

CHEMICAL DEPOSITION OF TIN(II) SULPHIDE THIN FILMS

M. RISTOV, GJ. SINADINOVSKI, I. GROZDANOV AND M. MITRESKI

Faculty of Natural Sciences and Mathematics, University "Kiril i Metodij", Skopje (Yugoslavia)

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A method is described, by which an SnS thin film can be deposited on a glass surface, from aqueous solutions of SnCl_2 and Na_2S or $(\text{NH}_4)_2\text{S}$. The SnS film is of p-type conductivity, with carrier concentration dependent on the alkalinity. An annealing of the SnS films for a short time above 280 °C changes the conductivity to n-type without detectable change in composition. Annealing for a longer time (over 24 h) changes the composition to SnS_2 . Oxidation of the films by annealing at higher temperatures (300–400 °C) in open air, changes the composition to SnO_2 .

1. INTRODUCTION

Up to now, very little attention has been paid to the applications of SnS, although it could be of interest for a photovoltaic cell, since its optical energy gap of 1.08 eV is similar to that of silicon^{1,2}. A development of chemical deposition method for SnS thin film preparation would be of practical interest, since chemical deposition is both simple and economic.

Tin forms several binary sulphides, such as SnS (orthorhombic)^{3,4}, SnS_2 (trigonal)⁵, Sn_2S_3 (rhombic)⁶ and Sn_3S_4 (tetragonal)⁷. All of these are semiconductors. Crystalline SnS is usually a p-type semiconductor, with optical and thermal energy band gaps of 1.08 eV and 1.20 eV respectively^{1,2,8}. The acceptor levels are created by the tin vacancies normally present in the lattice. An excess of tin changes the type of conductivity of SnS from p- to n-type. At temperatures above 265 °C, SnS slowly decomposes (disproportionates) to SnS_2 and tin. SnS_2 has an optical energy band gap of 2.07 eV and shows n-type conductivity⁹.

2. FILM PREPARATION

For the preparation of the SnS films, we applied a technique already used for preparation of Cu_2O and ZnO thin films^{10,11}. A previously cleaned glass substrate is successively immersed in a cold (18–25 °C) solution of Na_2S or $(\text{NH}_4)_2\text{S}$ with $c = 0.025 \text{ mol dm}^{-3}$, and then in a hot (80–90 °C) solution with the same concentration of SnCl_2 . Upon immersion in the hot solution, a chemical reaction takes place on the surface of the substrate and a brown precipitate is formed as a thin

film. If the solution's $\text{pH} < 3$, the precipitate does not hold tightly and can easily be rubbed away. At $\text{pH} > 3$, a transparent brown-red film deposits uniformly on both surfaces of the substrates. The adhesion under these conditions is very good and the films cannot be rubbed away easily. With successive immersions in the cold and the hot solution the films grow, and their total thickness can be controlled by the immersion number. At $\text{pH} \approx 7$, the growth rate is lower, as part of the dissolved SnCl_2 hydrolyses and precipitates as Sn(OH)_2 . If the solution of SnCl_2 is made more alkaline, by addition of NaOH , at about $\text{pH} \approx 10$ part of the precipitate forms Na_2SnO_2 , which dissolves back, and the growth rate increases again. The appearance of interference colours proves the good quality of the film. It is also possible to monitor the film thickness by the interference colours. At $\text{pH} = 10$, a red interference colour appears after each 20 immersions. By a weight method, it was found that the corresponding film thickness was $0.02 \mu\text{m}$. It was not possible to increase the growth rate by increasing the concentration of the Na_2S or $(\text{NH}_4)_2\text{S}$ solution, as a dissolving of the already deposited film occurred at higher concentrations. The further increase of alkalinity to $\text{pH} = 12$ changes the situation completely. At this pH , Sn^{2+} is in the form of Na_2SnO_2 . The film deposited at this pH is not uniform and it starts to grow up from isolated islands, spreading out to the whole surface of the substrate. The film appears black and it is not transparent to visible light. The interference colours are absent in this case, while the growth rate is twice as large as that observed at $\text{pH} = 10$. The increase of pH over 12 does not yield film deposition.

