Study of In$_2$S$_3$ Thin Films by Diffraction of Synchrotron Radiation

V. G. Bessergenev*,[1], A. V. Bessergenev†, E. N. Ivanova, and Yu. A. Kovalevskaya

*Institute of Inorganic Chemistry, 630090 Novosibirsk, Russian; and †Institute of Solid State Chemistry, 630091 Novosibirsk, Russia

The crystal structure of In$_2$S$_3$ thin films obtained by the chemical vapor deposition method from the volatile complex compounds indium(III) isopropyl xanthate and indium(III) diethyl dithiocarbonate was studied by synchrotron radiation diffraction. High photon beam intensity (3×10^{10} photons/mm$^2 \cdot$ s) and the high angular resolution ($0.02°$) of the reflexes made it possible to study weak reflexes to analyze the phase composition of samples in more detail, to determine the size of the particles (the size of coherency), and to evaluate the stress at the microscopic level. It is shown that for indium sulfide films deposited at $T = 230°$C, the structure is cubic (α-In$_2$S$_3$). For deposition temperatures $T = 250°$C and higher, the structure is tetragonal (β-In$_2$S$_3$). During annealing an α–β phase transition was observed at $T = 400$–$420°$C. For samples deposited at $430°$C, a splitting of the (5,0,15) reflex was observed, which can be assigned to monoclinic or hexagonal distortions of the lattice. © 1998 Academic Press

INTRODUCTION

The electrical properties of In$_2$S$_3$ thin films allow their use as conducting layers in microelectronics. Application of volatile complex compounds and the chemical vapor deposition (CVD) of the material opens the possibility of technological compatibility of fabrication of luminescent (1, 2) and conducting (3) layers. However, the electrical resistivity (ρ) of In$_2$S$_3$ films can vary in a wide interval depending on the deposition conditions even for the same deposition technique (4). Such variations of electrical resistivity can be due to the variations of the crystal structure of In$_2$S$_3$ films. Another promising conducting material, from our point of view, is In$_2$O$_3\langle$S$\rangle$, prepared by oxygenation of In$_2$S$_3$ films synthesized using butylindium thiolate (5) or indium(III) isopropyl xanthate (3). As was shown in ref 3, the electrical conductivity of the In$_2$O$_3\langle$S$\rangle$ films and the kinetics of the oxygenation process In$_2$S$_3 \rightarrow$ In$_2$O$_3\langle$S$\rangle$ depend essentially on the crystal structure and microstructure of the initial In$_2$S$_3$ films. Thus, studies of the crystal structure of In$_2$S$_3$

films and the dependence of the structure on fabrication conditions are important from both scientific and practical points of view.

It is known that indium sulfide exists in three crystal modifications—α, β, and γ (6). The basis of the α- and β-modifications of the crystal structure of In$_2$S$_3$ is a compact cubic packing of S atoms. For α-In$_2$S$_3$, 70% of the indium atoms are statistically distributed over octahedral sites and 30% over tetrahedral sites (7). The period of the cubic lattice of α-In$_2$S$_3$ is $a = 5.36$ Å with nonordered vacancies in this phase. For β-In$_2$S$_3$ the indium atoms are arranged in a spinel type crystal structure with the period of the crystal lattice $a = 10.72$ Å. It has been shown in further studies that for the β-In$_2$S$_3$ crystal structure, the cation vacancies are ordered and that the superstructure of β-In$_2$S$_3$ has tetragonal symmetry (8). The primitive cell for such a structure contains three cubic spinel cells along the c axis with crystal parameters $a = a_0(2^{1/2}/2)$ and $c = 3\,a_0$, where $a_0 = 10.77$ Å is the period of the spinel type crystal cell. The unit cell of the structure contains 16 formula units of In$_2$S$_3$. In the β-In$_2$S$_3$ crystal structure all octahedral sites and two-thirds of the tetrahedral sites are occupied by indium atoms, while one-third of the tetrahedral sites are vacant (9). At room temperature the β-In$_2$S$_3$ phase is stable. The phase transition $\beta \rightarrow \alpha$ for In$_2$S$_3$ appears at 420°C. A high temperature the γ-In$_2$S$_3$ phase exists at $T \geq 754°$C and has trigonal symmetry (6).

