



## Nano-scale Surface Modification of Polycrystalline Tin Sulphide Films during Plasma Treatment

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**Abstract:** In this work, we have carried out a comparative research of the nanoscale modification of the surface morphology of polycrystalline SnS films on glass substrates with two different preferred growth orientations during sputtering in inductively coupled argon plasma. We report a new effect of polycrystalline SnS film surface smoothing during plasma treatment, which can be advantageous for the fabrication of multilayer solar cell devices with SnS absorption layers.

**Keywords:** Plasma, Surface modification, Polycrystalline, SnS.

### اصلاح سطحی فیلم نازک سولفید قلع چند کریستال (SnS) در مقیاس نانو به روش پلاسما

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چکیده: در این مقاله، نتایج کارهای تجربی برای بهبود خواص سطحی فیلم نازک سولفید قلع چند کریستال روی که در زیر لایه شیشه لایه نشانی- شده با دو جهت رشد کریستالی متفاوت را در حین فرآیند پاشش پلاسمای القایی گاز آرگون، ارائه می‌شود. آزمایش‌ها نتایج جدیدی از تاثیر عملیات پلاسما روی هموارسازی سطح فیلم نازک سولفید قلع چند کریستال را نشان می‌دهند. این نتایج برتری‌های روش عملیات پلاسما برای اصلاح کیفیت سطوح برای ساخت چند لایه‌های سلول‌های خورشیدی با استفاده از SnS به عنوان لایه جذب را نشان می‌دهند بطوریکه روش عملیات پلاسما در مقیاس نانو کارایی خوبی برای بهبود خواص لایه فعال SnS دارد.

واژه‌های کلیدی: پلاسما، اصلاح سطحی، چند کریستالی و سولفید قلع.

## 1. Introduction

During the last decade, investigations of new materials have evoked considerable interest in SnS thin films due to their vast potential for use in thin film solar cells and other optoelectronic devices like holographic recording system, solar control device etc. [1–4]. Layered semiconductor SnS is a IV-VI compound crystallizing in the orthorhombic structure (space-group *Pnma*, GeS structure type) [5, 6]. Their unit cell spans two layers, which stack along the [010] axis of the crystal. In thin film form SnS is usually a p-type semiconductor with different band gap values in the range of 1.07–1.38 eV. The acceptor levels are created by double ionized tin vacancies [7, 8]. Tin sulfide thin films show high absorption coefficient ( $> 10^4 \text{ cm}^{-1}$ ) in the visible range [3]. They contain only relatively less-toxic materials and stable in the slight acidic media [9]. SnS has also a good thermoelectric properties and it may become a good thermoelectric material for future applications [10]. Hot wall vacuum deposition method (HWVD) has been used for thin IV-VI films deposition for some decades [11]. The method showed high efficiency and economy as HWVD is concerned with the film growth under conditions close to thermodynamic equilibrium and with a minimum loss of material [12–14].

Along with nanostructure lead chalcogenides [15], SnS is one of the most important IV-VI semiconductors of modern nanotechnology. It is prospective for thermoelectric devices [16], and its varied direct gap of 1.07–1.27 eV [17] laying in the optimum range for solar photo conversion makes tin sulphide extremely prospective for the application as an absorption layer in a new generation photovoltaic solar cell devices. Among the many methods of SnS films growth, the highly effective approach is a hot wall thermal evaporation method that allows to successfully obtain SnS films with the

stoichiometric composition under conditions close to the thermodynamic equilibrium phase [16, 17].

## 2. Experimental

Tin sulphide films with stoichiometric composition and 3.0–5.5  $\mu\text{m}$  thickness were grown on pre-cleaned Corning 7059 glass substrates using a hot wall epitaxy method [16, 17]. SnS film deposition was carried out in a sealed quartz tube at a pressure of  $5 \times 10^{-4}$  Pa and a temperature of the tube walls of 550°C, the distance between the evaporated SnS powder and the substrate was 12 cm, the duration was 10–50 min. For this work, two groups of samples were fabricated: at low and high substrate temperature of 212°C and 289°C, respectively.

Plasma treatment of the samples was carried out in high-density low-pressure radio-frequency inductively coupled plasma (RF ICP) in accordance with our recently elaborated method of lead chalcogenide film sputtering and nanostructuring [15]. The treatment parameters were as following: argon flow 10 sccm with a pressure of 0.07 Pa, inductive RF power 800 W, RF bias power on the aluminum substrate holder 300 W, self-bias potential  $200 \pm 10$  V, the treatment was carried out in two consecutive 30 s stages.

