

Structural and Electrical Properties of Annealed In–Bi₂S₃ Thin Films

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Received August 20, 1996; in revised form January 29, 1998; accepted February 2, 1998

Intrinsic bismuth sulfide deposited on indium thin films (~ 20 nm) change to *n*-type when annealed in air or nitrogen atmosphere. As deposited bismuth sulfide on the In films is amorphous and electrically very resistive. Annealing the films in air at 200, 300, and 400°C results in the formation of In₂O₃ as observed in the X-ray diffraction patterns of the films. The dark conductivity of the In + bismuth sulfide films nitrogen-annealed at 300°C attains a value of $600 \Omega^{-1} \text{cm}^{-1}$, which is an improvement by more than eight orders of magnitude compared with as-prepared films. This improvement is attributed to amorphous–crystalline transformation and the presence of metallic bismuth and In₂O₃ in the annealed films. An etching test in 1 M solution of HCl indicates that these films are rather stable in acid medium. © 1998 Academic Press

INTRODUCTION

In earlier papers from our laboratory, we reported on the photoconductivity and optical properties of chemically deposited bismuth sulfide thin films (1, 2) and their application in an imaging technique—metal sulfide thin film photography (3). The interest in these films arises mainly from their suitability for photovoltaic conversion of solar energy (4–6), owing to the relatively high conversion efficiency predicted by the Price-Loferski diagrams for the optical band gap of 1.45 eV of bismuth sulfide, Bi₂S₃ (7). The conversion of chemically deposited thin films, which are of intrinsic conductivity (1), to *n*-type is an important aspect of investigation toward the realization of such applications.

In the present work we report on the structural, electrical, and optical properties of composite thin films consisting of indium oxide, bismuth sulfide, and metallic bismuth. These films are produced by annealing at 300°C (in air or nitrogen) of bismuth sulfide thin films deposited from a chemical bath over glass substrates coated with thermally evaporated indium thin films. This approach of combining a chemically deposited semiconductor thin film with evaporated In film

has been suggested by the recent reports on the improved electrical conductivities obtained in composite films of CdS:In–In₂O₃ and CdSe:In–In₂O₃ produced by annealing of CdS–In (8) and CdSe–In (9) films. In the present case, the use of indium film on the glass substrate prior to deposition of the bismuth sulfide film (rather than over the semiconductor thin film as reported in (8) and (9)) was found to prevent the peeling of bismuth sulfide thin films (1) from glass substrates at intermediate film thicknesses (150 nm).

EXPERIMENTAL DETAILS

Two kinds of thin films samples were prepared in the present case: (i) bismuth sulfide thin films directly deposited on glass substrates following the procedure reported in (1) (described as Bi₂S₃ thin films); and (ii) bismuth sulfide thin films deposited on a glass substrate coated with an indium thin film (described as In + Bi₂S₃ thin films). For case (ii), indium thin films of about 20 nm thickness of indium were deposited on microscope glass slides by evaporating indium of 99.999% purity (Alfa Products) in a vacuum chamber evacuated to 10^{-6} Torr. We noticed that indium coatings are stable in the chemical bath for bismuth sulfide thin films.

Prior to the deposition of the films (In or Bi₂S₃), the glass substrates (75 × 25 × 1 mm) were immersed in sulfuric acid for 24 h to remove organic compounds and were subsequently washed in a solution of commercial detergent powder, rinsed in deionized water, and dried. The chemical bath for the deposition of bismuth sulfide thin films in both cases was prepared by mixing 10 ml of 0.5 M [Bi(TEA)_n]³⁺ (prepared by dissolving 24.25 g of Bi(NO₃)₃ · 5H₂O in 70 ml of 3.7 M triethanolamine and taken to 100 ml), 10 ml of 3.7 M of TEA, and 4 ml of 1 M thioacetamide, and adjusting the volume to 100 ml with deionized water. Baker Analyzed Reagents were used in this work. The bismuth sulfide films were deposited for 20 h at room temperature (20–25°C) in both cases. After the deposition, these films were washed in deionized water and dried in hot air. The films were annealed at 200, 300 and 400°C for 1 h each in air and at

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300–400°C in nitrogen at atmospheric pressure in a tubular furnace.

