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GROWING Sb_2Se_3 FILMS ENRICHED WITH SELENIUM USING CHEMICAL MOLECULAR BEAM DEPOSITION

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This study explores the growth of Sb_2Se_3 films on soda-lime glass (SLG) surfaces using the chemical molecular beam deposition (CMPD) method at a substrate temperature of 500°C. High-purity binary compounds, Sb_2Se_3 and Se, were employed as source materials for film deposition. Scanning electron microscopy (SEM) was employed to investigate the morphological characteristics of the Sb_2Se_3 films. Furthermore, the influence of temperature on the grain size and crystallographic orientation in selenium films was examined. Samples were obtained from a selenium source at temperatures of 370°C and 430°C. The results indicate that increasing the temperature of the selenium source results in the formation of larger grains and the presence of rod-shaped grains of Sb_2Se_3 aligned parallel to the substrate. A sample obtained at 370°C exhibited grains larger than 2 μm in size, evenly distributed across the substrate surface, indicating a uniform growth process. In contrast, when the temperature of the selenium source was raised to 430°C, considerably larger grains measuring approximately 4 μm were detected on the film surface substrate. X-ray diffraction analysis was conducted to gain insights into the crystalline phases and crystal structure of the Sb_2Se_3 films synthesized under different temperatures of the selenium source. The X-ray diffraction patterns displayed prominent peaks corresponding to the crystallographic planes (221) and (211), indicating the presence of strong crystalline phases. Additionally, peaks such as (020), (120), and (310) were observed in the X-ray patterns, further confirming the crystallinity of the films.
Keywords: *X-ray diffraction; Chemical molecular beam deposition; Sb_2Se_3; Selenium temperature*
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1. INTRODUCTION

Antimony selenide (Sb_2Se_3) has emerged as one of the most promising absorber materials for the development of next-generation thin-film solar cells, due to its outstanding photovoltaic performance. The remarkable properties of Sb_2Se_3, including its simple crystal structure, substantial absorption coefficient exceeding 10^5 cm^{-1}, ideal band gap within the 1.1–1.3 eV range, and significant mobility, approximately 10 $cm^2V^{-1}s^{-1}$ [1], make it a highly attractive candidate for advanced thin-film solar cells. One distinct advantage of Sb_2Se_3, compared to more established thin-film solar cells, specifically Copper Indium Gallium Selenide ($CuInGaSe(S)_4$, referred to as CIGS) and Cadmium Telluride (CdTe), is its cost-effectiveness. Both antimony (Sb) and selenium (Se), the constituent elements of Sb_2Se_3, are widely available and exhibit lower toxicity. As such, we can anticipate that Sb_2Se_3 technology will become a serious competitor in the mass production of thin-film photovoltaic modules. It has been discovered that [hk1]-oriented (vertically oriented) Sb_2Se_3 film is superior for efficient charge carrier transfer compared to the [hk0]-oriented Sb_2Se_3 compound film. However, controlling the orientation of the thin film remains a significant hurdle to further enhancing the efficiency of Sb_2Se_3-based solar cells. It should be noted that during the synthesis of Sb_2Se_3 films via physical methods, a considerable amount of Se is lost due to film decomposition into Sb, Se, and SbSe. This results in the formation of Se vacancies, which subsequently increase the density of recombination centers in the films [2]. These changes have a negative impact on the optical and electrophysical properties of the solar cells. To mitigate this issue, researchers propose additional heat treatment in Se vapor. Zhiqiang Lee [2] has successfully produced thin film Sb_2Se_3 using a co-evaporation method of Sb_2Se_3 and Se [3, 4], whilst Shongalova [5] has introduced a method for creating Sb_2Se_3 films by sputtering, followed by "selenized" annealing in a H_2Se gas atmosphere. These innovative solutions illustrate the ongoing advancements in the field, paving the way for the full realization of Sb_2Se_3 potential in next-generation solar technology.

Sb_2Se_3 films are used various methods precipitation: thermal evaporation [6-7], gas transport evaporation [8, 9] method sublimation in a closed vacuum [10] and magnetron sputtering [11]. In this work, first time to grows films Sb_2Se_3 for solar cells by chemical molecular beam deposition (CMBD) method. In this study, we investigate the growth of Sb_2Se_3 films on SLG substrates using the CMBD method.