For the examination of the physical properties of the SnS films, we used glass as a substrate. The films were deposited from aqueous solutions at pH values of 3, 10 and 12. A preparation at $\text{pH} = 7$ was not carried out because of the very small growth rate.

3. STRUCTURE OF THE FILMS

X-ray examination of the films prepared at different pH values showed the diffraction peaks that correspond to SnS (Fig. 1, curves a', a'' and a'''). The intensity of the [013] peak increases with increasing pH , which shows the increased degree of preferred crystallization. In addition to the characteristic peaks there appears a broad band diffuse reflection (background), whose intensity decreases with increasing pH (Fig. 1, curves a', a'', a''').

An examination of the film structure by transmission optical microscopy showed that the films prepared at pH values between 3 and 10 contain small crystals surrounded by a transparent glassy brown phase, which looks like the amorphous phase of SnS (Fig. 2(a)). The films prepared at $\text{pH} = 12$ contain only larger non-transparent crystals (Fig. 2(b)).

Scanning electron microscopy confirmed the same film structure (Fig. 3 is a scanning electron micrograph of the film prepared at $\text{pH} = 10$).

4. CONDUCTIVITY OF THE FILMS

The conductivity of non-annealed SnS films measured at 20°C and under

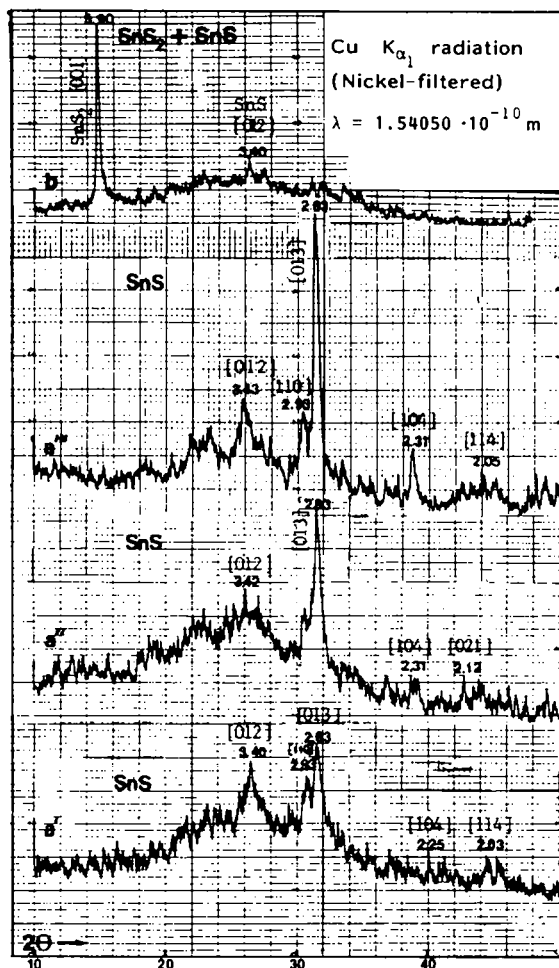


Fig. 1. X-ray diffraction spectra of SnS and SnS₂: curve a', pH = 3; curve a'', pH = 10; curve a''', pH = 12; curve b, annealed at 285 °C for 24 h.

daylight illumination was found to depend on the alkalinity of the SnCl₂ solution. The increase of pH from 3 to 12 led to an increase in conductivity by four orders of magnitude. For example, the films prepared at pH = 3, 10 and 12 with a thickness of 0.1 μm had conductivities of 1×10^{-7} , 5×10^{-5} and $6 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ respectively. It was also possible to increase the conductivity of the films by doping with Cu²⁺, which was achieved by adding CuSO₄ to the solution of SnCl₂. X-ray diffraction spectra of doped SnS films showed the characteristic peaks of Cu₂SnS₃. The film conductivity increased with increasing concentration of Cu²⁺.