## 3. Results and discussion

The sample crystalline structure study was performed using X-ray analysis methods on the DRON-3M diffractometer in the Bragg-Brentano scheme using  $\text{CuK}_\alpha$  radiation. The evaluation of the X-ray spectra of the films was conducted using a Joint Committee on Powder Diffraction Standard data. It was determined that all the films were polycrystalline and contained a single phase of SnS orthorhombic structure (card No. 00-039-0354). Furthermore, the samples grown with low substrate temperature had a (111) preferred orientation of the crystallites. For the

samples grown with high temperature, the major peak (111) was not observed, but the intensity of peaks (040) and (080) strongly increased indicating a (010) preferred growth orientation. These results correspond well to the previously reported [14, 15] consistent pattern for such films.

The study of the surface morphology of the film structures was conducted with scanning electron microscopy (SEM) using Supra 40 Carl Zeiss microscope. For the samples fabricated with low substrate temperature, which had a (111) preferred orientation, the surface was characterized with petal-like grains. Their density was  $9 \times 10^8 \text{ cm}^{-2}$  with a typical thickness of about 10 nm and other geometrical dimensions (width and height) of 200–900 nm. Between the grains there were vertically propagating voids. A typical SEM image of the surface of SnS film with such nano-petals is given in Fig. 2. The surface of these tin sulphide layers after plasma treatment underwent some significant changes. The nano-petal crystallites with a nano-scale thickness were almost completely etched away, while simultaneously a formation of an array of heterogeneous nano-hillocks took place on the smoothed surface (see the inset in Fig. 2). Density of the hillocks was up to  $1.4 \times 10^{10} \text{ cm}^{-2}$ , the lateral dimensions were 25–100 nm, height 70–350 nm. Additionally, on the surface there were larger hillocks with a height up to 750 nm with the density of the order of magnitude of the density of the nanopetals on the initial surface; and also the voids between the grains were still distinctly visible.

The samples with a (010) preferred orientation fabricated with high substrate temperature had a noticeably different grains on the initial surface (Fig. 3). In comparison with the previous case, these grains had larger size dispersion with the width of 750–1200 nm, and their thickness increased much more

significantly and was in the range of 75–750 nm. The density of the grains was accordingly lower —  $2 \times 10^8 \text{ cm}^{-2}$ . During plasma treatment of these films, a surface smoothing also took place, but it was even more profound. The smoothing was accompanied by a comparatively minor phenomenon of the 100–350 nm high nano-hillock formation (see the inset in Fig. 3).

The morphology of the sputtered surface of SnS polycrystalline films in both cases discussed above can be explained by the ongoing competing processes of the physical sputtering (protruding grain material removal) and the redeposition of the material (hillock array formation), which we have recently also observed for the polycrystalline lead chalcogenides based films. However, a crucial feature of the SnS polycrystalline films is that the sputtered material redeposition is significantly lower, which results in a much lower nano-hillock growth and stronger surface smoothing.

#### 4. Conclusion

The study of the plasma sputtering of SnS polycrystalline films with two different types of preferred growth orientation was performed. It was demonstrated that the plasma treatment can serve as a method for effective surface smoothing on nanoscale, which can be very prospective for the multilayered devices fabrication with active SnS layers, such as solar cells.