Dark and photocurrent measurements of the films were made using a Keithley 619 multimeter and a Keithley 230 programmable voltage source. For this, coplanar silver print electrodes (5 mm long, 5 mm separation) were painted over the film surface after performing the heat treatment mentioned above. A 250 W tungsten-halogen lamp was used as the illumination source, which produced at the plane of the film an intensity of illumination of 2000 W m⁻². The applied bias was in the 0.1–10 V range, so that current level was in the nA–μA range for the more resistive films (bismuth sulfide and In + bismuth sulfide as-prepared) and did not exceed the mA range in the less resistive films (In + bismuth sulfide annealed in nitrogen atmosphere). The sheet resistance was calculated for each film.

X-ray diffraction (XRD) patterns of the films were recorded on a Siemens D 500 system using CuK α radiation. The diffraction patterns of the films showed the XRD peaks superimposed on the background pattern of the glass substrate. This background was subtracted from the total spectra in most cases to prepare the figures. A Siemens SRS 300 X-ray fluorescence (XRF) spectrometer was used to confirm the presence of indium in the films. The XRF spectra were recorded using a LiF crystal (110), (2d = 0.2848 nm) for Bi-L _{α 1} fluorescence line ($2\theta = 47.36^\circ$), a LiF crystal (100), (2d = 0.4027 nm) for In-L _{α 1} fluorescence line ($2\theta = 139^\circ$), and a Pentaerythrite crystal (2d = 0.8742 nm) for S-K _{α 1,2} fluorescence line ($2\theta = 75.85^\circ$).

Optical transmittance spectra of the films were recorded on a Shimadzu UV-VIS-NIR 3101 PC Spectrophotometer.

Film thickness was determined using Alpha-Step 100 step thickness measuring equipment (Tencore Instruments, USA). It was found to be $(0.18 \pm 0.02) \mu\text{m}$ for the films deposited on the In-coated glass substrates or directly on the glass substrates.

RESULTS AND DISCUSSION

Structural analysis. Figure 1 shows the XRD patterns of bismuth sulfide films deposited directly on glass substrates and annealed at various temperatures in air. The as-prepared film is predominantly amorphous. Annealing at 200 and 300°C brings about crystallinity in the film with grain size of bismuthinite of 210 and 240 Å respectively, as calculated using the Scherrer formula (12). The patterns exhibit good agreement with the standard Bi₂S₃ (bismuthinite) XRD pattern. XRD patterns of the air-annealed films at 300°C suggest that there is a partial conversion of the material into metallic bismuth. Air-annealing at 400°C results in the formation of bismuth oxide sulfates, which leads to deterioration of electrical conductivity of the film as discussed later. These results are in accordance with earlier findings (2).

