As$_2$Se$_3$ thin films deposited by frequency assisted thermal evaporation – morphology and structure

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Abstract. Thin As$_2$Se$_3$ films with thicknesses of 60 and 250 nm were deposited from the initial compound by frequency assisted thermal evaporation in vacuum – a new approach for shaping thin films surface. Frequencies of 0, 50 and 4000 Hz were applied on the substrates during the deposition process. The morphology was evaluated using AFM and SEM techniques. Some main optical properties and specifics of the films were determined by the means of spectroscopic ellipsometry analysis. The structure of the samples was investigated by XRD. A possible mechanism for explanation of the observed peculiarities is proposed on the basis of the classical materials science and molecular thermodynamics.

1. Introduction

In order to satisfy the ever rising requirements of the contemporary electronics, in particular optoelectronic and sensing technologies, the scientists focus their efforts towards development of new methods and approaches for quality increase and price decrease of materials, which are already implemented and used in practice, as well as towards obtaining of materials with new properties.

The frequency assisted thermal evaporation in vacuum (FATEV) is new, cheap and simple approach for topography shaping of thermally deposited films. The technology is based on application of audible frequency vibrations on the substrates during thermal deposition in vacuum. For this purpose a source of mechanical vibrations with sonic wave frequency is mounted in standard equipment for thermal evaporation.

The physical meaning of the FATEV approach is the following: The vibrations with audible frequency are directly transferred from the source to the substrate and corresponding waves are distributed on its surface by forming a standing waves network. Each instant a small portion of the evaporated substance condenses on the excited substrate and nuclei formation takes place at the nodes and anti-nodes of the standing wave network. With the increase of the nuclei size islands are formed which coalesce and a continuous film is formed which copies the substrate topology.

Until now this technology was used for deposition of selenium and tellurium films [1], and change of their topography depending on the applied frequency was observed – undulated surfaces were obtained at near subsonic frequencies with rms roughness (Rq) maximum at 50 Hz. The excitement with frequency of 4 kHz led to formation of extremely smooth surfaces. The quantification of these
changes depends on the degree of crystallinity of the deposited material – the Rq deviations for amorphous selenium films are from 2.3 nm for frequency of 50 Hz to 0.2 nm for 4 kHz oscillations, while the Rq of crystalline tellurium decreases from 40 nm (at 50 Hz) to 13 nm (at 4 kHz). The mechanical distortions do not lead to any change in the crystallographic structure of the materials.

In this sense the aim of the present report is to investigate the influence of the mechanical vibrations with audible frequencies of 50 and 4000 Hz during deposition on the morphology, structure and optical properties of films of As₂Se₃ (a typical glassy chalcogenide semiconductor).

2. Experimental procedures

The source material, As₂Se₃, was synthesized by conventional melt quenching technique. Appropriate quantities of As and Se (purity of 5 N) were melted in evacuated to a residual pressure of 1.10⁻³ Pa quartz tubes. Two isothermal steps (300 and 550 °C) were performed during the synthesis, conformed to the physicochemical peculiarities of the source elements and the final phase. The melt was tempered for 2 hours at the last step and then rapidly quenched in ice-cold water (cooling rate of ~10-15 °C/s).

The frequency assisted thermal evaporation in vacuum (TEV) was performed in modified TEV equipment. A source of mechanical vibrations with acoustic wave frequency (2 inch 180 mW closed loudspeaker with frequency response in the interval 20-20000 Hz, situated normally to the evaporation flow) was set up in the vacuum chamber. The desired sine signal was generated using a computer program and translated through an amplifier towards the loudspeaker. Frequencies of 0, 50, and 4000 Hz were applied on a 2 inch Si (100) wafer during deposition. The amplitude of the vibrations was set to 80 % of the maximum loudspeaker output power.

Series of As₂Se₃ films with thicknesses of 60 and 250 nm were deposited at the three frequencies of the mechanical vibrations with deposition rate of ~0.5 nm/s. The residual pressure in the vacuum chamber was 7.10⁻³ Pa. The distance between the crucible and the substrate was 20 cm. The deposition rate and the thickness of the films during preparation were controlled using a quartz-crystal microbalance device Miki MSV 1841/A.