The thermal behaviour of the conductivity of SnS films prepared at pH = 10 is presented in Fig. 4, which shows $\ln R$ vs. $1/T$. The first straight part of the line corresponds to the activation of acceptor levels ($E_a = 0.3 \text{ eV}$) and the second straight

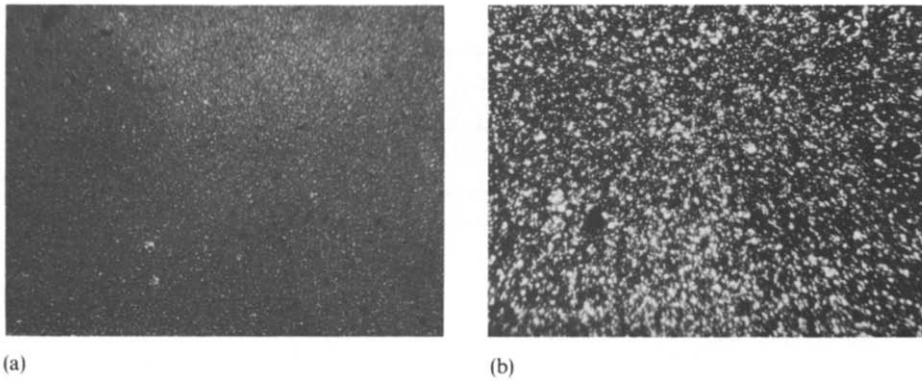


Fig. 2. Transmission optical micrographs of SnS films.

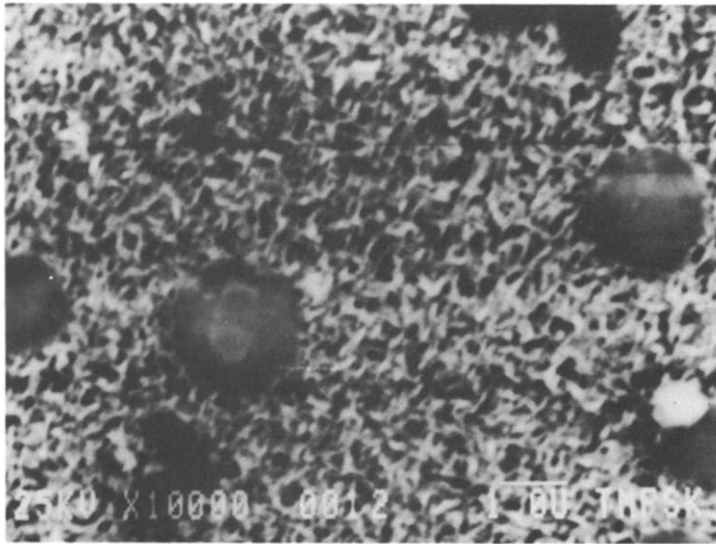


Fig. 3. Scanning electron micrograph of an SnS film.

part of the line corresponds to an activation trough forbidden gap ($E_g = 1.1$ eV). Acceptor levels are created by the Sn^{2+} vacancies formed during the preparation of the films.

5. ANNEALING OF THE FILMS

Annealing of the films at 285 °C for 4 h changed the composition to a mixture of SnS and SnS_2 . Short-time annealing (for 30 min) at 285 °C in open air changed the type of conductivity from p-type to n-type, as was found by thermoelectric probe measurements. The conductivity of the film was found to increase by one order of magnitude. X-ray diffraction spectra of these short-time-annealed films did not

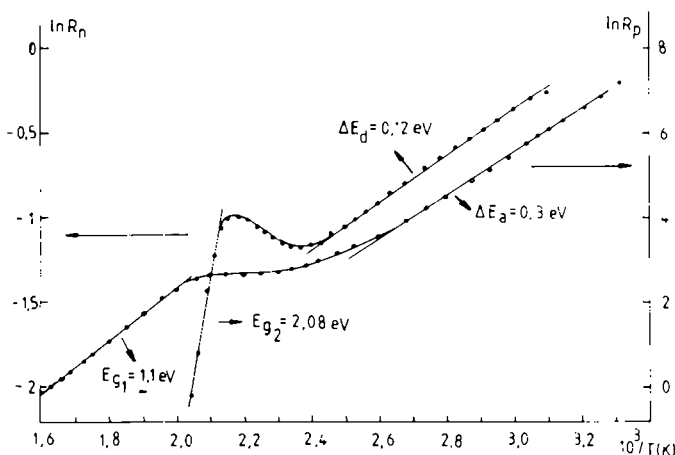


Fig. 4. Temperature dependence of the resistivity of SnS and SnS₂ thin films: R_p , resistance of p-type SnS; R_n , resistance of n-type SnS₂.

indicate any change in the film structure. The reason for the change of the type of conductivity is probably an undetectable excess of tin, released by the partial decomposition of SnS to tin and SnS₂, which shows n-type conductivity.