2. MATERIALS AND METHODS

Installed technological mode optimal grow Sb_2Se_3 films on surfaces SLG (soda- lime glass) by the method chemical molecular beam precipitation (Fig. 1). The experimental system was prepared by purging hydrogen to eliminate atmospheric pollutants. The SLG substrates with dimensions of 2.0×2.0 cm^2 were used for film deposition. To obtain Sb_2Se_3 films with enriched selenium content and stoichiometric composition, the partial pressure of Se in the steam phase was adjusted during

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the growth process. The substrate temperature was maintained at 500°C, while the temperatures of the source elements were varied within the ranges of 350°C to 430°C for Se and 700°C for Sb_2Se_3. The growth rate was controlled between 0.1 to 1 Å/sec, and a hydrogen flow rate of WH_2 = 20 cm^3/min was maintained.

Granules of Sb_2Se_3 and high-purity Se (99.999%) were utilized as the source materials. These compounds were placed in separate containers within the experimental setup. The morphological properties of the films were examined using a scanning electron microscope (SEM-EVO MA 10). The film compositions were determined by energy-dispersive elemental analysis (EDX) using an Oxford Instrument Aztec Energy Advanced X-act SDD detector. The crystal structure and phase composition were analyzed using X-ray diffraction (XRD) with a Panalytical Empyrean diffract meter, employing CuKα radiation (λ = 1.5418 Å) and 2θ measurements in the range of 20° to 80° with a step size of 0.01°. The phase composition analysis was conducted using the Joint Committee on Powder Diffraction Standards (JCPDS) database.

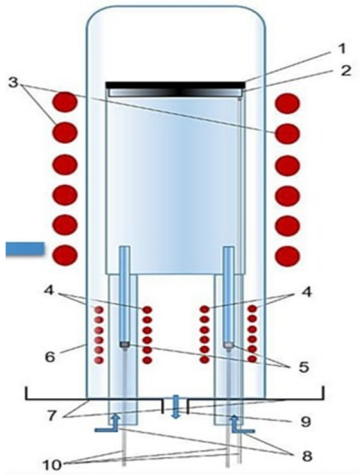

Figure 1. a) Schematic diagram of the system; b) Schematic image method chemical molecular beam deposition 1, 2 – substrate and its holder , 3- heater substrates , 4- heaters sources , 5-sources evaporated component (Sb_2Se_3 and Se), 6- hydrogen gas carriers (H_2), 7- flange holder, 8-hydrogen inlet, 9-hydrogen outlet, 10-thermocouple

3. RESULTS AND DISCUSSION

Morphological properties. The obtained SEM images revealed the morphological characteristics of the Sb_2Se_3 films, while the EDX analysis confirmed their elemental composition.

This study investigates the influence of temperature on grain size and crystallographic orientation in selenium films. A sample was obtained from a selenium source at temperatures of 370°C and 430°C. The characterization of the samples was performed using microscopy techniques, and the results were analyzed to understand the relationship between temperature and the observed grain size and crystallographic orientation. Our findings indicate that increasing the temperature of the selenium source leads to the formation of larger grains and the presence of rod-shaped grains of Sb_2Se_3 aligned parallel to the substrate. These observations are consistent with the collected data, which also revealed an increase in the peak texture coefficients (hk0) at the temperature of 430°C.

Upon analyzing the sample obtained at 370°C, grains larger than 2 μm in size were observed. These grains exhibited a uniform distribution across the substrate surface, indicating a uniform growth process. However, when the temperature of the selenium source was raised to 430°C, considerably larger grains measuring approximately 4 μm were detected on the film surface substrate. The increase in temperature led to the formation of larger grains, which can be attributed to enhanced diffusion and coalescence processes during film growth.

Furthermore, rod-shaped grains of Sb_2Se_3 were observed in the sample obtained at 430°C. These grains aligned themselves parallel to the substrate, as depicted in Figure 2. The formation of Sb_2Se_3 grains can be attributed to the reaction between antimony (Sb) impurities present in the selenium source and the substrate material. The alignment of these rod-shaped grains suggests an epitaxial growth mechanism on the substrate surface.

The XRD analysis revealed that the peak texture coefficients (hk0) began to exhibit an increase at the temperature of 430°C. This finding indicates a preferential crystallographic orientation in the film, which can be attributed to the growth conditions and the interaction between the deposited selenium and the substrate material. The increased peak texture coefficients further support the observed larger grain size and the presence of Sb_2Se_3 rod-shaped grains.

These observations are consistent with our data, as the presence of larger grains can positively impact the performance of solar cells by reducing recombination losses. Larger grains tend to have fewer defects along their boundaries, which can lead to improved efficiency in converting solar energy. In conclusion, our results demonstrate that temperature influences grain size and texture in the selenium film. The larger grain size observed at higher temperatures suggests the potential for enhanced solar cell performance.