Depending on the precursor species as well as the conditions and the method of synthesis, it is possible to prepare either the α- or β-phase modification of In$_2$S$_3$ films. According to ref 10, β-In$_2$S$_3$ thin films can be grown at $T_{sub} = 350°$C on a glass substrate by spraying a solution prepared by dissolving InCl$_3$ in thiourea. According to ref 11, α-In$_2$S$_3$ thin films can be prepared by thermolysis of indium complexes at $T_{sub} = 190$–$270°$C on glass, silicon, and carbon substrates.

Conducting properties of the films essentially depend on the degree of the ordering of the In vacancies. A disordered α-phase of indium sulfide has a much higher conductivity compared with the β-phase. Also, thin films of In$_2$O$_3\langle$S$\rangle$ prepared from β-In$_2$S$_3$ have a higher conductivity compared with films prepared from α-In$_2$S$_3$ (3).

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[1]To whom correspondence should be addressed. Present address: Algarve University UCEH, Campus de Gambelas, P-8000, Faro, Portugal.

In this work the crystal structure and the phase composition of In$_2$S$_3$ thin films prepared from volatile complex compounds by the CVD method have been studied.

EXPERIMENT

The In$_2$S$_3$ films were deposited using low-pressure CVD by decomposition of indium(III) isopropyl xanthate (samples 1–7) and indium(III) diethyl dithiocarbamate (sample 8) on $6 \times 9\,\mathrm{cm}^2$ glass substrates in a vacuum apparatus (type UVN). The thickness of the films varies from the center of the substrate to the edges within 10%. Before loading into the chamber, the substrates were washed in a detergent solution, rinsed in distilled water, immersed in an H$_2$SO$_4$–K$_2$Cr$_2$O$_7$–H$_2$O solution (184:4:100 by mass) for 24 h, thoroughly washed in distilled water, and blown dry from boiling propan-2-ol. The temperature of the vapor source was varied in the range 120–190°C and the substrate temperature was stabilized in the range 210–450°C. The apparatus is initially evacuated to the pressure 10^{-4} Pa. During synthesis, the pressure of volatile decomposition products is 10^{-2}–10^{-1} Pa. After the decomposition the films cool to room temperature with average rate of 5 grad/min in vacuum.

The study of the crystal structure of the samples was done using the synchrotron radiation from the VEPP-3 electron–positron collider at the Institute of Nuclear Physics Siberian Branch of the Russian Academy of Sciences. The phase composition of the films was studied by the "diffraction cinema" VEPP-3 instrument (12). This instrument has the following parameters: the monochromatization magnitude is 10^{-3} and the photon flow on the sample is 3×10^{10} photons/mm^2·s. The high intensity of the synchrotron radiation makes possible the measurement of low-intensity diffraction peaks, which are very important for the analysis of thin films composed of highly oriented particles. Diffractograms were obtained in reflection conditions.

Determination of the size of the particles (coherent length) was performed using the "anomalous scattering" setup at VEPP-3 (12). The instrument has a monochromatization magnitude of 4×10^{-4} and an instrument broadening of 0.02°. The instrumental broadening makes it possible to determine the physical width of the reflexes. Diffractograms were obtained under reflection conditions (θ–2θ scan with the step 0.005°). To determine the size of the particles and the parameters of the microstress (lattice distortion of the second order, $\Delta d/d$ (13)), five orders of reflex, (1 1 1) in the case of the α-phase or (103) in the case of the β-phase, were analyzed. The size of the particles and the parameters of the microstress were calculated according to the following expression:

$$B = \frac{0.9\lambda}{L\cos\theta} + \frac{\Delta d}{d}\tan\theta \qquad [1]$$

where B is the physical width of the reflex, λ is the wavelength, L is the average size of the particles, d is the interplanar spacing, and θ is the Bragg angle. The first term in this equation is connected with the size of the particles, and the second one with the parameters of the microstress. The parameters L and $\Delta d/d$ were calculated from the root mean square (rms) of the B term using measurements of all five orders of the reflexes.

