. Deposition rate 0.02 nm/s.

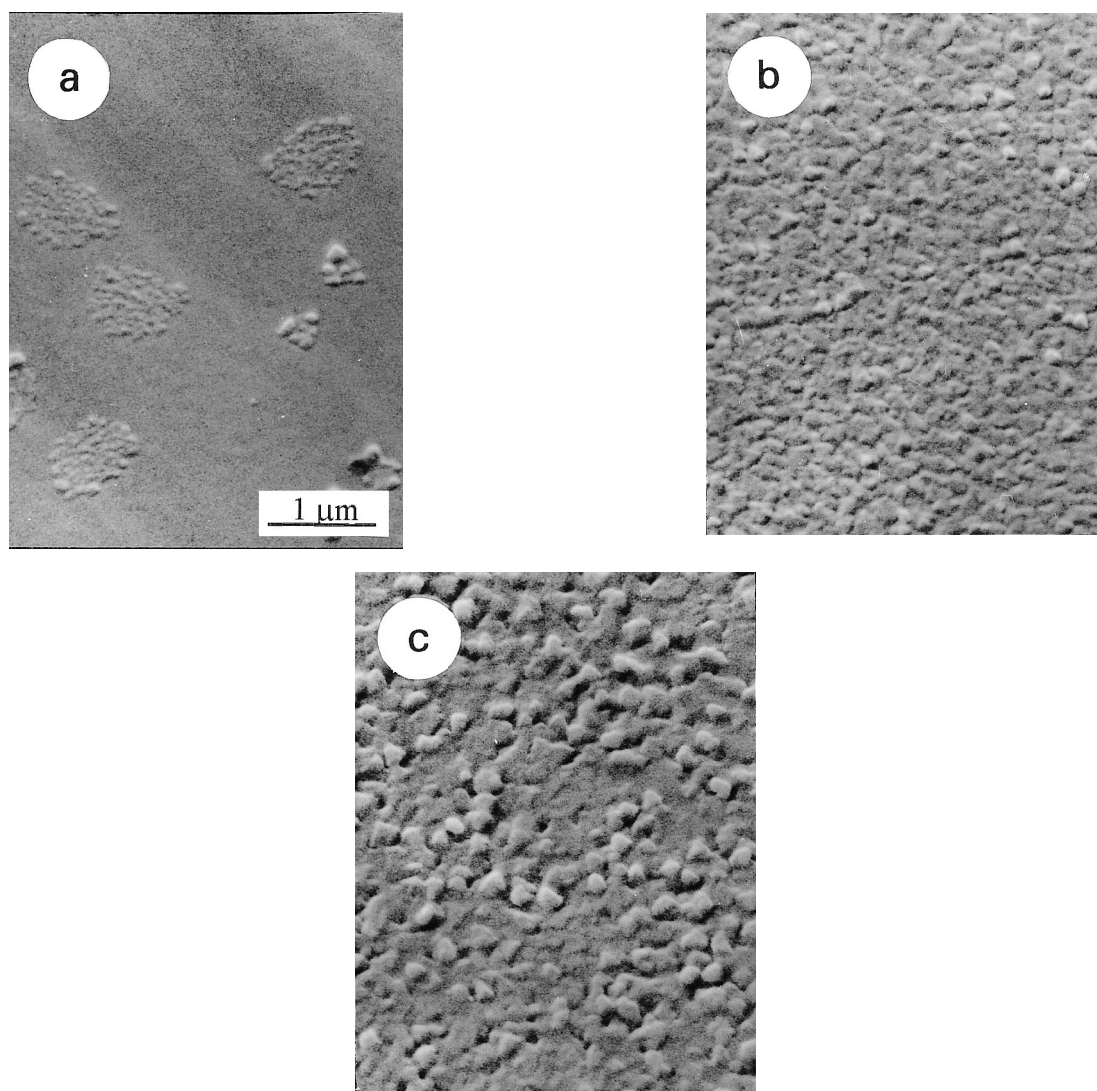


Figure 3. Scanning electron micrographs of the top surface of 100 nm thick As-S films grown on air-cleaved NaCl single crystal at: 25°C (a), 35°C (b) and 45°C. Deposition rate 0.02 nm/s.

