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In-situ growth of high room temperature thermoelectric performance Ag₂Se thin films

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Abstract: In this work, well-crystalline Ag₂Se thermoelectric thin film with high power factor at room temperature was successfully fabricated at solid substrate by a facile *in-situ* growth method via co-evaporation deposition. Micro-structure characterizations show that the thin films prepared under proper growth temperature have single α -Ag₂Se phase and stable chemical valence states, leading to a high electrical conductivity. Additionally, the carrier concentration is optimized after adjusting growth temperature and further contributes to a high Seebeck coefficient. As a result, a maximum power factor of 15.34 $\mu\text{Wcm}^{-1}\text{K}^{-2}$ is achieved, demonstrating that our *in-situ* growth method is an effective way to fabricate high performance Ag₂Se thermoelectric thin films.

Keywords: Thermoelectric; Thin film; Ag₂Se; Power factor

1. Introduction

Recently, achieving high performance thermoelectric (TE) thin film for portable and wearable electronic applications have received great attention by researchers [1]. The performance of TE material is evaluated by a dimensionless figure-of-merit ($ZT = S^2\sigma T/\kappa$, where S , σ , $S^2\sigma$, T , and κ are the Seebeck coefficient, electrical conductivity, power factor, absolute temperature, and thermal conductivity, respectively) [2]. Due to the lack of high performance of TE thin films at room-temperature, environmentally unfriendly Te-based materials are still the choice for fabricating thin film devices [3]. Thus, it is extremely urgent to prepare environmentally friendly TE thin films for

practical application.

Environmentally friendly *n*-type Ag₂Se has excellent thermoelectric performance with *ZT* value of 0.96 at 300 K for bulk Ag₂Se, reported by X. Shi [4]. Many thin film deposition methods, including physical vapor deposition (PVD) and chemical vapor deposition (CVD) were employed to fabricate Ag₂Se based thin film in order to replace the fabrication of traditional Te-based materials [5-8]. For instance, Hou et al. have prepared flexible silver selenide films by a simple vacuum thermal evaporation method, exhibiting a *PF* of 17 $\mu\text{Wcm}^{-1} \text{K}^{-2}$ at 300K [9]. Lu et al. have synthesized a PEDOT/Ag₂Se compound via chemical method, demonstrating a *PF* of 16.03 $\mu\text{Wcm}^{-1} \text{K}^{-2}$ [10]. Comparatively, PVD method is more suitable for preparing thin films whose components are easily oxidized. Moreover, thermal evaporation is one of the most common PVD methods used for preparing TE thin films [9-11]. However, Ag₂Se thin films prepared by this method [12] have lower power factor than using other methods until now [13-15]. In this work, a facile *in-situ* growth mechanism is employed to fabricate Ag₂Se thin films by using co-evaporated Ag and Se. To precisely control the micro-structure of thin films, the growth temperature was varied. As a result, a high power factor of 15.34 $\mu\text{Wcm}^{-1}\text{K}^{-2}$ of Ag₂Se thin film is achieved under proper growth temperature, which can be compare with the record value of the evaporated Ag₂Se from the report [10], indicating that our *in-situ* method can be used for high-performance TE thin films and show great potential to apply for the miniature thermoelectric devices.

2. Experiment

Ag₂Se films were deposited at BK7 substrate by vacuum thermal co-evaporation method. High purity Ag powder and Se powder were fixed in a vacuum deposition chamber by using tantalum evaporator boats. The evaporating current of Ag and Se is 130 A and 40 A, respectively, with a co-deposition time of 15 min. Before thin film deposition, the substrate was heated to a set temperature to realize *in-situ* growth. The deposition temperature was set as 363 K, 393 K, 423 K, 453 K and 483 K, respectively. X-ray diffraction (XRD) was applied to analyze the crystal structure and scanning electron microscope (SEM) was used to conduct morphological analysis of microstructure with an energy dispersive X-ray spectroscopy (EDS) to measure the composition of Ag₂Se thin films. Additionally, the thickness of the thin films was

measured by using the cross-sectional SEM images, and the results are shown in Fig. S1 (Supporting information). X-ray photoelectron spectroscopy (XPS) provided semi-quantitative information of the elemental valence states. The electrical conductivity and Seebeck coefficient were measured by utilizing a Seebeck coefficient and electrical conductivity measurement apparatus. Van der Pauw Hall measuring instrument was applied to investigate the carrier concentration and mobility.

