NOTES Bull. Chem. Soc. Jpn., 62, 939—941 (1989)

Preparation of Bismuth Sulfide Thin Films by Solution Pyrolysis of Bismuth Dithiocarbamate Complexes

Ryoki NOMURA,* Kouichi KANAYA, and Haruo MATSUDA
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamada-Oka, Suita, Osaka 565

(Received October 8, 1988)

Synopsis. Solution pyrolysis of $\mathrm{Bi(S_2CNRR')_3}$ in *p*-xylene or chloroform on a glass substrate at 350 °C under Ar atmosphere gave polycrystalline and low resistive ($10^2\ \Omega$ cm in dark) bismuth sulfide thin films which showed large photoelectric effect.

Bismuth sulfide ($\mathrm{Bi_2S_3}$) is the direct band gap material with E_g of 1.3 eV[1] and useful for photodiode arrays or photovoltaics.[2,3] Preparation of photoconducting $\mathrm{Bi_2S_3}$ thin layers has so far been limited to the physical methods such as vacuum evaporation[4] or sintering.[5] However, to develop the chemical thin film process has been considered to be indispensable to produce large area chalcogenide layers in low cost.[6,7] Thus, some chemical processes such as dip-dry method,[2] chemical liquid deposition (CLD)[7,8] and solution-gas interface technique[9] have already examined, but they generally supplied highly resistive and amorphous $\mathrm{Bi_2S_3}$ films. Recently, we have reported the preparation of several polycrystalline oxide or sulfide thin films via a "solution pyrolysis" technique (printing method) using organometallics[10] and/or metal dithiocarbamate complexes.[11] The printing method is the most convenient procedure for the preparation of thin layers,[11] however, the method remains unemployable state yet bacause of a lack of suitable precursor compounds for $\mathrm{Bi_2S_3}$ layers. Therefore we attempted to prepare $\mathrm{Bi_2S_3}$ films via the solution pyrolysis using bismuth dithiocarbamate complexes ($\mathrm{Bi(S_2CNRR')_3}$) on the basis of their thermal analysis data.

Experimental

General. Characterization of the obtained bismuth sulfide films were performed with a Rigaku Rota-flex X-ray diffractometer (Cu *Kα*, 40 kV), a Shimadzu ESCA 650B, a Hitachi S-405 type scanning electron microscope (SEM), and a Shimadzu UV-200S spectrophotometer. Resistivity was measured by means of four probe method using a Tycoon 841 type apparatus. Thermal analysis of the bismuth dithiocarbamate complexes was done with a SEIKO TG/DTA 20 type thermal analyzer. Commercial bismuth(III) oxide (Mitsuwa, purity >99.9%) was used without purification. Other reagents and solvents were used after distillation.

Preparation of $\mathrm{Bi(S_2CNRR')_3}$. Preparation of $\mathrm{Bi(S_2CNRR')_3}$ was conducted with the procedure reported previously.[12] Into a suspension of $\mathrm{Bi_2O_3}$ (6 mmol) in methanol (20 ml), carbon disulfide (50 mmol), and amines (40 mmol) were added dropwise in this order. The mixture was stirred for 19—48 h at room temperature and the resulting yellow precipitates were recrystallized from methanol or chloroform. **$\mathrm{Bi(S_2CNEt_2)_3}$:** Mp 194—196 °C (lit,[13] 194—195 °C); IR (KBr) 1490 cm^{-1}. **$\mathrm{Bi(S_2CNBu^n{}_2)_3}$:** Mp 98—99 °C; IR (KBr) 1480 cm^{-1}; Found: C, 39.42; H, 6.60; N, 5.11; S, 23.42%. Calcd for $\mathrm{C_{27}H_{54}BiN_3S_6}$: C, 39.45; H, 6.62; Bi, 25.42; N, 5.11; S, 23.40%. **$\mathrm{Bi(S_2CNHex^n{}_2)_3}$:** Mp 80—81 °C; IR (KBr) 1480 cm^{-1}; Found: C, 45.31; H, 8.24; N, 4.38; S, 20.10%. Calcd for $\mathrm{C_{36}H_{78}BiN_3S_6}$: C, 45.30; H, 8.24; Bi, 21.90; N, 4.40; S, 20.16%. **$\mathrm{Bi(S_2CNHBu^i)_3}$:** Mp 140 °C (decomp); IR (KBr) 1510 cm^{-1}; Found: C, 27.47; H, 4.45; N, 6.26; S, 29.03%. Calcd for $\mathrm{C_{15}H_{30}BiN_3S_6}$: C, 27.55; H, 4.63; Bi, 31.96; N, 6.43; S, 29.43%.