Table 1 presents the chemical composition of the elements in the deposited Sb_2Se_3 films. The analysis using an energy dispersive elemental analyzer revealed that the Sb/Se atomic concentration ratio decreased as the selenium

temperature increased from 350°C to 430°C, approaching the stoichiometric composition of Sb/Se≈0.66. This indicates that the selenium content in the Sb_2Se_3 thin films increased with higher selenium flow. At a selenium source temperature of 350°C, the Sb_2Se_3 film was selenium-poor. However, at higher temperatures, the compound films approached a stoichiometric composition with an Sb/Se ratio of 0.68, which was achieved at a selenium source temperature of 430°C. It is evident that the temperature of the selenium source plays an important role in obtaining high-quality Sb_2Se_3 films.

Stoichiometric, vertically oriented Sb_2Se_3 grains larger than 4 μm were successfully obtained at a selenium temperature of 430°C, which are considered beneficial for charge carrier transport.

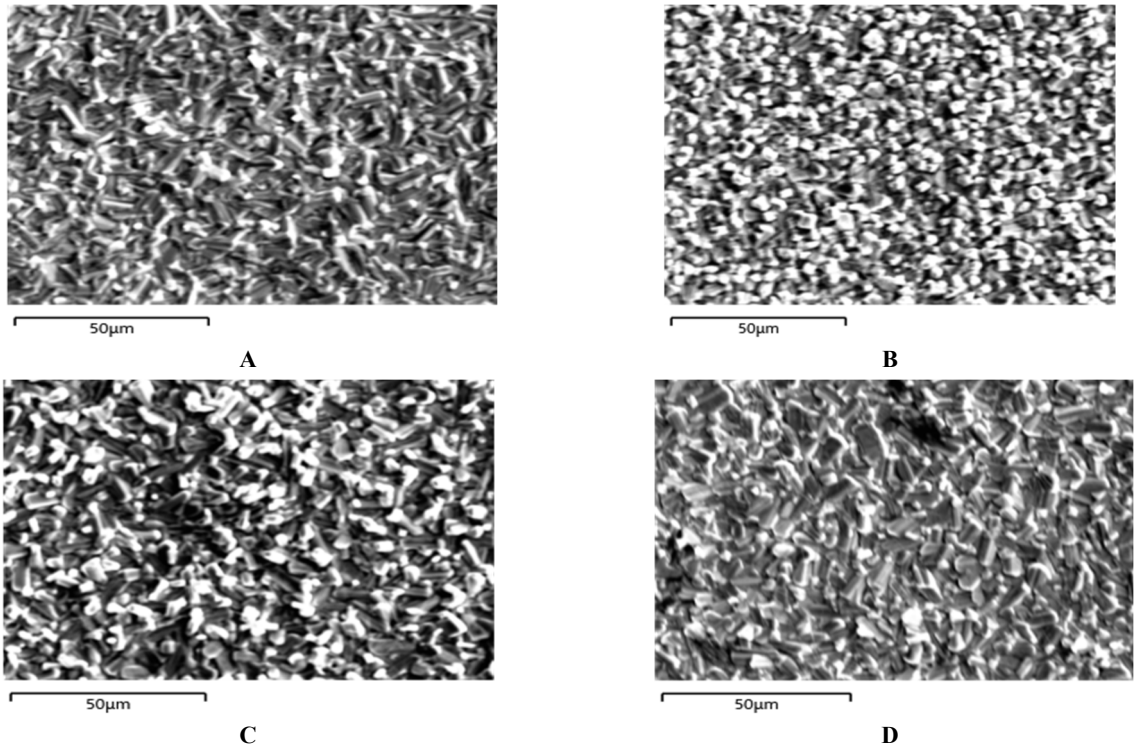

Figure 2. SEM images of Sb_2Se_3 films at different selenium temperatures: a) 350°C; b) 370°C; c) 400 °C; d) 430°C

It is worth noting that Sb_2Se_3 films exhibit p-type conductivity. However, some samples of Sb_2Se_3 may exhibit n-type conductivity due to the presence of Sb impurities. Additionally, the presence of (V_{Se}) defects can also contribute to n-type conductivity or act as donors [12].