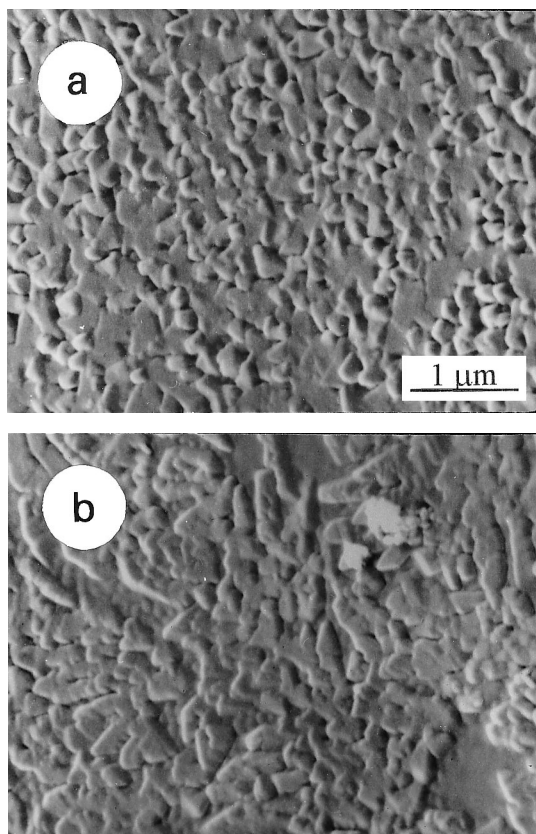


Figure 4. Scanning electron micrographs of the top surface of 100 nm thick As-S films grown on air-cleaved NaCl single crystal (a) and Na-Ca-silicate glass (b). Deposition rate 0.02 nm/s.

formation, its growth being favored at the advanced condensation stages. This is clearly seen from the direct TEM image presented in Figure 1(e). The analysis of the selected area diffraction pattern shows that a crystalline phase of orthorhombic As_4S is epitaxially grown on the NaCl surface. Obviously, the composition of this phase differs substantially from the stoichiometric As_2S_3 used for the evaporation. As shown by the scanning electron micrograph in Figure 2 the existence of an amorphous and a crystalline phases is also observed in 1000 nm thick film. However, the X-ray diffraction spectra of this sample showed the presence of crystalline β -AsS. Evidently, the composition of the crystalline phase changes drastically during the film growth. Summarizing the results obtained it can be concluded that under experimental conditions studied, partially crystalline As-S films are formed in the range of thicknesses between 10 and 1000 nm.

It is known⁵ that the heating of the substrates increases the mobility of the condensed vapor species, thus facilitating their ordering during the film growth. Figure 3 demonstrates the influence of the substrate temperature on the surface microstructure of 100 nm As-S films vacuum evaporated on NaCl single crystals at deposition rate of 0.02 nm/s. The inhomogeneous microstructure of the film obtained at room temperature of the substrate is clearly seen from the SEM micrograph in Figure 3(a). Simultaneously, it is evident that the samples deposited on heated substrates (Figure 3(b) and (c)) are characterized by a higher percentage of the crystalline-like phase. The analysis of the selected area diffraction patterns reveals the presence of poly-

crystalline AsS (pararealgar). Therefore, it can be concluded that the condensation of As_2S_3 on heated substrates at low deposition rates results in the formation of crystalline but non-stoichiometric films. Further increase of the substrate temperature above 46°C does not improve the film growth process due to the occurring of the undesirable effect of reevaporation.