AFM measurements were performed on scanning probe microscope Multimode V (Veeco, Santa Barbara, CA). The images were taken in tapping mode, as each sample has been investigated on multiple points of the surface. Measurements in scale of 1, 3 and 10 µm have been performed with scanning rate in the interval 0.5-2.0 Hz and images resolution of 512 lines per scan direction. Al-coated silicon cantilevers TAP150-Al-G (Budget Sensors Innovative Solutions Bulgaria Ltd., Bulgaria) with nominal resonant frequency of ~150, and spring constant of 5 N/m have been used. The radius of the cantilever’s tip is smaller than 10 nm. The root mean square roughness (Rq) of the samples was determined in scale of 10 µm. The images have been just flattened before the analysis.

SEM observations have been made using e-Line EBL equipment in SEM mode (Raith GmbH, Germany), working with accelerating voltage of 10 kV. The As₂Se₃ films were observed on cross-section with magnification from 20 to 150 thousand times.

The structure of the films was evaluated through grazing incidence X-ray diffraction (GIXRD) using Rigaku SmartLab X-ray thin film diffraction system (Rigaku Corporation, Japan) at CuKα₁,₂ irradiation (λ=1.5418 Å) and angle of incidence of 0.35 °. The XRD patterns were taken in Bragg angle (2θ) range from 10 to 100 ° with step of 0.01 °.

Ellipsometric measurements in the UV-VIS-NIR region were carried out with an automatic M2000D spectroscopic ellipsometer (J.A. Woollam, Germany, bought on FP7 INERA REGPOT-2012-2013-1 NMP project) within the spectral range of 193-1000 nm and angles of incidence from 45 to 65 ° by 5 °. The films thicknesses and optical constants were determined by the means of Tauc-Lorentz oscillator model using Woollam’s CompleteEASE program.

3. Results and discussion

Cross-section SEM microphotographs of as-deposited As₂Se₃ films are presented in figure 1.

The SEM observations show homogeneous and smooth surface, without cracks or other inclusions. Only some shell-like formations (cracks), typical for glassy materials, were observed.
The films thicknesses (table 1) were evaluated using the SEM microphotographs. The obtained values were confirmed during the spectroscopic ellipsometry (SE) investigations, the results of which are also present in table 1. The determined values are in good agreement.

![Figure 1. Cross-section SEM microphotographs of as-deposited As₂Se₃ films.](image1)

A representative SE data, as well as the corresponding fit, used for determination of the thickness and the optical constants of the films are presented in figure 2. The SE study showed a fair agreement of the optical constants with the literature data (optical band gap $E_g=1.8$ eV [2], refractive index $n≈3$ [3], and extinction coefficient $k≈0.04$ [3]). The results are presented in table 1.

The applied frequencies do not influence the optical properties of the films. As it can be seen in table 1 the optical band gap $E_g(As₂Se₃)≈1.78$ eV, and $n$ and $k$ at He-Ne laser wavelength ($\lambda=632.8$ nm) are around 3.2 and 0.05, respectively, and vary insignificantly depending on the frequency of the applied vibrations.

![Figure 2. Typical SE data and fit model for As₂Se₃ films (250 nm film, deposited at 50 Hz is presented).](image2)

### Table 1

| Sample       | $d_{SEM}$, nm | $d_{SE}$, nm | $R_q$, nm | $E_g$, eV | $n$  | $k$    |
|--------------|---------------|--------------|-----------|-----------|------|--------|
| 60 nm, 0 Hz  | 55            | 56.4         | 1.21      | 1.78      | 3.18 | 0.05587|
| 60 nm, 50 Hz | 57            | 57.9         | 1.70      | 1.80      | 3.16 | 0.04621|
| 60 nm, 4000 Hz | 53          | 53.4         | 2.09      | 1.79      | 3.17 | 0.04823|
| 250 nm, 0 Hz | 236           | 235.0        | 0.509     | 1.75      | 3.22 | 0.07655|
| 250 nm, 50 Hz| 247           | 246.1        | 0.449     | 1.78      | 3.19 | 0.05887|
| 250 nm, 4000 Hz | 240        | 239.1        | 0.448     | 1.78      | 3.19 | 0.05723|

The results from the X-ray diffraction measurements at grazing incidence (GIXRD) are presented in figure 3. Because of the small thickness, some peaks of the Si wafer appear on the XRD pattern.