Table 1. Chemical compound Sb_2Se_3 films at various temperatures selenium source

T_{Se}, (Temperatures of Selenium source °C)	*T* substrate, °C	weight percentage, %		Atomic percentage, %		Sb/Se
		Sb	Se	Sb	Se	
350	500	53.3	46.7	0.43	0.59	0.74
370	500	52.6	47.4	0.43	0.60	0.72
400	500	51.8	48.2	0.42	0.61	0.70
430	500	51.2	48.8	0.42	0.618	0.68

The implications of the Sb/Se atomic concentration ratio approaching the stoichiometric composition in Sb_2Se_3 films are significant. The stoichiometric composition represents the ideal ratio of antimony (Sb) to selenium (Se) atoms in Sb_2Se_3. When the Sb/Se ratio approaches this stoichiometric composition, the film exhibits optimal electrical properties. This means that the film is more likely to have the desired characteristics for its intended applications, such as solar cells. Achieving the stoichiometric composition helps in attaining the desired electronic band structure and charge transport properties. Reduced Defects: Deviations from the stoichiometric composition can introduce defects in the crystal structure of the material. By approaching the stoichiometric composition, the number of defects, such as vacancies or impurities, can be minimized. Fewer defects lead to improved electrical and optical properties, as defects act as recombination centers for charge carriers, reducing their lifetime and overall device performance.

Structural properties of Sb_2Se_3 films. Figure 3 present the outcomes of the X-ray diffraction analysis, providing insights into the crystalline phases and crystal structure of the Sb_2Se_3 films synthesized under different temperatures of the selenium source. The X-ray patterns exhibit distinct features, with notable observations regarding the intensity variations of specific peaks in response to increasing temperature of the selenium source. The X-ray diffraction patterns display prominent peaks corresponding to the crystallographic planes (221) and (211), indicating the presence of strong crystalline

phases. Additionally, peaks such as (020), (120), and (310), are also obviously in the X-ray patterns. Notably, these peak intensities demonstrate a dependence on the temperature of the selenium source, with alterations observed as the temperature increases. The selenium source temperature of T_{Se} = 370°C, the XRD analysis reveals the disappearance of weak peaks, including (020), (120), (310), (230), (240), (002), and (320), while the strong peaks (221) and (211) remain raised. This suggests a distinct influence of the temperature on the crystal structure, leading to the elimination of certain crystallographic planes at temperatures up to T_{Se} = 370°C. Furthermore, a subsequent increase in temperature to T_{Se} = 430°C induces a decrease in the intensities of the (221) and (211) peaks, while the weak peaks (020), (120), (230), and (240) become significantly more pronounced. This temperature-dependent variation highlights the dynamic nature of the crystal structure and phase composition of the Sb_2Se_3 films. Moreover, an additional observation is made at 2θ = 29.66°, where a low-intensity reflex is detected in correspondence to the (101) peak. This reflex indicates the formation of the Se phase, providing evidence of a distinct phase transition or phase presence within the Sb_2Se_3 films under the given experimental conditions. In summary, the XRD analysis of the Sb_2Se_3 films elucidated valuable information regarding their crystal structure and phase composition. The obtained results demonstrate the influence of the selenium source temperature on the intensities of specific peaks, emphasizing the temperature-dependent alterations in the crystal structure. Additionally, the identification of the Se phase further contributes to the understanding of the film's structural properties.

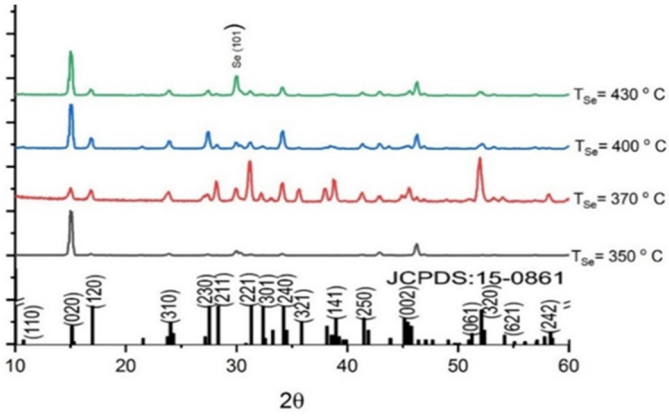

Figure 3. X-ray diffraction pattern of Sb_2Se_3 films at different temperatures of the selenium source

To quantitate vela, study the orientation of Sb_2Se_3 films, the texture coefficients (T_C) of diffraction peaks were calculated based on the following equation [13]:

$$T_c = \frac{I_{(hkl)}}{I_{0(hkl)}} \Big/ \left(\frac{1}{N} \sum_{i=1}^{N} \frac{I_{(h_i k_i l_i)}}{I_{0(h_i k_i l_i)}} \right). \quad (1)$$