The In$_2$S$_3$ films were annealed under vacuum to determine if they undergo an $\alpha \rightarrow \beta$ phase transition. Thermal treatments were performed by step-by-step heating with stops at 340, 400, and 430°C with simultaneous *in situ* measurements of the electrical resistivity of the film.

RESULTS AND DISCUSSION

The phase composition has been investigated for samples of different thickness deposited at different temperatures. It has been shown that In$_2$S$_3$ films are strongly oriented so that close packed (111) planes of the α-phase (or (103) planes of the β-phase) are parallel to the surface of the samples and only reflection orders from these planes can be observed. Such orientation of the particles makes the phase analysis difficult because the difference between the α- and β-phases is defined only by order or disorder of indium atoms over tetrahedral sites. This difference cannot be determined using reflexes from the (111) or (103) planes because the ordering takes place in these planes and does not affect the intensity of the reflexes and interplanar spacing of these planes. Ordering of indium atoms over tetrahedral sites leads to the appearance of new reflexes. However, the intensities of these reflexes are relatively small because only tetrahedral In atoms (one-fourth of the total number of In atoms) contribute to these reflexes.

The identification of samples as β-In$_2$S$_3$ can be made based on relatively lower reflexes corresponding to this phase: (008), (107), (1,1,10), (305), and (244). For example, the list of reflexes for samples 1 and 6, identified as the α- and β-modifications, respectively, is presented in Table 1.

It should be noted that the intensity of the reflexes for our samples does not always correspond to standard (ASTM) values. The reason for such a phenomenon, in our opinion, is a high orientation of the crystallites in the films.

The results of the phase analysis of the films are shown in Table 2. It can be seen that for the deposition temperature 230°C indium sulfide film forms an α-In$_2$S$_3$ crystal modification (samples 1 and 2). Increasing the temperature of the synthesis leads to ordering of the indium atoms over tetrahedral sites and to the appearance of additional reflexes of the β-phase. Annealing at 430°C of sample 3 originally deposited at 230°C in the α-modification leads to a phase transition to the β-phase. The size of the particles in the films and the parameters of the microstress depend on the

TABLE 1
Identification of the Diffractograms for Samples 1 and 6

	Sample 1					Sample 6			
2θ (deg)	d (Å)	I/I_{max}	hkl	Phase	2θ (deg)	d (Å)	I/I_{max}	hkl	Phase
					11.53	7.452	3		β-In$_2$S$_3$
13.71	6.248	100	111	α-In$_2$S$_3$	13.71	6.25	100	103	β-In$_2$S$_3$
					21.43	4.011	17	008	β-In$_2$S$_3$
					22.51	3.823	11	200	β-In$_2$S$_3$
					22.63	3.800	7		
					24.98	3.449	3		
26.50	3.255	5	311	α-In$_2$S$_3$	26.51	3.253	30	213	β-In$_2$S$_3$
27.70	3.116	29	222	α-In$_2$S$_3$	27.69	3.118	41	206	β-In$_2$S$_3$
28.65	3.015	3							
					31.13	2.780	4	1,1,10	β-In$_2$S$_3$
					32.07	2.701	12	220	β-In$_2$S$_3$
					34.15	2.541	2	301	β-In$_2$S$_3$
					35.02	2.480	3	303	β-In$_2$S$_3$
					36.65	2.373	4	305	β-In$_2$S$_3$
					37.46	2.323	1	314	β-In$_2$S$_3$
					39.10	2.230	1	307	β-In$_2$S$_3$
					39.64	2.200	4	2,0,12	β-In$_2$S$_3$
42.12	2.076	20	333	α-In$_2$S$_3$	42.11	2.076	39	309	β-In$_2$S$_3$
					43.46	2.015	1	0,0,16	β-In$_2$S$_3$
					45.29	1.938	1		
46.23	1.646	1	533	α-In$_2$S$_3$	46.00	1.909	23	400	β-In$_2$S$_3$
					48.25	1.825	2	143	β-In$_2$S$_3$
					51.11	1.729	1		
					51.89	1.705	1	240	β-In$_2$S$_3$
					52.94	1.674	1		
					53.14	1.668	1	244	β-In$_2$S$_3$
					53.94	1.645	6	419	β-In$_2$S$_3$
					54.65	1.625	1	2,0,18	β-In$_2$S$_3$
57.25	1.557	20	444	α-In$_2$S$_3$	57.23	1.558	35	4,0,12	β-In$_2$S$_3$