Preparation of Bismuth Sulfide Films by Solution Pyrolysis Method. A detailed technique for the solution pyrolysis was reported previously.[10,11] About a 100 μl of 10 wt-% solution of $\mathrm{Bi(S_2CNRR')_3}$ in the prescribed solvent was dropped onto a glass substrate (IWAKI Code 2926 WSLID-P, 76×26 mm) and spread over the whole surface by tipping. Thus the substrate was heated in a quartz tube under Ar atmosphere. A heating sequence was as follows: 1) 100 °C for 1 h, 2) cooling to room temperature, 3) 250—350 °C for 1 h. Chloroform and *p*-xylene were selected as the solvents for $\mathrm{Bi(S_2CNEt_2)_3}$ and for $\mathrm{Bi(S_2CNBu^n{}_2)_3}$ and $\mathrm{Bi(S_2CNHex^n{}_2)_3}$, respectively.

Results and Discussion

We first investigated on the thermal properties of $\mathrm{(BiS_2CNRR')_3}$, in order to optimize the process for

Table 1. Thermal Analysis Data of Bismuth Dithiocarbamate[a)]

Compound	TG			DTA
	Weight loss		%-weight loss (calcd)[b)]	
	Start/°C	End/°C		Endothermic peak[c)]/°C
$\mathrm{Bi(S_2CNEt_2)_3}$	248	350	60.0 (60.7)	$\underline{192}$, 328
$\mathrm{Bi(S_2CNBu^n{}_2)_3}$	262	348	67.5 (68.7)	$\underline{99}$, 317
$\mathrm{Bi(S_2CNHex^n{}_2)_3}$	266	346	76.0 (72.9)	$\underline{79}$, 313
$\mathrm{Bi(S_2CNHBu^i)_3}$	100	218	55.6 (60.7)	146

a) Conditions: instrument, SEIKO TG/DTA 20; $\mathrm{N_2}$ flow; heating program, 10 °C min^{-1}, rt—500 °C. b) Values of total %-weight loss are presented. Calcd means the weight loss to give $\mathrm{Bi_2S_3}$ and is indicated in the parentheses. c) Underlined temperatures showed the melting points.

preparation of Bi_2S_3 films, and the results are summarized in Table 1. It was found that the $Bi(S_2CNRR')_3$ employed here decomposed with endotherms. Three dialkyl derivatives decomposed at around 310—330 °C and gave Bi_2S_3 powders quantitatively till 350 °C. While $Bi(S_2CNHBu^i)_3$ decomposed at ca. 150 °C and also gave Bi_2S_3 powders. Although $Bi(S_2CNHBu^i)_3$ seemed to be a more suitable precursor for the preparation of Bi_2S_3 only from its decomposition temperature, it decomposed with a significant degree of vaporization, and its solubility was too low to use in the solution pyrolysis. Therefore, we investigated to prepare Bi_2S_3 films using the dialkyldithiocarbamate complexes.

If the solution on the substrate was directly heated at the pyrolysis temperatures (250—350 °C), only Bi_2S_3 powders deposited and no film was obtained. While, a "preheating" at 100 °C for 1 h which preceded the calcination was found to be effective to inhibit the formation of powders and the two step heating process gave smooth and homogeneous thin layers. In the following discussion, the term "temperature" will indicate the second step temperature.

The X-ray diffraction patterns of the obtained films are displayed in Fig. 1. The intensities of the diffraction peaks increased with temperature rising from 250 to 350 °C. The Bi_2S_3 films obtained from $Bi(S_2CNBu^n{}_2)_3$ at 350 °C possessed the polycrystalline texture as shown in Fig. 2. The surface morphology of this film rather resembled the vacuum-evaporated Bi_2S_3 films[9] than those obtained by CLD method.[7a] Observation by ESCA on the surface and the cross sectional composition indicated that the film was the stoichiometric Bi_2S_3.