The intensities of the diffraction peaks, denoted as $I_{(hkl)}$ and $I_{0(hkl)}$, respectively, correspond to the measured and standard X-ray diffraction patterns of Sb_2Se_3 (JCPDS 15-0861) for the crystallographic planes (hkl). The determination of the peak intensity is crucial for analyzing the crystal orientation and structural properties of the material under investigation. Notably, the texture coefficient, TK, associated with the diffraction peaks signifies the level of orientation prevalence along a specific direction. In the case of the examined samples, the high TK values observed for the diffraction peaks indicate a pronounced orientation in the corresponding direction. Interestingly, at a selenium source temperature of 370°C, the TC values for crystallographic planes (hk0) in our samples tend to decrease. This initial decrease suggests a deviation from the dominant orientation, possibly due to the effect of elevated temperature on the crystal lattice arrangement. However, as the temperature of the selenium source continues to rise 370°C, a subsequent increase in the TK values for the (hk0) planes is observed. The temperature of the selenium source plays a significant role in influencing the crystal orientation and can result in distinct variations in the diffraction patterns of Sb_2Se_3. Further investigation is necessary to comprehensively understand the underlying mechanisms behind these observed temperature-dependent changes in crystal orientation and their implications for the materials properties.

4. CONCLUSIONS

In this study, we investigated the effect of temperature on grain size and crystallographic orientation in selenium films. The results indicate that increasing the temperature of the selenium source leads to the formation of larger grains and the presence of rod-shaped grains of Sb_2Se_3 aligned parallel to the substrate. The observed grain sizes and crystallographic orientations are in line with the collected data, as evidenced by the increased peak texture coefficients at the temperature of 430°C. These findings contribute to a better understanding of the growth mechanisms and properties of selenium films, which can aid in the development of tailored thin film technologies for various applications. Further studies exploring the influence of other parameters on grain formation and crystallographic orientation are warranted to expand our knowledge in this field. At a selenium source temperature of 430°C, large rod-like grains can be observed on

the surface of the Sb_2Se_3 film. Sb_2Se_3 films Se -deficient at a selenium source temperature of 350°C. As the temperature of the selenium source increases, the composition of the $Sb_2Se_{3\ film}$ approaches stoichiometric.

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ВИРОЩУВАННЯ ПЛІВОК Sb_2Se_3, ЗБАГАЧЕНИХ СЕЛЕНОМ, ЗА ДОПОМОГОЮ ХІМІЧНОГО МОЛЕКУЛЯРНОГО ОСАДЖЕННЯ

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У цьому дослідженні вивчено ріст плівок Sb_2Se3 на поверхнях вапняно-натрієвого скла (SLG) за допомогою методу хімічного молекулярно-променевого осадження (CMPD) при температурі підкладки 500°C. Вихідними матеріалами для осадження плівок були використані високочисті бінарні сполуки Sb_2Se_3 та Se. Для дослідження морфологічних характеристик плівок Sb_2Se_3 використовували скануючу електронну мікроскопію (SEM). Крім того, було досліджено вплив температури на розмір зерен і кристалографічну орієнтацію в плівках селену. Зразки отримували з джерела селену при температурах 370°C і 430°C. Результати показують, що підвищення температури джерела селену призводить до утворення більших зерен і наявності стрижнеподібних зерен Sb_2Se_3, розташованих паралельно підкладці. Зразок, отриманий при 370°C, показав зерна розміром понад 2 мкм, рівномірно розподілені по поверхні підкладки, що свідчить про рівномірний процес росту. Навпаки, коли температуру джерела селену підняли до 430°C, на поверхні плівки підкладки були виявлені значно більші зерна розміром приблизно 4 мкм. Рентгеноструктурний аналіз був проведений, щоб отримати уявлення про кристалічні фази та кристалічну структуру плівок Sb_2Se_3, синтезованих за різних температур джерела селену. На рентгенівських дифракційних картинах відображені помітні піки, що відповідають кристалографічним площинам (221) і (211), що вказує на наявність сильних кристалічних фаз. Крім того, такі піки, як (020), (120) і (310), спостерігалися на рентгенівських картинах, що додатково підтверджує кристалічність плівок.

Ключові слова: *рентгенівська дифракція; хімічне молекулярно-променеве осадження; Sb_2Se_3; температура селену*