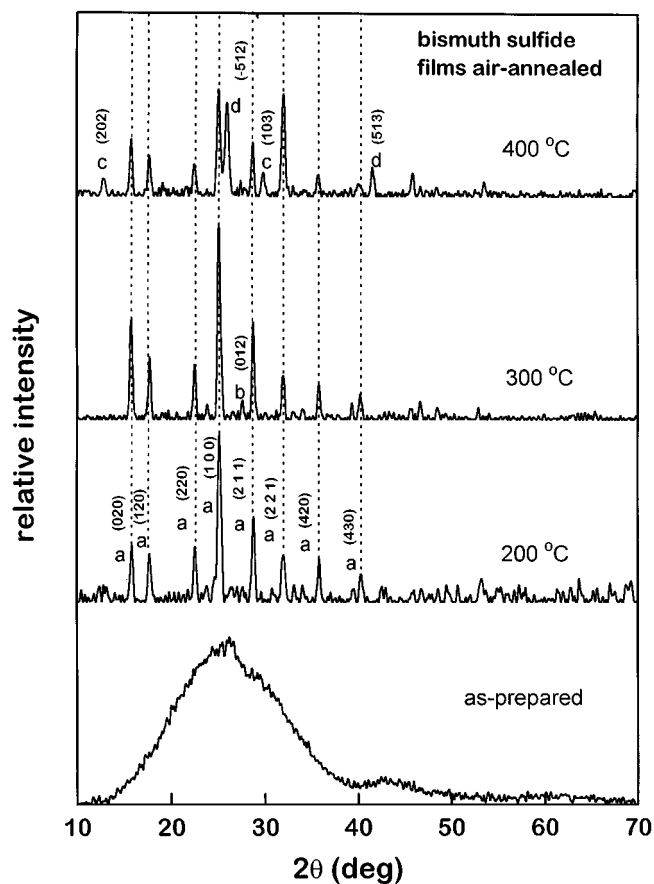


FIG. 1. X-ray diffraction patterns (CuK α) of bismuth sulfide films as prepared and air-annealed at 200–400°C. The presence of metallic Bi is noted in the film annealed at 300°C. (a) Bi₂S₃ (bismuthinite, JCPDS 17-0320); (b) metallic Bi (JCPDS 5-0519); (c) bismuth oxide sulfate (JCPDS 41-0688); (d) bismuth oxide sulfate (JCPDS 41-0687).

Figure 2 shows the XRD patterns of In + bismuth sulfide thin films subjected to the same annealing conditions as the bismuth sulfide films given in Fig. 1. The XRD pattern of the as-prepared indium film (20 nm), which served as the substrate film for deposition of the bismuth sulfide film, is also given. This pattern shows the peaks due to metallic indium at $2\theta \cong 33^\circ$ for (101) planes and $2\theta \cong 69^\circ$ for (202) planes. The same peaks are observed in the as-prepared In + bismuth sulfide film. Air-annealing of this film at 200°C results in the formation of In₂O₃ with XRD peak positions at $2\theta \cong 30.6^\circ$ for (222) planes and leads to the partial crystallization of the bismuth sulfide thin film, producing peaks corresponding to Bi₂S₃ (previous works indicate that such transitions are possible in bismuth sulfide films (10)). The continued presence of metallic indium is, however, noted. Annealing of the film in air at 300°C leads to the disappearance of the peaks corresponding to metallic indium at $2\theta \cong 33^\circ$ and $2\theta \cong 69^\circ$. The pattern is now dominated by the In₂O₃ (222) peak. Additionally, in the XRD pattern of

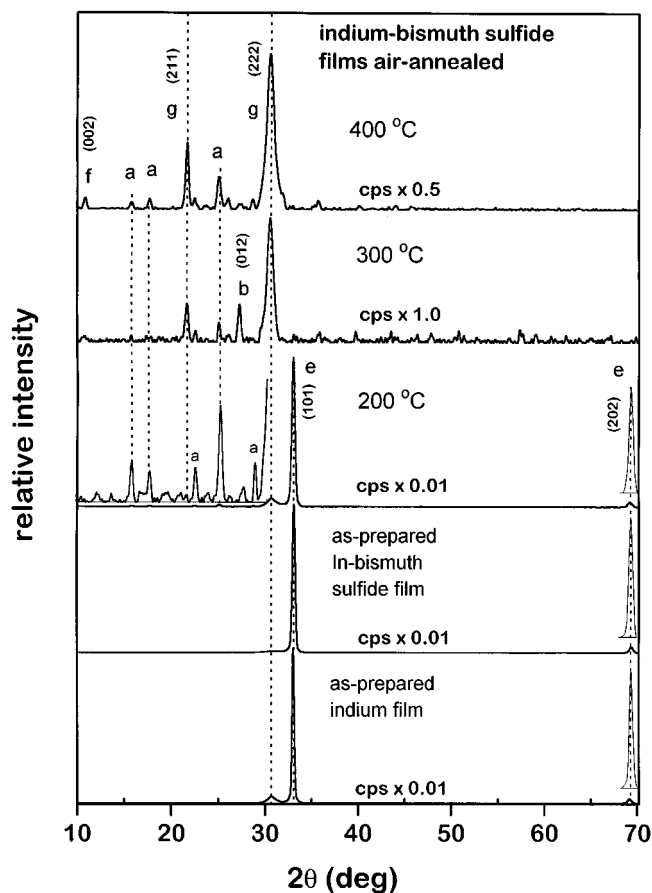


FIG. 2. X-ray diffraction patterns ($\text{CuK}\alpha$) of metallic In and In + Bismuth sulfide as prepared and air-annealed at 200–400°C. (e) metallic In (JCPDS 5-0642); (f) In_6S_7 (JCPDS 19-0587); (g) In_2O_3 (JCPDS 6-0416).

