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## **ON THERMAL STABILITY OF ANTIMONY THIN FILMS FOR SOLAR CELLS APPLICATIONS**

Antimony has received considerable attention due to structural archetype for a variety of sulfide and sulfosalt minerals. In this work Sb thin films with thickness of ~ 300 – 400 nm were grown by radio frequency magnetron sputtering, in order to use as a precursor to synthesize chalcogenide semiconductors for solar cells applications. It was shown the influence of annealing temperatures to the structure of the as-deposited Sb films. Antimony thin films were deposited on a glass substrate and subsequently were annealed at different temperatures 300 °C, 400 °C, 500 °C in argon gas ambient. Structural characterization of the films analyzed by Raman scattering spectroscopy, two different excitation wavelengths were used: 532, 632.8 nm. Raman bands both the symmetric ( $A_{1g}$ ) and nonsymmetrical ( $E_g$ ) phonons were identified. Transmittance measurements and morphology studies of the films showed stability of annealed films at temperatures at 400 °C and the results of Raman spectroscopy showed their high polycrystalline structure.

**Key words:** antimony thin films, RF magnetron sputtering, RTP, Raman spectra.

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### **Күн элементтерінде қолдану үшін жұқа антимониум қабықшаларының жылу тұрақтылығы**

Сурьма (Sb) әртүрлі сульфид және сульфотталған минералдарға құрылымдық архетиптердің арқасында үлкен көңіл бөлінді. Бұл жұмыста қалыңдығы 300–400 нм болатын жұқа Sb қабыршақтары радиожиілік магнетронды шашырау әдісімен өсіп, оларды кальцогенидті жартылай өткізгіштерді өндіру және оларды күн батареялары саласында қолдану үшін прекурсор ретінде пайдалану мақсатында жасалды. Тұндырылған Sb қабықшаларының құрылымына жану температурасының әсері көрсетілген. Sb жұқа пленкалары шыны субстраттарға қойылып, аргон ортасында әртүрлі температурада: 300 °C, 400 °C, 500 °C қыздыруға ұшырады. Қабықшалардың құрылымдық сипаттамасы Раман спектроскопиясын пайдалана отырып, екі түрлі толқын ұзындығы 532, 632,8 нм пайдаланып талданды. Екі симметриялы ( $A_{1g}$ ) және ассиметриялық ( $E_g$ ) фонндардың аралас шашыраңқы белдестері анықталды. Тасымалдау спектрі мен морфологиялық зерттеулерді өлшеу 400 °C температура кезінде пленкалардың тұрақтылығын көрсетті және Раман спектроскопиясының нәтижелері олардың жоғары поликристалды құрылымын көрсетті.

**Түйін сөздер:** сурьма жұқа қабыршақтары, магнетронды шашырау, тез пісетін пеш, комбинациялық ыдырау спектрі.

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### Термическая устойчивость тонких пленок антимонии для применения в солнечных элементах

Сурьма (Sb) получила значительное внимание из-за структурного архетипа для различных сульфидных и сульфосольтовых минералов. В этой работе тонкие пленки Sb толщиной ~ 300–400 нм выращивались методом радиочастотного магнетронного распыления с целью использования их в качестве прекурсора для получения халькогенидных полупроводников и их применения в области солнечных элементов. Было показано влияние температур отжига на структуру осажденных пленок Sb. Тонкие пленки Sb были осаждены на стеклянные подложки и в дальнейшем подвержены отжигу при различных температурах: 300 °С, 400 °С, 500 °С в аргоновой среде. Структурную характеристику пленок проанализировали с помощью спектроскопии комбинационного рассеяния света, при использовании двух разных длин волн возбуждения: 532, 632,8 нм. Были идентифицированы полосы комбинационного рассеяния как симметричных ( $A_{1g}$ ), так и несимметричных ( $E_g$ ) фононов. Измерения спектров пропускания и морфологические исследования пленок показали стабильность отожженных пленок при температурах 400 °С, а результаты спектроскопии комбинационного рассеяния показали их высокую поликристаллическую структуру.

**Ключевые слова:** тонкие пленки сурьмы, магнетронное распыление, печь быстрого отжига, спектры комбинационного рассеяния.