Three X-ray amorphous halos are observed on the XRD patterns (figure 3), the positions of which...
correspond to the pattern of monoclinic As$_2$Se$_3$ [4], but are shifted towards lower 2θ angles, most probably due to internal stress in the films.

The possibility for formation of nanocrystalline objects, caused by the frequency excitation, in the as-deposited films was examined. For this purpose the main peaks of the XRD patterns were fitted using Lorentz model in order to obtain the exact position of the peak and its full width at half maximum (FWHM) – table 2. Using the obtained values, the average crystallite sizes (D) and the microstrain (ε) of the samples were calculated using Eq. (1), and Eq. (2), respectively:

$$D = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)
$$\beta = 4\varepsilon \frac{\sin \theta}{\cos \theta}$$  \hspace{1cm} (2)

where K - Scherrer constant (shape factor, K=0.94) [5]; β – line broadening (FWHM in radians); θ – Bragg angle; λ – X-ray wavelength (λ=0.15418 nm). The results are presented in table 2.

![Figure 3. GIXRD of as-deposited As$_2$Se$_3$ films. PDF 26-0122 - JCPDS card of bulk As$_2$Se$_3$ [4].](image)

**Table 2.** Position (2θ) and full width at half maximum (FWHM) of the main XRD peak, average crystallite size (D) and microstrain (ε) of as-deposited As$_2$Se$_3$ films.

| Sample          | 2θ, deg | FWHM, deg | D, nm | ε     |
|-----------------|---------|-----------|-------|-------|
| 60 nm, 0 Hz     | 30.69   | 8.42      | 1     | 0.13385 |
| 60 nm, 50 Hz    | 30.43   | 8.60      | 1     | 0.13798 |
| 60 nm, 4000 Hz  | 29.81   | 10.87     | 0.8   | 0.17827 |
| 250 nm, 0 Hz    | 30.76   | 8.64      | 1     | 0.13712 |
| 250 nm, 50 Hz   | 30.55   | 9.78      | 0.9   | 0.15624 |
| 250 nm, 4000 Hz | 30.93   | 8.55      | 1     | 0.13485 |

The estimated crystallite size value is with a fair approach towards accuracy due to the following factors: 1) the investigated peak is too complex and the obtained FWHM could differ a little, 2) the value of the Scherrer constant could be different since we do not know the exact shape of the crystallites. However, the obtained values are around 1 nm in diameter or below, which roughly corresponds to the cell parameters of the As$_2$Se$_3$ JCPDS file (a=6.69 Å, b=13.86 Å, c=10.00 Å, β=113.8 °) [4], and are a proof for the glassy nature of the deposited films. Other proof for the disordered structure of the films is the relatively high strain, observed in them.

AFM images of the as-deposited samples are presented in figure 3. The topology of the samples, revealed from the AFM measurements, is in good correlation with the SEM observations – the films are homogeneous and no crystalline formations were seen. The root mean square roughness Rq of the samples was determined and the results are presented in table 1.

Two facts are of particular interest: 1) the rms surface roughness of the films decreases with the increase of their thickness, and 2) the effect, caused by the mechanical excitement during deposition, is significantly smaller or even absent in comparison to the results obtained during the investigation of Se and Te films, deposited by the FATEV approach at the same conditions [1].

These deviations could be explained taking into account the following facts:

- The stable state of As$_2$Se$_3$ is glassy and it is hardly obtained in crystalline form by thermal evaporation in vacuum [6].
- The evaporated As$_2$Se$_3$ molecules and structural fragments tend to attach to any place forming a disordered glassy network due to their high viscosity in gas and liquid state and thus to reach
unimpeded the glass-transition temperature and freeze as a supercooled liquid [7].