this sample, the (211) peak of In_2O_3 at $2\theta \cong 21.5^\circ$ and the (012) peak of metallic bismuth at $2\theta \cong 27.2^\circ$ are well noted. The relative intensity of the peak of metallic bismuth in In + bismuth sulfide films (compare Figs. 1 and 2 at 300°C) increases, while its grain size diminishes as shown in Table 1.

The indium oxide ((211) and (222) reflections) in the In + bismuth sulfide film (see Fig. 2 at 200–400°C) increases, as does grain size, (see Table 2). In the films annealed at 400°C, the presence of In_2O_3 and bismuth sulfide is clearly noted. The peak at $2\theta \cong 11^\circ$, which appears in the film annealed at 300°C and becomes more pronounced in the film annealed at 400°C, may be considered an indication of the formation of In_6S_7 .

The presence of the In_2O_3 peaks in the annealed films indicates that metallic indium from the substrate diffuses to the surface on annealing and reacts with the available oxygen at the intergrain region of the bismuth sulfide film and from the atmosphere, forming small crystallites of In_3O_3 with grain size $\sim 70\text{--}155 \text{ \AA}$ (see Table 2).

Films of bismuth sulfide and In + bismuth sulfide were nitrogen-annealed at 300°C with the expectation that the electrical properties of the films would be enhanced by preventing any degradation of bismuth sulfide film due to reaction with atmospheric oxygen. However, the dominant effect observed was an increase in the relative concentration of metallic bismuth compared to air-annealed films (Figs. 1 and 2). Figure 3 shows XRD patterns of bismuth sulfide and In + bismuth sulfide films annealed under nitrogen atmosphere. The peak intensity corresponding to metallic bismuth in In + bismuth sulfide film is higher than the peak intensity of metallic bismuth in bismuth sulfide film, while the grains of metallic bismuth in both films have almost the same size (170 Å). This result suggests that metallic bismuth is more developed in the In + bismuth sulfide film. In the case of bismuth sulfide film there is also the formation of sulfur, with a peak located at $2\theta \cong 26^\circ$ for (130), (212) reflections.

Figure 4 shows X-ray fluorescence (XRF) data on the relative intensity of bismuth, indium, and sulfur in the as-prepared and annealed In + bismuth sulfide films. XRF analysis demonstrates that the annealing process (up to 400°C) does not cause depletion of indium in the material. The reason the XRF signals for indium are weaker in the

TABLE 1
Grain Size of Metallic Bismuth Calculated Using the Scherrer Formula (12) for Various Bismuth Sulfide Films with the (012) Reflection Located at $2\theta \cong 27.3^\circ$

Films annealed at 300°C		Grain size of metallic bismuth (Å)	Relative intensities						
			(020)	(220)	Bi_2S_3 (%) (100)	(211)	(420)	$\text{Bi}/\text{Bi}_2\text{S}_3$ (012)/(100)	$\text{Bi}/\text{In}_2\text{O}_3$ (012)/(222)
Bi_2S_3	air	210	50	30	100	40	20	0.1	—
Bi_2S_3	N_2	170	40	0	100	30	10	0.3	—
In + Bi_2S_3	air	170	6	50	100	0	25	—	0.2
In + Bi_2S_3	N_2	160	0	0	0	0	0	—	0.8

Note. The relative peak intensities $\text{Bi}(012)/\text{Bi}_2\text{S}_3$ (100) and $\text{Bi}(012)/\text{In}_2\text{O}_3$ (222) have been estimated by assigning 100% peak intensity to Bi_2S_3 (100) reflection and In_2O_3 (222) reflection.