Annealing of the films at 285 °C for 24 h, changed the composition mainly to SnS₂, with small quantity remains of SnS, as seen in Fig. 1, curve b. The absence of peaks other than the [001] peak of SnS₂ shows that preferred recrystallization occurred during annealing. A fraction of the tin produced by thermal decomposition of SnS reacted with the excess of sulphur, some of tin serving as a donor. The remaining fraction of tin probably oxidized to SnO and SnO₂ in quantities too small to be detected.

The thermal behaviour of the conductivity of the annealed films is presented in Fig. 4. The type of the conductivity found by the thermoelectric probe measurement remained n-type in the temperature range from 0 to 300 °C. The donor activation energy $E_d = 0.1$ eV and thermal band gap energy $E_{g2} = 2.1$ eV were determined graphically. The optical transmission spectrum of this film was typical for SnS₂ with an absorption edge at 2.04 eV (Fig. 5, curve 1b).

Annealing the films at 400 °C in open air changed their colour from brown to white. Chemical analysis showed that the films had been changed to SnO and SnO₂. The conductivities of these films were not as high as those reported for SnO₂ films obtained by the spray pyrolysis method¹².

6. DISCUSSION

SnS thin films chemically deposited on a glass substrate, were found to be mixtures of crystalline and glassy brown amorphous-like phases. It was possible to vary the degree of crystallinity by a pH variation of the aqueous solution. These conclusions were drawn from X-ray spectra, optical microscopy, resistance measurements and optical transmission spectra. It was possible to vary the optical band gap from 2.04 eV to 1.08 eV by variation of degree of crystallinity. Short-time

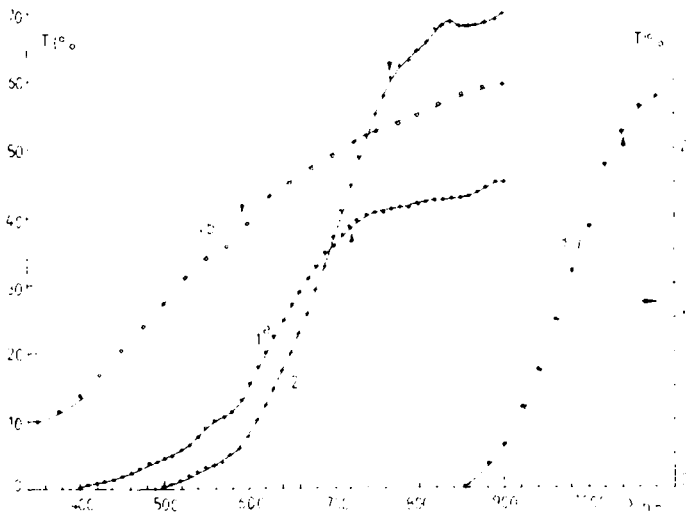


Fig. 5. Optical absorption spectra of SnS and SnS₂ films: curve 1^a, pH = 3; curve 1^b, pH = 3, annealed at 285 °C for 24 h; curve 2, pH = 10; curve 3, pH = 12.

annealing at 285 °C led to a change in the type of conductivity from p type to n type, at the same time increasing the conductivity by an order of magnitude. SnS films could also be doped by Cu²⁺ up to degeneracy.

Long-time annealing of the films at 285 °C made most of the SnS disproportionate to SnS₂. By short-time annealing a film followed by another chemical deposition over the annealed film it was possible to prepare an n-p homojunction. In a similar way, by long-time annealing, it was possible to make an n-p heterojunction of n-SnS₂-p-SnS. By chemical deposition, it was also easy to prepare a heterojunction n-CdO-p-SnS, which was superior in photovoltaic respect. A CdO thin film served as a transparent window electrode¹³.

Long-time annealing of SnS films at temperatures above 400 °C transformed SnS to SnO and SnO₂. Such films are very resistant to acids and could serve as protective coatings.

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