Generally, it is well-known that the Bi_2S_3 films prepared by the chemical process show high resistivity (10^6—10^{13} Ω cm) and low sensitivity of the photoelectric response.[2,3,7] In contrast, the Bi_2S_3 films obtained by the solution pyrolysis of $Bi(S_2CNRR')$ in this study possessed relatively low resistivity (10^{2-3} Ω cm in dark) as shown in Table 2. It is obvious that the degree of the photoelectric effect increases with an increase of the crystallinity. The specimen prepared from $Bi(S_2CNBu_2)_3$ at 350 °C showed the largest photoelectric response and the difference of the dark and the light resistivities was found to be more than two orders of magnitude. In addition, optical band gap energy $(E_g)_{opt}$ of this sample was also estimated to be 1.40 eV by UV-visible spectrometry, which was lower than those of the Bi_2S_3 films obtained by other chemical method (1.47—1.65 eV)[3,5] and slight larger than the value for single crystal (1.3 eV).[1]

Thus, polycrystalline and low resistive Bi_2S_3 thin films can be conveniently prepared from bismuth

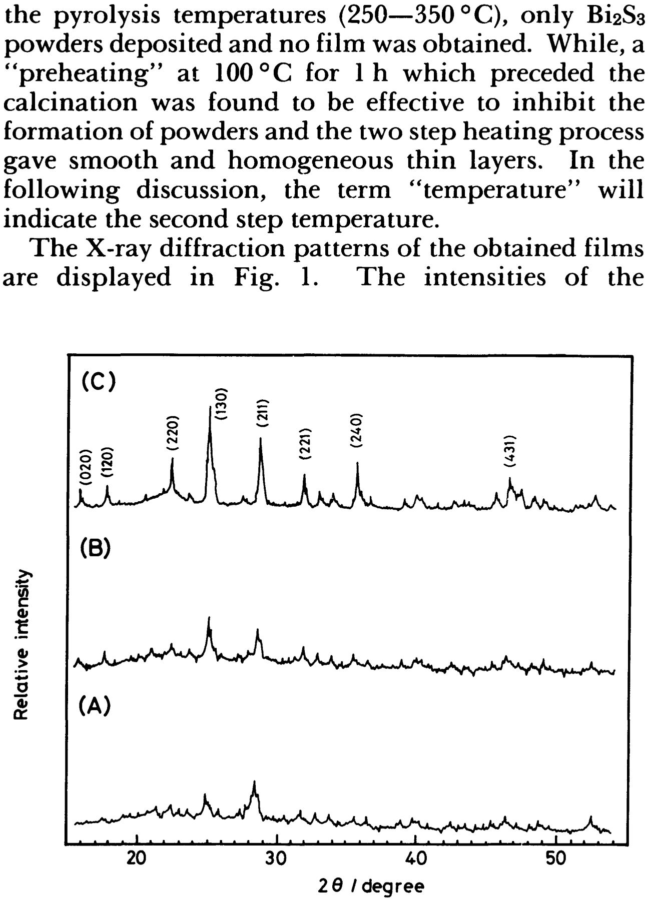

Fig. 1. Typical X-ray diffraction patterns of as-deposited bismuth sulfide thin films obtained by solution pyrolysis of $Bi(S_2CNBu^n{}_2)_3$ at 250°C (A), 300°C (B), and 350°C (C), under Ar atmosphere for 1 h.