TABLE 2

Average Grain Size of Indium Oxide Calculated Using the Scherrer Formula (12) for Air-Annealed In + Bismuth Sulfide Films with the (211) and (222) Reflections Located at $2\theta \cong 21.5^\circ$ and $2\theta \cong 30.6^\circ$, Respectively, and Relative Intensities of Bi₂S₃ and In₂O₃

In-Bi ₂ S ₃ films air-annealed (°C)	Grain size of indium oxide (Å)	Relative intensities (%)						
		(020)	(220)	Bi ₂ S ₃			In ₂ O ₃	
				(100)	(211)	(420)	(211)	(222)
200	70	30	20	100	16	0	0	100
300	140	6	50	100	0	25	20	100
400	155	20	30	100	30	20	20	100

case of the as-prepared films may be the partial absorption, by bismuth atoms in the top layer of bismuth sulfide, of the X-ray fluorescence emission of L_{α1} radiation from indium at $2\theta = 139.0^\circ$ (for LiF (100) planes), corresponding to an energy of 3.28694 keV. For example, the combined energy of the transitions M_{III}O_{IV,V} (3.153 keV.) and N_{VII}O_V (0.133 keV.) is 3.286 keV (11) and hence, a partial absorption of In-L_{α1} fluorescence radiation in the bismuth atoms may be considered possible. XRF data on the films obtained after annealing at 300 and 400°C show an apparent loss of bismuth and sulfur in the films. This may be explained as absorption of the XRF emission from bismuth and sulfur by the indium in the In₂O₃ layer formed over the film, as mentioned above.

Optical transmittance spectra. Figure 5a shows optical transmittance curves of bismuth sulfide thin films recorded in as-prepared films and air-annealed films at 200–400°C.

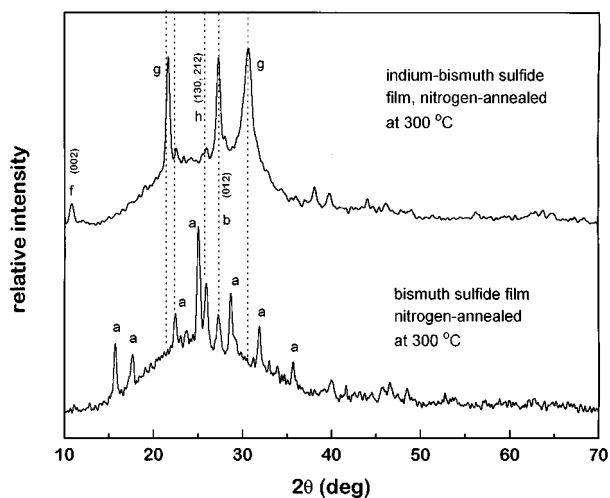


FIG. 3. X-ray diffraction patterns (CuK α) of bismuth sulfide and In + bismuth sulfide films nitrogen-annealed at 300°C. Higher relative presence of metallic bismuth is noted in the In + bismuth sulfide film, while in the bismuth sulfide film the presence of metallic bismuth and sulfur is seen. (h) sulfur (JCPDS 34-0941).

The absorption edge shifts to higher wavelengths in the case of annealed films. This effect could be related to the grain size increase of the crystallites of bismuthinite. Note that the film annealed at 400°C has undergone partial chemical decomposition (see Fig. 1) to bismuth oxide sulfates.