It is well known that the initial stages of thin film growth are of great importance to their morphology and microstructure. For that reason in a series of experiments the samples were prepared at an extremely low deposition rate of 0.005 nm/s. Besides, this deposition rate was gradually reached by a very slow increase of the evaporation temperature up to the necessary value. Thus, the first layers of the films were obtained at the possibly lowest nucleation rate. The surface microstructure of 100 nm thick films, deposited on an air-cleaved NaCl(a) and a Ca-Na silicate glass plate (b) is shown in Figure 4(a,b). As seen from the figure, in both samples, crystalline-like phase is observed, which is more perfect in the film deposited on the single crystalline substrate. This is confirmed by the direct TEM images and SAD patterns, presented in Figure 5(a,b). The results obtained demonstrate the important role of the deposition rate and substrate surface during the film growth. The analysis of the electron diffraction pattern and X-ray diffraction spectra (Figure 6(a,b)) showed that the film deposited on NaCl substrate consists of α -AsS, textured along [111]. The As/S ratio in this sample was also confirmed by EDS analysis in TEM. Simultaneously, a stoichiometric composition of the film obtained on the glass substrate was established. However, the identification of the crystalline phase in this sample

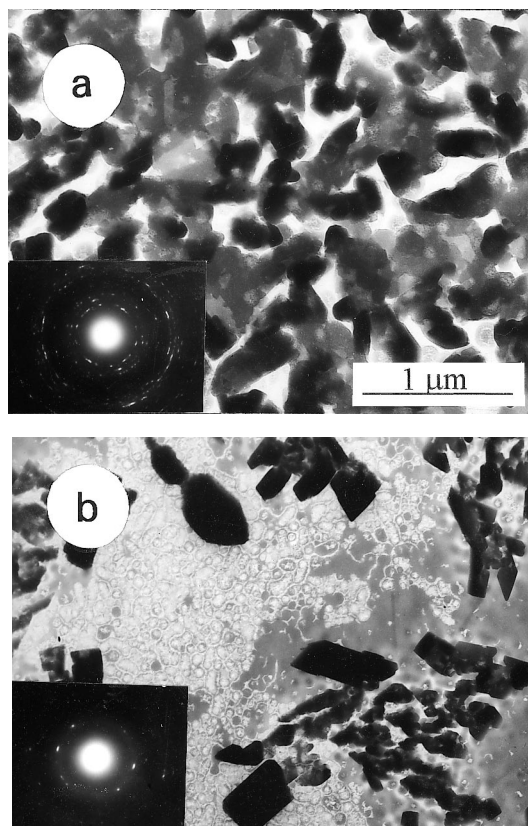


Figure 5. Transmission electron micrographs and corresponding SAD patterns of the samples on Fig. 4.

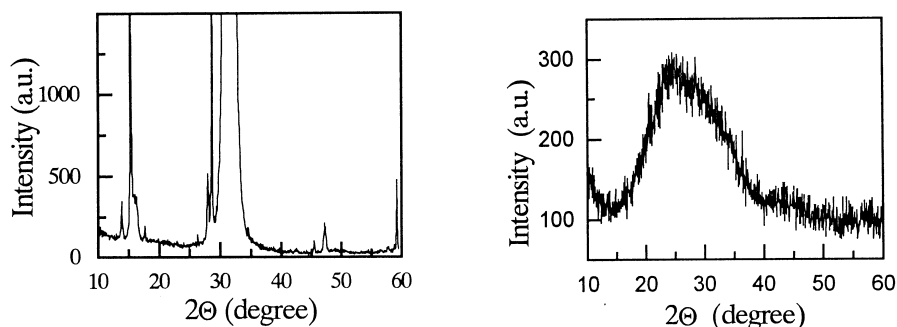


Figure 6. X-ray diffraction spectra of the samples on Figs. 4 and 5.

was hindered by the occurring of electron beam induced amorphisation.

Conclusion

The present study represents a first attempt to prepare thin crystalline films of arsenic sulfide. It is established that by applying some basic experimental conditions for epitaxial growth it is possible to obtain As-S films with crystalline microstructure. The composition of the crystalline films differs from stoichiometric As/S ratio and strongly depends on the vacuum condensation conditions. It is reasonable that an improvement of the epitaxial growth could be expected by further optimization of the experiments, including a cleavage of NaCl crystals under oil-free vacuum conditions and using of crystalline As_2S_3 as a starting material for the evaporation.

Acknowledgements

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