temperature of deposition and can be determined from the measurements of the width of the reflexes. According to Sherrer's formula, in the absence of microstress the width B is

$$B = \frac{0.9\lambda}{L\cos\theta} \qquad [2]$$

$B\cos\theta$ should remain constant for several orders of the same reflex. It has been shown that at higher diffraction angles the width of the reflexes increases faster than it takes place for the diffraction from particles of finite size. Such increases in the width can be caused by the microstress in the samples or by splitting reflexes (111) into (111) and (11$\bar{1}$) for the α-phase or (103) into (103) and (10$\bar{3}$) for the β-phase.

TABLE 2
Deposition Conditions, Phase Composition, and Parameters of the Crystal Structure of the Samples

Sample	T_{dep} (°C)	Thickness of film (Å)	Phase comp	$d(5\,5\,5)$ or $d(5\,0\,15)$ (Å)	Coherence size (Å)	Microstress ($\Delta d/d$)
1	230	2500	α-In$_2$S$_3$	1.2442 ± 0.0004	190 ± 13	0.0058 ± 0.0004
2	230	2300	α-In$_2$S$_3$			
3	230, anneal at 430°C	2500	β-In$_2$S$_3$	1.2524 ± 0.0004	260 ± 16	0.0031 ± 0.0002
4	250	1800	β-In$_2$S$_3$	1.2436 ± 0.0004	210 ± 14	0.0042 ± 0.0002
5	370	1300	β-In$_2$S$_3$	1.2444 ± 0.0004	220 ± 14	0.0048 ± 0.0004
6	370	7500	β-In$_2$S$_3$	1.2443 ± 0.0004	290 ± 20	0.0022 ± 0.0002
7	430	2300	β-In$_2$S$_3$	1.2466 ± 0.0004	260 ± 16	0.0061 ± 0.0004
				1.2524 ± 0.0004	240 ± 16	0.0080 ± 0.0004
8	450	3600	β-In$_2$S$_3$			

For the films synthesized at 230–370°C, neither splitting nor asymmetry of the reflexes has been found. Therefore, the increase of the width of the reflexes can be attributed to the microstresses in the samples. When the deposition temperature increases, the coherence size increases and the value of the microstress decreases.

Annealing the samples synthesized at low temperatures leads as well to an increase in the coherence size and to a decrease of microstress. The values of the d spacing between close-packed planes (111) of α-In$_2$S$_3$ (or (103) of β-In$_2$S$_3$) for all samples synthesized at $T = 230$–370°C are close to each other and practically do not depend on the crystal modification, the deposition temperature, or the film thickness. This confirms the conclusion that at higher deposition temperatures ordering of the In atoms in the crystal lattice takes place. The ordering does not change the spacing d but has a strong influence on the electrical conductivity of the films. The electrical resistivity of In$_2$S$_3$ films at room temperature changes from 10^{-1} to $(4$–$5) \times 10^2$ ohm·cm (3) (Fig. 1).

For sample 7 deposited at 430°C, splitting of the reflexes (103) was observed. This splitting is most evident at large angles θ (Fig. 2). In this case the intensities of the reflexes (5,0,15) and (5,0,-15) are not identical. This may be related to the existence of two phases in the film. One phase is tetragonal β-phase indium sulfide and the other is the β-phase with lattice distortion. Similar splitting of the reflexes can be seen for hexagonal or monoclinic structures (13). The increase of the parameter B $\cos\theta$ in the sample due to the microstress can be seen from the reflex splitting as well. At the 430°C deposition temperature both the sizes of the particles and the value of microstress increase. The increase of the microstress may be caused by the lattice distortion which can be seen for this sample.