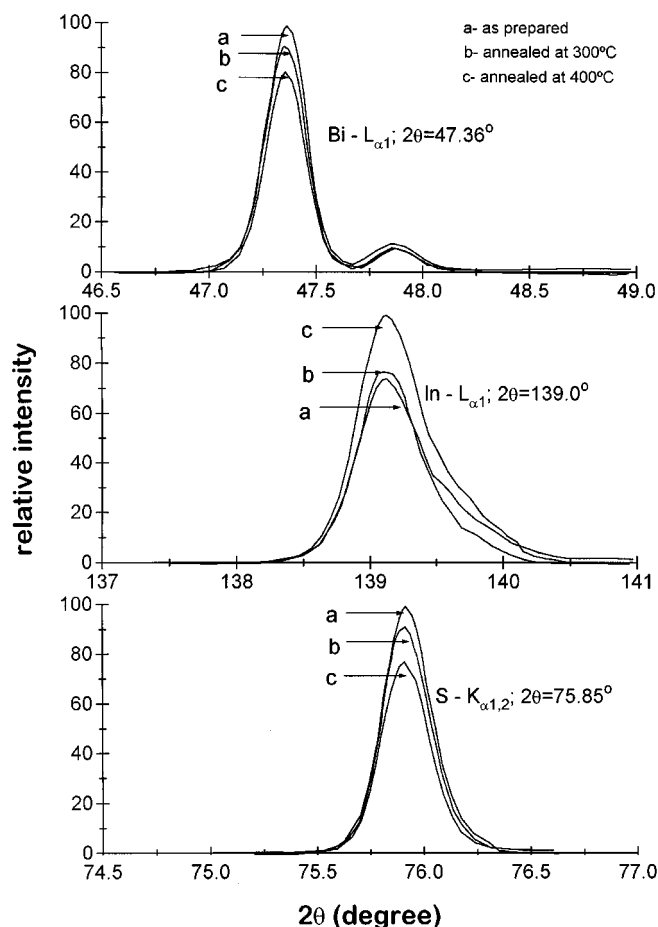


FIG. 4. X-ray fluorescence patterns of In + bismuth sulfide thin films: (a) as prepared and (b) annealed in air at 300°C; and (c) at 400°C.

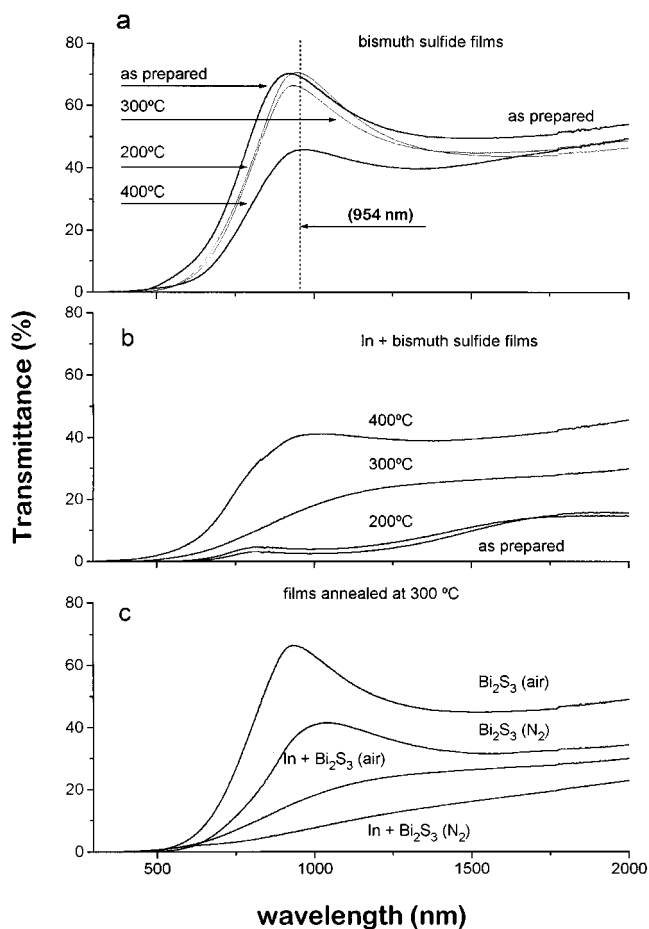


FIG. 5. Optical transmittance ($T\%$) spectra of the (a) bismuth sulfide and (b) In + bismuth sulfide films air-annealed at 200–400°C, and (c) films annealed in nitrogen at 300°C.

The optical transmittance of In + bismuth sulfide films, as-prepared as well as air-annealed, is shown in Fig. 5b. The as-prepared In + bismuth sulfide film is nearly opaque due to the underlying indium film. The annealing process of these films at 200°C for one hour does not change the optical transmittance too much because temperature and annealing–time were not great enough to induce chemical reactions between metallic indium and oxygen. Metallic indium can still be seen in the film after annealing at 200°C for one hour (see Fig. 2). A temperature increase from 200 to 400°C leads to the diffusion and reaction of indium with oxygen present at the intergrain region of the bismuth sulfide film and from the atmosphere to form transparent crystallites of In₂O₃. These indium oxide crystallites in the bulk of the composite layer increase the transparency of the films.