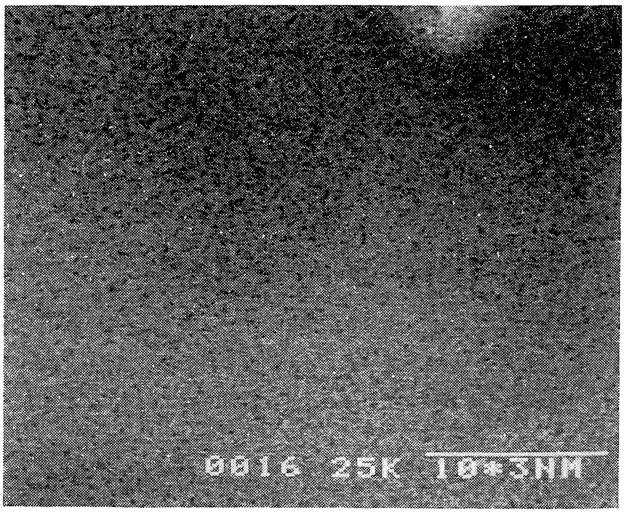

Fig. 2. Surface profile of as deposited Bi_2S_3 films from $Bi(S_2CNBu^n{}_2)_3$ at 350 °C. The measure bar indicates 10 μm.

Table 2. Resistivity of Bi_2S_3 Thin Films Prepared from $Bi(S_2CNR_2)_3$

Precursor $Bi(S_2CNR_2)_3$ R=	T/°C	Resistivity[a)]/Ω cm Dark	Light[c)]	Thickness[b)]/nm
Et	350	3.1×10^3	3.2×10^2	870
Bu^n	300	2.3×10^3	3.7×10^2	200
	350	2.6×10^3	1.0×10^1	250
Hex^n	350	8.2×10^2	4.1×10^2	200

a) Four probe method. b) SEM cross section. c) Under irradiation of a 60 W tungsten lump (distance from the specimen, 30 cm).

dithiocarbamate complexes by solution pyrolysis at 350 °C under Ar atmosphere. In addtion, preparation of Bi_2S_3 films is now feasible under the innert atmosphere such as Ar without the use of the hazardous sulfuration reagents such as H_2S and CS_2 which are necessary in other chemical process to maintain the Bi_2S_3 stoichiometry.[2,3,7,8)]

References

1) J. Black, E. M. Conwell, L. Seigle, and C. W. Spencer, *J. Phys. Chem. Solids,* **2**, 240 (1957).

2) B. B. Nayak, H. N. Acharya, G. B. Mitra, and B. K. Mathur, *Thin Solid Films,* **105**, 17 (1983).

3) S. H. Pawar, P. N. Bhosale, M. D. Uplane, and S. Tanhankar, *Thin Solid Films,* **110**, 165 (1983).

4) A. Lopez-Otero, *Thin Solid Films,* **49**, 3 (1978); C. Ghosh and B. P. Vorma, *ibid.*, **60**, 61 (1979); J. George and M. K. Radhakrishnan, *J. Phys. D,* **14**, 899 (1981); P. A. Krishna Moorthy and G. K. Shrivakumar, *Thin Solid Films,* **121**, 151 (1984).

5) M. J. Chokalingam, K. N. Rao, N. Rangarajar, and C. V. Suryanarayan, *J. Phys. D,* **3**, 1641 (1970).

6) N. Croitoru and S. Jakobson, *Thin Solid Films,* **56**, L5 (1979).

7) a) P. Pramanik and R. N. Bhattachrya, *J. Electrochem. Soc.,* **127**, 2087 (1980); b) R. N. Bhattacharya and P. Pramanik, *ibid.*, **129**, 332 (1982); c) S. Biswas, A. Mondal, D. Mukherjee, and P. Pramanik, *ibid.*, **133**, 48 (1986).

8) B. B. Nayak, S. K. Singh, and B. S. Acharya, *Phys. Stat. Solidi (A),* **105**, 455 (1988).

9) P. Pramanik and S. Bhattachrya, *J. Mater. Sci. Lett.,* **6**, 1105 (1987).

10) R. Nomura, S.-J. Inazawa, H. Matsuda, and S. Saeki, *Polyhedron,* **6**, 507 (1987); R. Nomura, A. Moritake, K. Kanaya, and H. Matsuda, *Thin Solid Films,* in press.

11) R. Nomura, K. Kanaya, and H. Matsuda, *Chem. Lett.*, **1988**, 1849.

12) R. Nomura, A. Takabe, and H. Matsuda, *Polyhedron,* **6**, 411 (1987).

13) G. E. Manoussakis and P. Karayannidis, *Inorg. Nucl. Chem. Lett.,* **6**, 71 (1970).