The investigation of the phase diagram for the system In–S (14) has shown (Fig. 3) that in the range of compositions from InS$_{1.35}$ to InS$_{1.50}$ a continuous row of solid
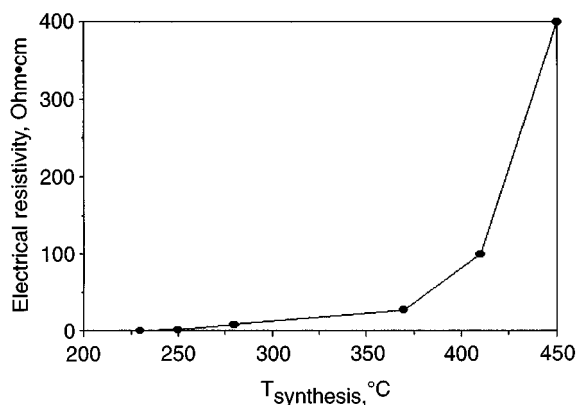

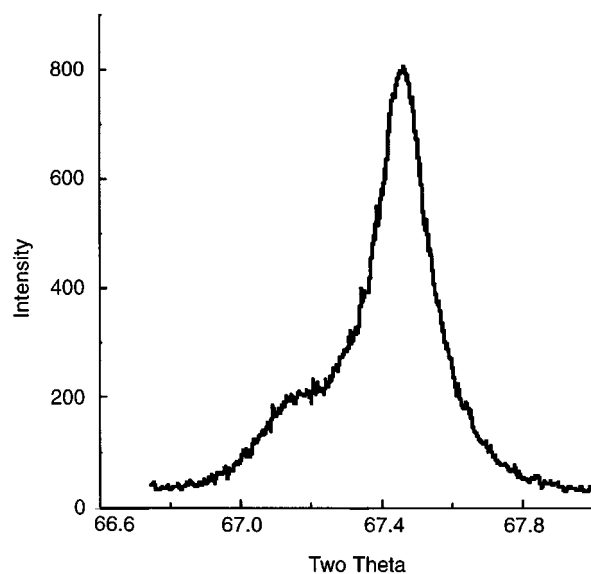**FIG. 2.** Splitting of the reflex (5,0,15) for sample 7 ($\lambda = 1.3845$ Å).

solutions exists with a linear dependence of lattice parameter on the S content. Comparing the lattice parameter $a_0 = 5\sqrt{3}d$ for our samples 1, 2, and 4–6 with the lattice parameter in (14), one may conclude that the S content corresponds to 0.60. This fact verifies that stoichiometric indium sulfide was prepared in our experiments. However, for sample 3, deposited at 230°C and then annealed at 430°C, the d value turns out to be significantly higher. For sample 7 there are two values of d, corresponding to the splitting reflexes. The value $d = 1.2466$ Å is higher than the values of d for samples that were deposited at low temperatures. However, the value $d = 1.2524$ Å overlaps with d for

FIG. 1. Electrical resistivity of In$_2$S$_3$ films at room temperature versus temperature of the synthesis.
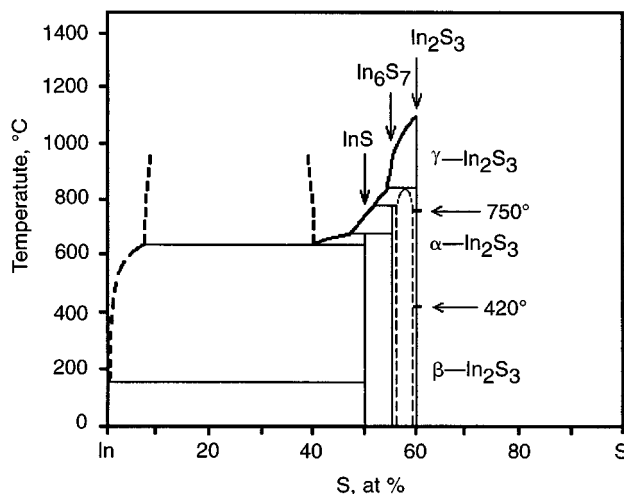

FIG. 3. Phase diagram for the In–S system.

sample 3. It has been shown (10, 14) that the lattice para-meter a_0 for the cubic (or c ($c = 3a_0$) for the tetragonal) modification of In_2S_3 increases with an increase in the sulfur content of the sample. According to this observation, it is possible to assume that for samples deposited at 430°C the sulfur content is higher. However, this assump-tion does not agree with the data for sample 3, which was annealed under vacuum and for which the parameter d in-creased as well, because annealing under vacuum should lead to a loss of sulfur or stoichiometric evaporation of the In_2S_3 (8).