## Introduction

Thin film solar cells (SC) based on CIGS (copper indium gallium selenide), CdTe (cadmium telluride) have been extensively studied due to their semiconducting properties and they were always cheaper than first generation SC due to technology of producing. CIGS and CdTe has reached solar cells achieving certified solar energy conversion efficiencies of 20.81 and 20.4%, respectively. However, researches on photovoltaic area are aimed at reducing the cost, which include raw material and the manufacturing process. The scarcity of In and Ga in CIGS and high toxicity of Cd in CdTe made research to search for alternative materials. As an alternative material in last decades high interest is caused by such compounds based on Sb such as antimony selenide  $Sb_2Se_3$ , stibnite  $Sb_2S_3$ , copper antimony sulfide  $CuSb_xS_y$ , antimony telluride  $Sb_2Te_3$ . Among the listed structures  $Sb_2Se_3$  appears to be a promising candidate for photovoltaic because of the following advantageous features:  $Sb_2Se_3$  has an ideal low-band-gap value (1.2–1.0 eV) and a high optical absorption coefficient (around  $10^5 \text{ cm}^{-1}$  near the absorption onset) [1, 2], which permits a strong visible–near-infrared sunlight absorption. The constituent elements of Sb and Se in  $Sb_2Se_3$  are relatively earth-abundant, inexpensive, and low-toxic. Antimony can be grown on different

substrates. For example antimony forms an abrupt interface with III-V semiconductors such as InP or GaAs [3] without chemical reactions. Also, on the Si [111] substrate films were polycrystalline and displayed a preferential orientation about the (111) axis in a direction perpendicular to the film plane of the substrate [4]. Also, there are several studies on changes in structure characteristics with growth pressure [5, 6]. Like other semi-metals of the group V-A, antimony crystallizes at ambient conditions in the trigonal A7 structure (space group  $R\bar{3}m$ , No. 166) [7].

One of the most important discoveries in the field of solid-state physics and chemistry is that the properties of a body depend directly on the microstructure, i.e. from the chemical composition, the bounding nature (atomic structure), and body dimensions in one, two or three directions. Other words, if one of the set of parameters changes, then the properties of the body also changes. In this work we analyzed the influence of the annealing temperatures to the structure of the Sb films using Raman scattering spectroscopy.

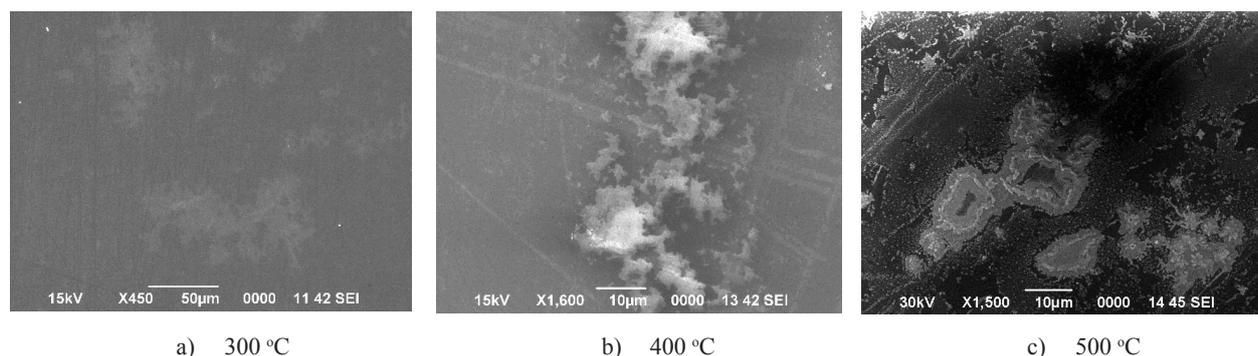
## Experimental methods

Antimony thin films were deposited by radio frequency magnetron sputtering technique from Sb target onto the glass maintained at room temperature