#### 5. References

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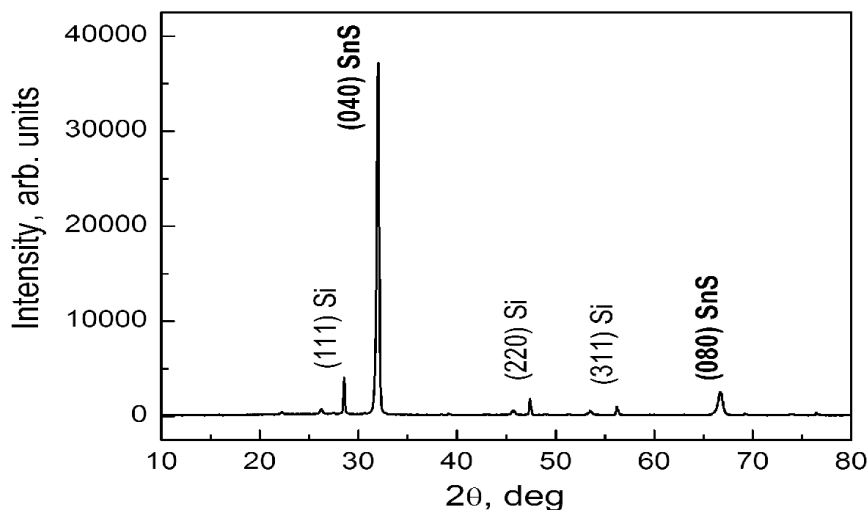
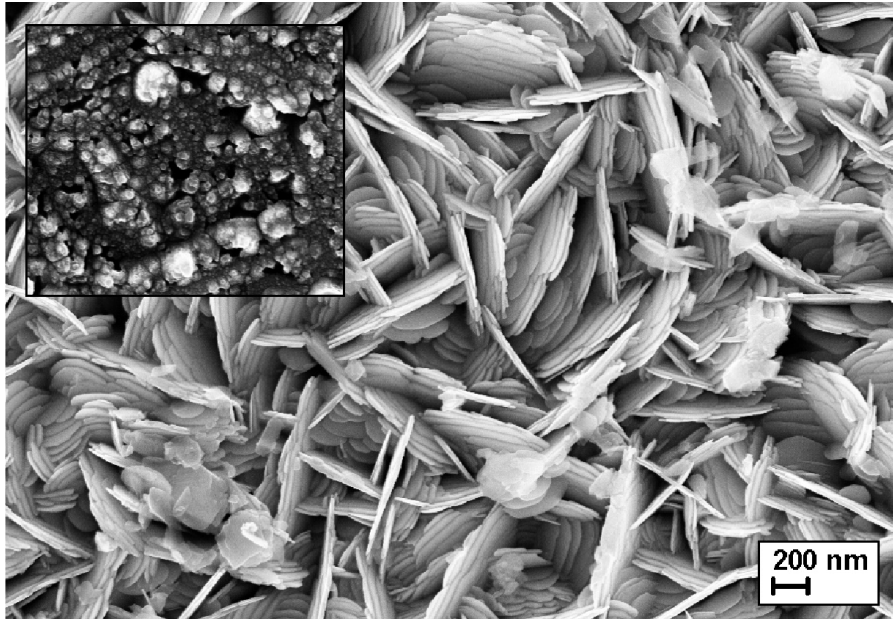
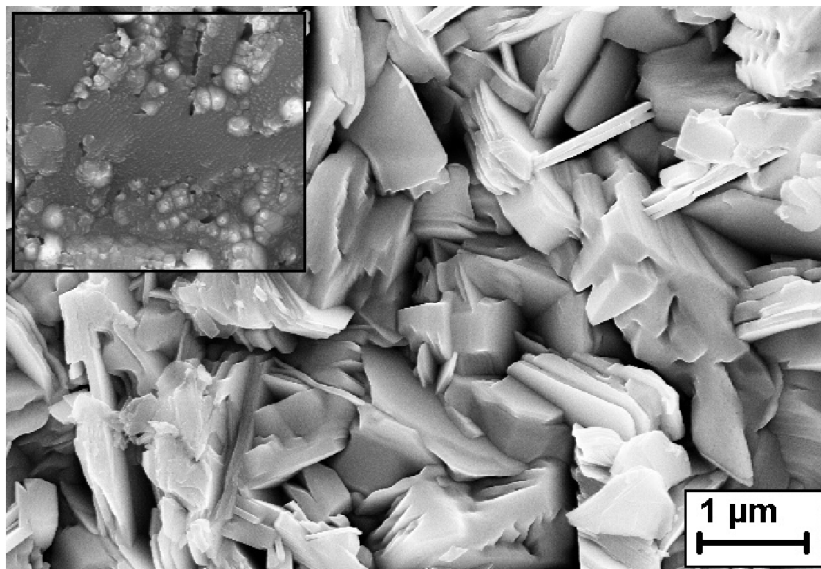


Fig. (1): Typical XRD spectrum of the SnS thin film.



**Fig. (2):** SEM image of the surface of SnS film grown with low substrate temperature.



**Fig. (3):** Typical SEM image of the surface of SnS film grown with high substrate temperature.