From our point of view the increase of the spacing d and consequently the increase of the lattice parameter can be explained by the changes in the crystal structure of the samples that are connected with the $\beta\text{-}In_2S_3 \rightarrow \alpha\text{-}In_2S_3$ phase transition which starts at 420°C (6). At this temper-ature, the cooperative movement of the tetrahedral indium atoms over neighboring tetrahedral sites just begins. As a result of this movement there is a shift of the sulfur layers (15). The value of this shift exceeds the changes in Δd corresponding to the microstress. There are anomalies in DTA and electrical conductivity dependencies for $\beta\text{-}In_2S_3$ crystals at the same temperature (15). According to our data, the appreciable increase of the electrical resisitvity of the samples which begins at $T = 400°C$ can be explained as the beginning of the phase transition. At $T = 420°C$ this pro-cess is going much faster. For sample 3, which was annealed at 430°C and cooled to room temperature at the rate of 9 grad/min, the crystal structure corresponds to $\beta\text{-}In_2S_3$ with the increased lattice parameters.

The splitting of the reflexes (5, 0, 15) for In_2S_3 has been observed for the first time. The reason for this splitting is not clear at present. The effect has not been observed for the annealed sample. This leads us to conclude that the splitting is connected with the specifics of the growth processes at this temperature.

The data of the present work on the phase compositions of the In_2S_3 films obtained by the CVD method at different temperatures are in agreement with other experimental re-sults. Several methods of indium sulfide fabrication have been described in the literature. The main difference in the methods consists in the temperature of the process. As a rule, it is possible to obtain $\alpha\text{-}In_2S_3$ only in a low-temper-ature process, for example, by precipitation of an indium salt solution and H_2S (7). Samples of $\alpha\text{-}In_2S_3$ irreversibly transform into $\beta\text{-}In_2S_3$ by heating at temperatures above 350°C. The other methods of fabrication (for example from the melt or from the gas phase) are performed at temper-atures $T > 450°C$, and as a result the $\beta\text{-}In_2S_3$ phase is always obtained after cooling to room temperature. An important factor that determines the phase state of the sample is stoichiometry. For example, it was shown in ref 6 that the $\alpha\text{-}In_2S_3$ phase can be stable at room temperature only if there is a lack of sulfur.

The results on the fabrication of $\alpha\text{-}In_2S_3$ at the relatively low temperature $T = 230°C$ using the method described herein are in agreement with data for powders (7) and for films (11). Low diffusive mobility of the components of the material at this temperature leads to a nonordered distribu-tion of the indium vacancies. Thus, $\alpha\text{-}In_2S_3$ was prepared. This phase is not in thermodynamic equilibrium at these low temperatures. A small increase in the deposition tem-perature up to 250°C leads to $\beta\text{-}In_2S_3$. It has been shown in this work that the $\alpha\text{-}In_2S_3$ phase can be transformed into the $\beta\text{-}In_2S_3$ phase by sample annealing under vacuum at tem-peratures $T > 400°C$.

CONCLUSIONS

Phase analysis of the In_2S_3 films deposited by the CVD method from volatile complex compounds has been per-formed using the diffraction of the synchrotron irradiation. It has been shown that the films obtained at $T = 230°C$ crystallize as cubic $\alpha\text{-}In_2S_3$. At the deposition temperature $T = 250°C$ and higher, the films crystallized in the tetrag-onal β-phase. The annealing of the films synthesized at 230°C leads to $\beta\text{-}In_2S_3$ phase formation as well. The size of the particles (coherent size) increases as the deposition tem-perature increases. The values of the interplanar spacing d for close-packed planes are similar to each other for all samples deposited at temperatures $T = 230\text{–}370°C$ and practically do not depend on the crystal modification, the deposition temperature, and the thickness of the samples.

By calculation of the width of the reflexes the values of microstresses have been determined. It has been shown that microstresses decrease after annealing or for higher depos-ition temperatures (up to 370°C). For the sample deposited at 430°C, a splitting of the reflex (5, 0, 15) has been observed, which can be explained as a monoclinic or hexagonal distor-tion of $\beta\text{-}In_2S_3$.

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