at sputtering pressure  $5 \cdot 10^{-3}$  mbar. The Sb target was made by powdering of the bulk material and then annealing of the powder at about  $700^\circ\text{C}$  in furnace for rapid thermal processing (RTP). Sputtered thin films (thickness of  $\sim 500$ - $600$  nm) were annealed at different temperatures in the RTP furnace at  $300^\circ\text{C}$ ,  $400^\circ\text{C}$ ,  $500^\circ\text{C}$  in Ar ambient (300 sccm) during 10 minutes at maximum temperatures. The morphology of the films were studied on SEM (JEOL). Transmittance spectra of antimony films were measured on the QEX10 Quantum Efficiency/Spectral Response (SR) with a measurement range of 190-1100 nm. The Raman spectroscopy (RS) measurements were done using Solver Spectrum. The RS were analyzed by a single-stage spectrograph with a multichannel CCD detector and excited with the 532 nm line of an Ar-ion laser and with the 632.8 nm HeNe laser. The surface of the specimen was focused with the help of  $100\times$  objective with a laser spot diameter of  $\sim 1$   $\mu\text{m}$  when an HeNe laser line (632.8 nm) is used as excitation source and  $\sim 0,72$   $\mu\text{m}$  when an HeNe laser line (632.8 nm).

## Results and discussion

**Morphology and transmittance studies.** The morphology of antimony films annealed at different temperatures from  $300^\circ\text{C}$  to  $500^\circ\text{C}$  is shown in figure 1 a, b. The surface of the specimens annealed at  $300^\circ\text{C}$  and  $400^\circ\text{C}$  are smooth and no visual changes after annealing, their thickness remained in its original form, which demonstrates the stability of the films at about  $400^\circ\text{C}$ . Also, the stability of the antimony thin films confirmed by transmittance spectroscopy. The results of transmittance measurements are illustrated in figure 2. The transmittance spectra of the as-deposited and annealed films at  $300^\circ\text{C}$  and  $400^\circ\text{C}$  can be divided into two parts, from 300 nm to 400 nm and from 400 nm to 1100 nm. In part 300-400 nm spectra films has highly transparency. From 400 nm absorbance of the annealed films goes up because of a higher orderliness of the crystal structure. In case of film obtained at  $500^\circ\text{C}$  became almost transparency (fig.2), there is remains of antimony on top of glass can be observed (fig.1 c).



**Figure 1** – SEM of antimony films prepared at different annealing temperature

**Structure analysis.** The A7 structure of Sb-I is trigonal, with six atoms per hexagonal unit cell occupying the 6c position (fig.3). Changes in a condition of growth lead to lattice distortions. The structure is rhombohedral distortion of simple cubic structure, which forms layers of atoms arranged along the hexagonal axis. Two distortion modes lead from the parent cubic-primitive (cP1) to the A7 (hR2) structure: a rhombohedra elongation along a cubic [111] direction and a pairing of the original cubic (111) lattice planes. Atoms in red mark opposite corners of the distorted cube. According to

the group-theory there are two Raman active modes for the A7 structure at ambient-pressure:  $A_{1g}$  mode at  $150\text{ cm}^{-1}$  and a two-fold degenerated  $E_g$  mode at  $115\text{ cm}^{-1}$ .

Our thin films were investigated with two different excitation wavelengths: 532 nm, 632.8 nm. RS from 50 to  $350\text{ cm}^{-1}$  under different excitation wavelengths. The laser power for each laser wavelength are the same 50 mW, integration time were kept at 60s for both red and green laser lines. All spectra were measured through a 100X objective.

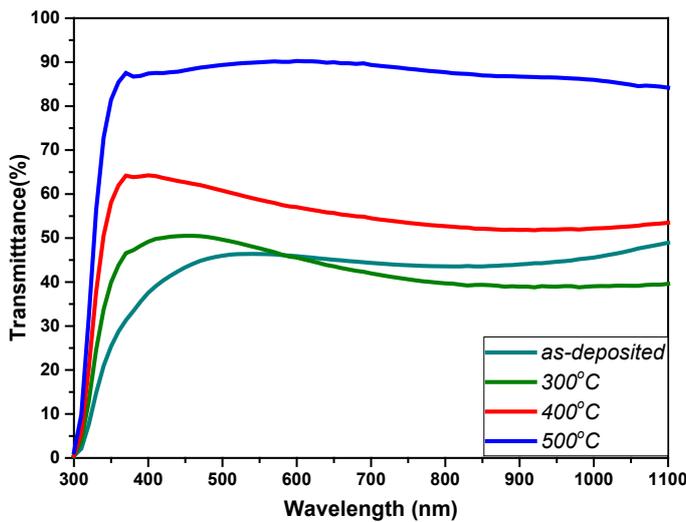


Figure 2 – Transmittance spectra of as-deposited and annealed at different temperatures antimony films