3.Result and Analysis

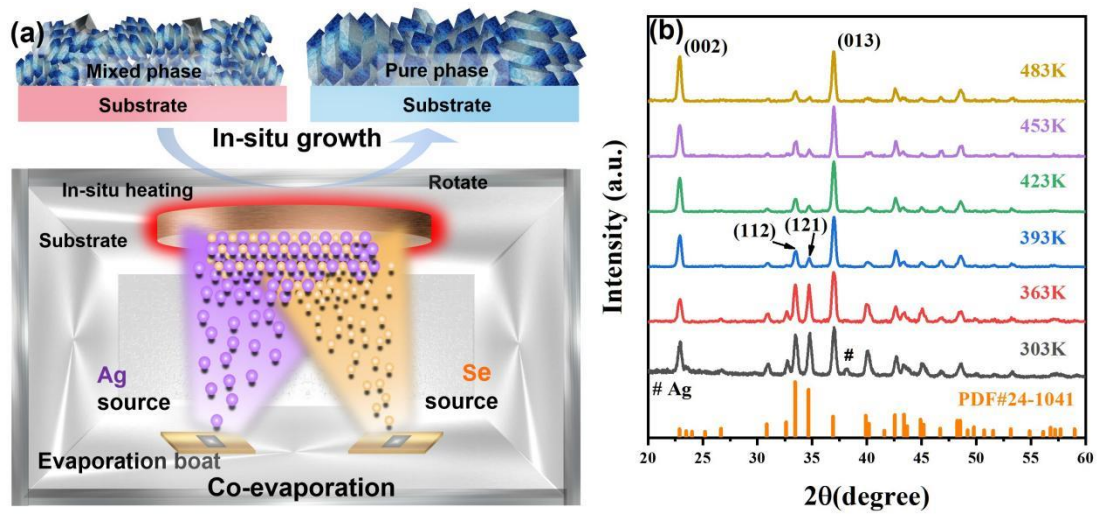


Fig.1. (a) A diagram of co-evaporation deposition process. (b) Phase characterization of the Ag₂Se thin film with different deposition temperature.

Fig.1(a) shows the schematic of co-evaporation process. The composition of the synthesized samples was controlled by adjusting the mass ratio of Ag/Se. Fig.1. (b) presents the XRD patterns of the synthesized Ag₂Se thin films, including the sample deposition at room temperature (303 K). The sample deposited at room temperature confirms that this sample has primary orthorhombic Ag₂Se phase, comparing to the standard diffraction pattern PDF#24-1041. But some minor impurity peaks related to Ag phases are observed. Similarly, all the samples grown at heated substrate have primary Ag₂Se phase, and no impurity peaks are observed when the deposition temperature is over 393 K.

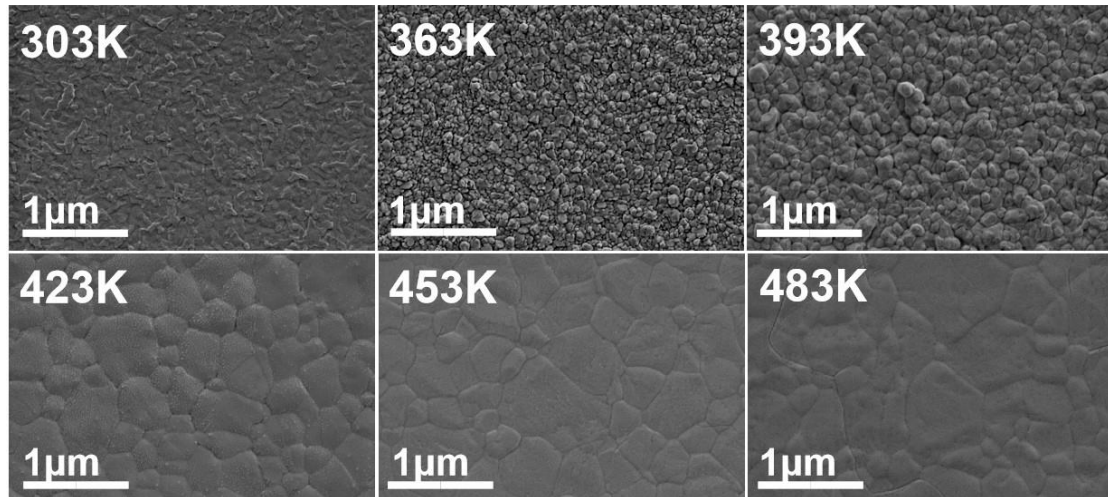


Fig.2. (a)-(f) SEM images of Ag_2Se films deposited at different deposition temperature.

Fig.2 presents the SEM images for all the samples. Dense surface is obtained from the as-deposited thin film, but the grains are very small which causes poor electrical transportation due to plenty of grain boundaries. In comparison, samples grown on heated substrate shows larger grain sizes and the grain sizes increase with the increasing deposition temperature. In many cases, large grain size will lead to high electrical conductivity. The chemical composition analyzed by EDS are shown in Table 1, which confirms that all the samples have the atomic ratio closed to 2:1. But the Se content has slightly decreased with the increase of growth temperature.

Table 1. Composition content of Ag_2Se thin films measured by EDS.