![AFM images of As₂Se₃ films](image)

**Figure 3.** AFM images at scale of 3 μm of as-deposited As₂Se₃ films. The maximum height scale is 5 nm for all 250 nm thick films, while for the thin ones it is 10 nm for 0 Hz and 50 Hz, and 20 nm for 4 kHz.

- Recently it has been theoretically predicted during molecular dynamics simulation of the effect of a standing surface acoustic wave on adatom diffusion on face centred crystal surface, that the main mechanism responsible for a structuring effect is the inertia [8].

- The same authors state that the diffusion of atoms from the substrate could also take place during the excitement [8].

In our case, the impurities present in the glassy matrix of As₂Se₃ worsen their optical properties, but do not cause their crystallization [9]. Therefore, as the influence of the inertial momentum decreases with the increase of the thickness, and since there is no typical crystallographic orientation of the deposit, only the glassforming ability of the material takes place. This should be the reason for the registered flat surfaces of the As₂Se₃ films with thickness of 250 nm and the significantly rougher ones of the 60 nm thick films.

The observed unusual increase of the Rq at excitement with 4 kHz wave in the 60 nm films can be explained by the high viscosity of As₂Se₃ [10] and its lack of crystallization tendency – the dynamic curvature of the substrate’s surface gives an additional momentum to the deposit, which is not related to the initial frequency, but to the mobility of its adatoms, i.e. the deposited film starts to resonate at its own frequency. Thus when the condensate “freezes” an undulated surface is formed. It has to be noted that the films, deposited at 0 Hz could also be subjected to a certain extent to uncontrollable vibrations, caused by equipment imperfections. However, it can be said that the increase of the frequency of the substrate mechanical excitement during deposition leads to formation of rougher films (than those obtained by conventional thermal deposition in vacuum), whose curvature is caused not directly by the standing waves network, but by the viscous movement of the material adatoms, excited by the vibrations. In the case of 250 nm films, when there is enough quantity of the deposited material, and taking into account the above statement that the excitement effect decreases with the thickness, it is not surprising that the thicker films are significantly smoother and not influenced by any excitement frequency.
Taking into account the results obtained from the investigation of the FATEV deposited selenium and tellurium films [1] it can be concluded that the vibration excitement of the substrate during thermal deposition is highly influenced by the viscosity and the tendency towards crystallization of the condensates – the high viscosity [10] and priority trend towards formation of disordered structures (in the case of As$_2$Se$_3$) dull the excitement effect; the almost equal viscosity [11] but existence of certain crystallization affinity even at room temperature if crystallization centres are present [12] (in the case of Se) lead to formation of undulated surfaces at near sub-sonic frequencies and extremely smooth ones at 4 kHz, while the typically crystalline material (in the case of Te) follows the last path but the changes are significantly larger.

4. Conclusions

Glassy As$_2$Se$_3$ films were deposited by frequency assisted thermal evaporation in vacuum at excitement frequencies of 0, 50 and 4000 Hz. The thicknesses of the films were determined to be 60 and 250 nm by cross-section scanning electron microscopy and spectroscopic ellipsometry. The optical properties of the samples coincide with the literature data about the same compound and do not change depending on the applied vibrations. A profound study of the films structure was preformed by the means of XRD analysis. The results show that the films are amorphous with particle sizes below the lattice parameters of the corresponding As$_2$Se$_3$ crystal. This, together with the SEM observations (appearance of shell-like cracks in cross-section) makes us believe that the deposited samples possess glassy nature. The excitement during deposition does not lead to noticeable changes of the crystalline structure. The AFM measurements reveal an unusual deviation of the surface roughness both with the thickness and the excitement frequency increase. The films surface roughness decreases with the increase of the thickness and stays equal for all 250 nm thick films, while the excitement of the 60 nm films leads to increasing curvature with the increase of the vibrations frequency. These specifics were explained by the means of molecular thermodynamics taking into account the physical properties of As$_2$Se$_3$. A comparison with other materials, previously deposited by the same method, was preformed.

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