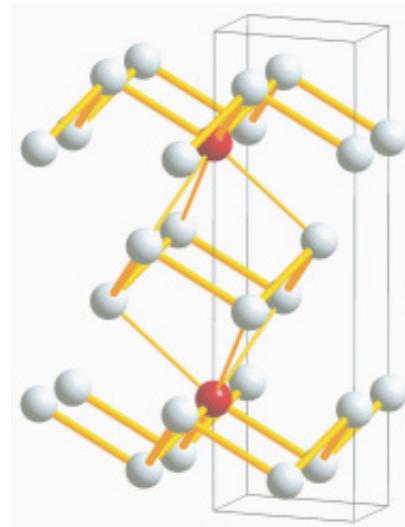


Figure 3 – Crystal structure of Sb-I (hexagonal setting) [6]

In figure 4 shown Raman spectra of our work and adapted literature data of polycrystalline and amorphous antimony recorded at room temperature [6, 8]. Since the spectra have different intensities, for correct comparison spectra of the testing samples were divided by maximum intense peak, for each spectra maximum is different at about 150  $\text{cm}^{-1}$ . The  $E_g$  mode at 115  $\text{cm}^{-1}$  identified in the red laser line. The reason of sensitivity of Sb-I phase on the excitation wavelength either high integration time or dependence of Raman scattering efficiencies

well-known  $1/\lambda^4$  ( $\lambda$  is the excitation wavelength) [9]. Proceeding from the last assumption, more phonon modes should be identified with less exciting wavelength. The Raman spectroscopy results of annealed samples at temperatures of 300 and 400  $^{\circ}\text{C}$  confirm the morphology and transmittance spectroscopy study results of the films. The crystal structure of the films is polycrystalline with the A7 structure showed two peaks at 115  $\text{cm}^{-1}$  and 150  $\text{cm}^{-1}$ , in agreement with [5, 10], whereas amorphous antimony phonon ( $a\text{-Sb}$ ) modes at  $\sim 145\text{-}150 \text{ cm}^{-1}$  [8].

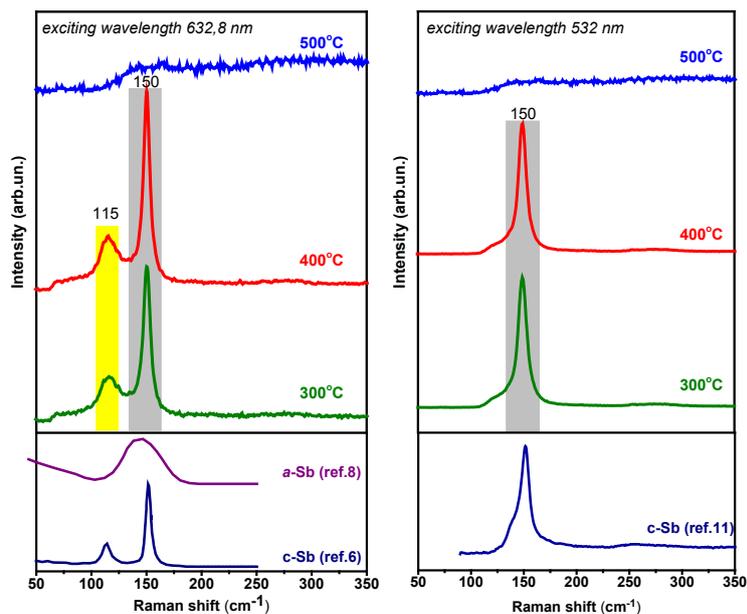


Figure 4 – Raman spectra of antimony

## Conclusion

Thin films of antimony have been grown on glass substrate using RF magnetron sputtering technique and then annealed at different temperatures in order to test stability of the film structure. Analyzes of the transmission spectra and the study of surface morphology showed the stability of thin films of antimony up to 400 °C, which confirmed by high quality Raman spectroscopy measurements. The data obtained by the Raman spectroscopy method are in good agreement with the literature data obtained from high-purity antimony powders, which are  $A_{1g}$  mode at 150  $\text{cm}^{-1}$  and a two-fold

degenerated  $E_g$  mode at 115  $\text{cm}^{-1}$ . In the future, the films will serve as precursors for chalcogenide structures.

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