The optical transmittance of the bismuth sulfide and In + bismuth sulfide films air-annealed and nitrogen-annealed at 300°C is shown in Fig. 5c. It is seen that a higher optical transmittance is achieved during air-annealing of

In + Bi₂S₃ films, as compared to that obtained during nitrogen annealing, due to the reduced formation of metallic bismuth (Figs. 2 and 3). In the case of bismuth sulfide films annealed in nitrogen as well, the formation of metallic bismuth is promoted (Fig. 3), which leads to higher electrical conductivity and a lower optical transmittance, as compared to air-annealed film.

Photoconductivity. Figure 6a shows the sheet resistance of bismuth sulfide thin films obtained from the dark and photocurrent response curves. The sheet resistance of the as-prepared film under the illumination is one order lower than that in the dark. In annealed films, the difference in dark and photocurrent is not significant. Annealing the films in air improved the electrical conductivity to $\sim 10^{-3} \Omega^{-1} \text{cm}^{-1}$, corresponding a reduction in sheet resistance.

The improvement in the conductivity is substantial in the case of the In + bismuth sulfide films annealed in air (Fig. 6b), as compared to annealed bismuth sulfide films (Fig. 6a). Photocurrent and dark current in these films keep

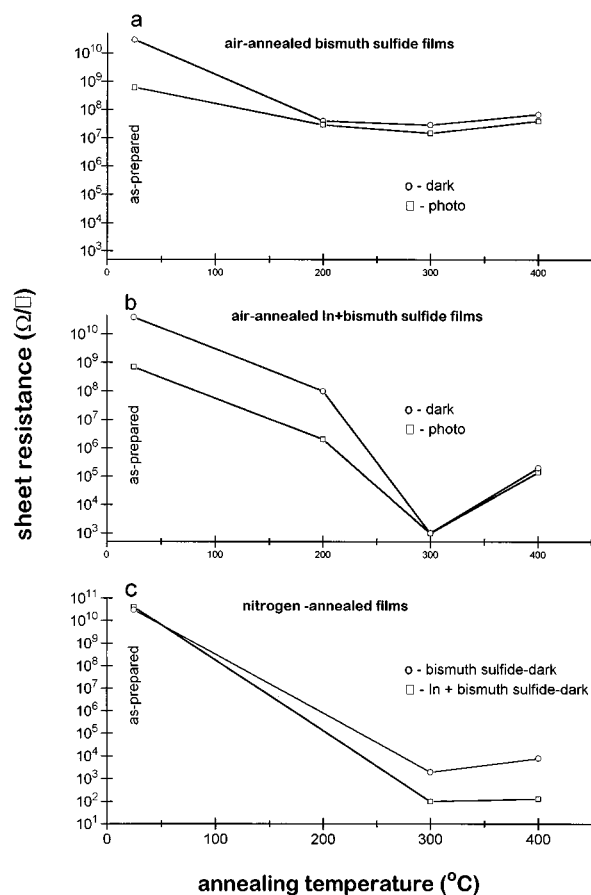


FIG. 6. (a) Sheet resistance of bismuth sulfide films air-annealed at various temperatures; (b) sheet resistance of In + bismuth sulfide films air-annealed under the same conditions; and (c) sheet resistance of the bismuth sulfide and In + bismuth sulfide films nitrogen-annealed at various temperatures.

the same trend with annealing as the bismuth sulfide films. Changes in the electrical conductivity must be attributed to structural and compositional modifications in the bismuth sulfide. The sheet resistance of this composite film is about 900 Ω/\square after annealing at 300°C due to the presence of metallic bismuth, indium oxide, and indium sulfide, as illustrated in Fig. 2.

Figure 6c shows that nitrogen-annealing improves the electrical conductivity of bismuth sulfide films by more than three orders of magnitude compared with air-annealed film (Fig. 6a). At annealing temperature 300°C, the sheet resistance for the nitrogen-annealed bismuth sulfide film is 2.5 k Ω/\square , which for film thickness 0.15 μm , indicates an electrical conductivity of 25 $\Omega^{-1}\text{cm}^{-1}$.