Deposition temperature (K)	303	363	393	423	453	483
Se (at%)	33.70	32.73	32.83	32.34	32.55	32.20
Ag (at%)	66.30	67.27	67.17	67.66	67.45	67.80
Atomic ratio (Ag : Se)	1.97	2.06	2.05	2.09	2.07	2.11

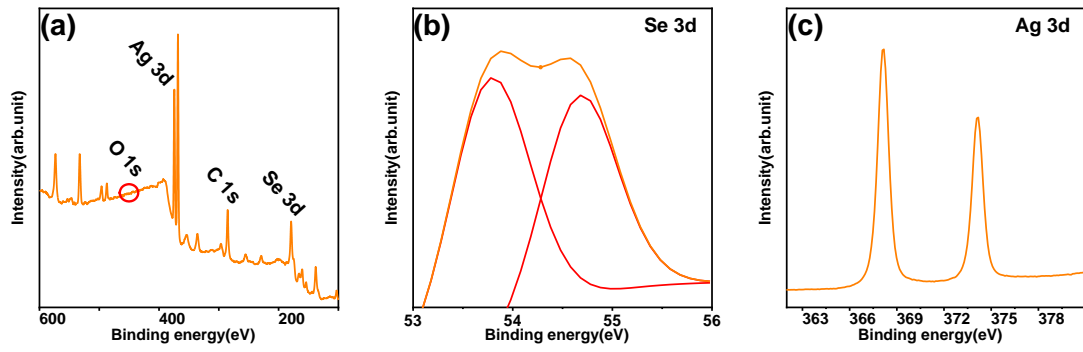


Fig. 3 (a) XPS survey scans of the Ag_2Se thin film deposited at 423 K, (b) Se 3d spectra, (c) Ag 3d spectrum

The XPS survey spectra of the Ag_2Se sample deposited at 423 K is shown in Fig. 3(a). As shown in Fig. 3(b), a broad peak ranging from 53 to 56 eV is observed. This peak is identified into two symmetric peaks related to Se $3d_{5/2}$ and Se $3d_{3/2}$ located at ~ 53.9 and ~ 54.8 eV, which meets the spin-orbit phenomena of Se^{2-} . Peaks located at ~ 368.3 eV and ~ 372.1 eV are shown in Fig. 3(c), which are indexed to the binding energy of Ag $3d_{5/2}$ and Ag $3d_{3/2}$. This result suggests the sample has stable Ag^{1+} state. Additionally, no Ag or Se related oxidation states are observed from the whole XPS patterns. Therefore, the XPS results indicate that the synthesized samples have pure Ag and Se chemical valence states, which can be supported by XRD results and benefit to achieve high TE performance for Ag_2Se thin films.

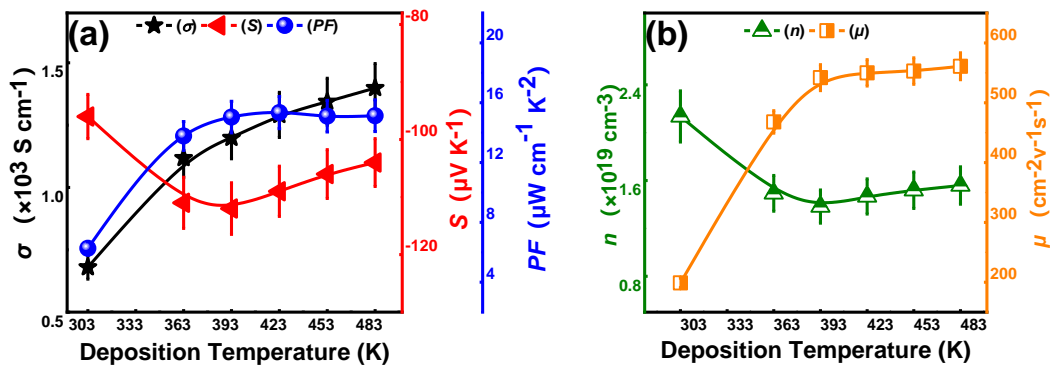


Fig.4 (a) Room-temperature electrical conductivity, Seebeck coefficient and power factor as a function of deposition temperature. (b) Carrier concentration and mobility as a function of deposition temperature.

Fig.4(a) displays the room temperature thermoelectric properties of Ag_2Se thin

films. The σ of as-deposited sample is 680 S cm^{-1} and this value is much lower than that of the reported value [9]. But it dramatically increases with the increasing growth temperature. Based on the carrier concentration and mobility results shown in Fig.4(b), the enhanced electrical conductivity is mainly due to the increase of carrier transport, supported by the increase of grain size observed in Fig.2. In addition, the as-deposited samples show low absolute Seebeck coefficient values. However, the S values are enhanced to over $100 \mu\text{VK}^{-1}$ while the deposition temperature raised to over 363 K. This can be attributed to the decrease of carrier concentration with increasing growth temperature. Consequently, the sample grown at 423 K has a maximum power factor of $15.34 \mu\text{W cm}^{-1} \text{K}^{-2}$, which is about twice enhancement of the as-deposited sample.

4. Conclusion

Ag_2Se thin films are fabricated by a facile *in-situ* co-evaporated growth process. Micro-structure analysis revealed that all the samples have stoichiometric ratio. The synthesized samples have single Ag_2Se phase when the deposition temperature was over 423K. Both electrical conductivity and Seebeck coefficient are enhanced at proper growth temperature due to the decrease of carrier concentration and the increase of mobility. Observed maximum power factor in this research is of $15.34 \mu\text{W cm}^{-1} \text{K}^{-2}$, which is about twice enhancement compared to the as-deposited thin film.

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