In the case of In + bismuth sulfide films, the sheet resistance attained on annealing at 300°C in nitrogen is about 90 Ω/\square , which for film thickness 0.18 μm of the composite film (see Fig. 3) suggests an overall electrical conductivity of nearly 600 $\Omega^{-1}\text{cm}^{-1}$.

A hot probe thermoelectric test showed *n*-type conductivity for air-annealed and nitrogen-annealed bismuth sulfide and In + bismuth sulfide thin films. The *n*-type conductivity is expected in these films from compositions of the type Bi₂S₃ + Bi, in the case of bismuth sulfide films, and Bi₂S₃ + Bi + In₂O₃ in the case of annealed In + bismuth sulfide films. The separation of metallic phase (Bi) as well as the usual presence of nonstoichiometric Bi₂S_{3-x} and In₂O_{3-y} are known to give rise to electrical conductivity dominated by electrons.

Figure 7 shows the relative stability of the electrical properties of the films air annealed and nitrogen annealed at 300°C, which were immersed in a solution of 1 M HCl. Their sheet resistance was determined as a function of etching time in the solution. The stability of the films may be attributed to the presence of indium oxide (Figs. 2 and 3),

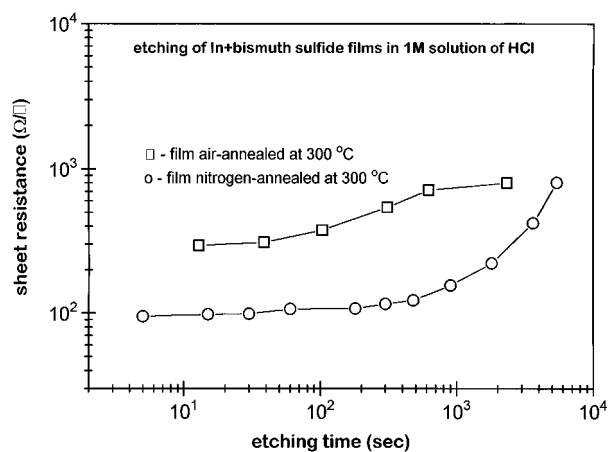


FIG. 7. Chemical stability for sheet resistance vs etching time of the air-annealed and nitrogen-annealed (300°C, 1 h) In + bismuth sulfide films in 1 M solution of HCl.

a component of the composite film that covers the bismuth sulfide and metallic bismuth grains.

CONCLUSIONS

In the present work, we reported the feasibility of depositing bismuth sulfide thin films on indium coated glass substrates. The primary intention of this work was to identify a deposition technique for bismuth sulfide thin films without the occasional risk of the film peeling from glass substrates under certain deposition conditions. In addition, we observed interesting changes in the structure and composition and the electrical and optical properties of these (In + bismuth sulfide) films compared with bismuth sulfide films, when subjected to annealing.

Changes in the structure of bismuth sulfide films from amorphous to crystalline phase and the formation of other compounds with indium were established on the basis of XRD and XRF analyses. Results of the electrical conductivity of the films presented here showed that the presence of indium prevents the degradation of bismuth sulfide when the samples are annealed in air through the formation of surface and intergrain layers of In₂O₃. There is evidence for the reaction of indium with sulfur ions of the bismuthinite producing In₆S₇ and the reduction of bismuth cations to metallic bismuth: $\text{Bi}^{3+} + 3\text{e}^- \rightarrow \text{Bi}$.

The most notable feature of the composite film resulting from annealing In + bismuth sulfide film is the increase in its electrical conductivity by a factor of more than eight orders of magnitude (nitrogen annealing at 300 or 400°C). The films are reasonably stable in an acid medium, suggesting possible application of the films in photoelectrochemical solar cells (6). Application of the films in solid state solar cells may also be a possibility. The present work supplements earlier results on chemically deposited CdS + In and CdSe + In films (8, 9), suggesting that the chemical deposition technique may be combined with thermal evaporation of metallic films to produce coatings with interesting electrical properties.

ACKNOWLEDGMENTS

The authors are grateful to Oscar Gomez-Daza and José Campos for assistance in the experimental work and to CONACYT México for financial support.

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