Applied Organometallic Chemistry (1990) 4 607–610
0268-2605/90/060607-04$05.00

SHORT PAPER

Useful and accessible organometallic precursors for preparation of zinc sulfide and indium sulfide thin films via solution pyrolysis (printing) method

Ryôki Nomura,* Kazuhisa Konishi, Satoshi Futenma and Haruo Matsuda
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-Oka, Suita, Osaka 565, Japan

Received 18 May 1990 *Accepted 16 July 1990*

Polycrystalline β-zinc sulfide thin films were prepared by solution pyrolysis of an ethylzinc isopropylthiolate–zinc bis(dibutyldithiocarbamate) combined precursor ($EtZnSiPr—Zn(S_2CNnBu_2)_2$) in chloroform solution on glass or silicon(111) substrates at 300 °C. Homogeneous but amorphous indium sulfide thin films were obtained from butylindium bis(isopropylthiolate) ($nBuInSiPr_2$) in *p*-xylene on these substrates at 300 °C similarly. The sulfide thin films obtained were characterized by means of X-ray photoelectron spectroscopy (XPS), X-ray fluorescence microanalysis, scanning electron microscopy (SEM) and optical band gap measurements.

Keywords: Organozinc thiolates, organoindium thiolates, zinc dithiocarbamates, zinc sulfide thin films, indium sulfide thin films, solution pyrolysis

INTRODUCTION

Thin films of metal sulfides are arousing much interest as promising optoelectronic device materials and various processes for their production have been developed.[1] Among these thin-film techniques, chemical processes such as printing are essentially most suitable for preparation of large areas and complex-patterned films.[2] It is pointed out, however, that introduction of more sophisticated precursors for such chemical thin-film processes so as to prepare high-qualtiy sulfide thin films is still needed. In two recent papers,[3,4] we have reported limited success in the preparation of indium(II) sulfide (InS) thin films via the solution pyrolysis of dibutylindium thiolates. That finding opened a new approach for the preparation of sulfide thin films using a single organometallic precursor by a printing process. In this paper, we describe the preliminary results of the preparation of more important and useful thin sulfide films such as zinc sulfide (ZnS) and indium(III) sulfide (In_2S_3) from the corresponding organometallic thiolates.

EXPERIMENTAL

General

^1H NMR and UV–vis spectra were recorded on a Hitachi R90H FT spectrometer and a Shimadzu UV-200S spectrophotometer, respectively. Thermal analysis was performed with a Seiko TG/DTA 30 model. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) scans were obtained by a Hitachi S-800-type microscope and a Rigaku Rota-flex diffractometer (Cu Kα, 40 kV), respectively. Surface composition was observed by using a Shimadzu ESCA 650B (XPS) and a Rigaku 0600-type ultratrace X-ray fluorescence microanalyzer. Tributylindium was prepared from indium trichloride and butylmagnesium chloride as reported earlier.[5] Diethylzinc was purchased from Aldrich Japan Inc., Tokyo. All the preparative handling was carried out carefully under a dry nitrogen atmosphere using syringe techniques.

---

† Author to whom correspondence should be addressed.

Table 1 Preparation of zinc sulfide and indium sulfide thin films

Precursor	Temperature (°C)	Composition[a]	$(E_g)_{opt}$ (eV)
nBuInSiPr$_2$[b]	300	In_2S_3[c]	2.25
	350	In_2S_3[c]	2.12
	400	In_2S_3[c]	2.22
EtZnSiPr[d]	300	$ZnS_{0.9}$[e]	3.45
	400	$ZnS_{0.7}$[e]	3.22
	500	ZnO[f]	3.20
EtZnSiPr-Zn($S_2CNnBu_2)_2$[g]	300	ZnS[e]	3.55

[a] Determined by XPS and X-ray fluorescence microanalysis. [b] Coating solution: 12 wt % in *p*-xylene. [c] Amorphous indium sulfide films were obtained; observed by XRD. [d] Coating solution: 10 wt % in chloroform. [e] Typical XRD patterns for β-ZnS were observed (JCPDS no. 5-566). [f] Typical XRD patterns for hexagonal ZnO were observed (JCPDS (Joint Committee on Powder Diffraction Standards) no. 5-664). [g] Coating solution: total concn 10 wt % in chloroform, EtZnSiPr/Zn$(S_2CNnBu_2)_2$ = 1:0.5 (molar ratio).

Preparation of organometallic precursors

Butylindium bis(isopropylthiolate) (BuIn(SiPr)$_2$) was prepared by the reaction of tributylindium with two molar equivalents of 2-propanethiol and was purified by vacuum distillation.[5] In a similar fashion, ethylzinc isopropylthiolate (EtZnSiPr) was prepared from diethylzinc and 2-propanethiol in hexane[6] or in chloroform and was isolated as a colorless oil.

EtZnSiPr: ^{1}H NMR (CDCl$_3$, 90 MHz): δ 3.35 (septet, 1H, *J*7.4 Hz, C*H* in iPr), 1.35 (d, 6H, C*H*$_3$ in iPr), 1.2–1.6 (bd, 5H, *Et*). Analysis: Found: C, 36.28; H, 7.44. Calc. for $C_5H_{12}SZn$: C, 35.41; H, 7, 7.13%.

The zinc thiolate possessed a higher lability than the indium analog and gradually solidified into an insoluble solid on standing for several days in bulk even under an inert atmosphere. Thus, we employed EtZnSiPr as freshly prepared in chloroform after checking purity by ^{1}H NMR in our further study.

Preparation of sulfide thin films

Substrates (10 mm × 10 mm) such as glass or silicon(111) were coated by a small portion (*ca* 50 μL) of the precursor solution in *p*-xylene or chloroform by using a spin-coater (1500 rpm); then the specimens were heated in a quartz tube under an argon atmosphere at prescribed temperatures for 1 h (Table 1). The detailed pyrolysis technique was described in the earlier papers.[3,4]

RESULTS AND DISCUSSION

As reported previously,[7] BuIn(SiPr)$_2$ decomposed at around 250 °C with an exotherm to give In_2S_3 up to 330 °C. EtZnSiPr stepwise lost ethyl and isopropyl groups at 104 and 270 °C, respectively, and finally gave ZnS up to 358 °C as shown in Fig. 1. Consequently we attempted to prepare the corresponding metal sulfide thin films on glass or Si(111) substrates via solution pyrolysis of the

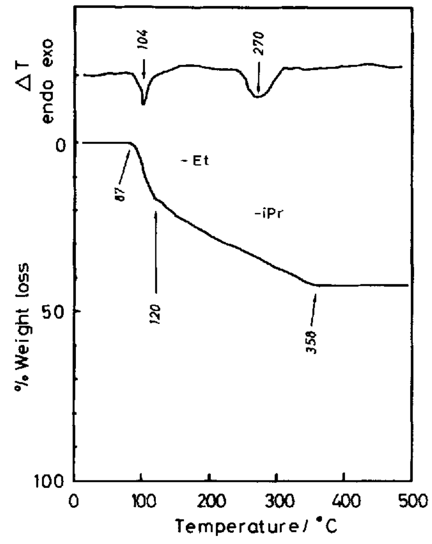

Figure 1 Thermogram of EtZnSiPr. Conditions: sample weight 10 mg, start temperature 20 °C, limit temperature 600 °C, program rate 10 °C $\min^{-1}$, under N_2 flow.

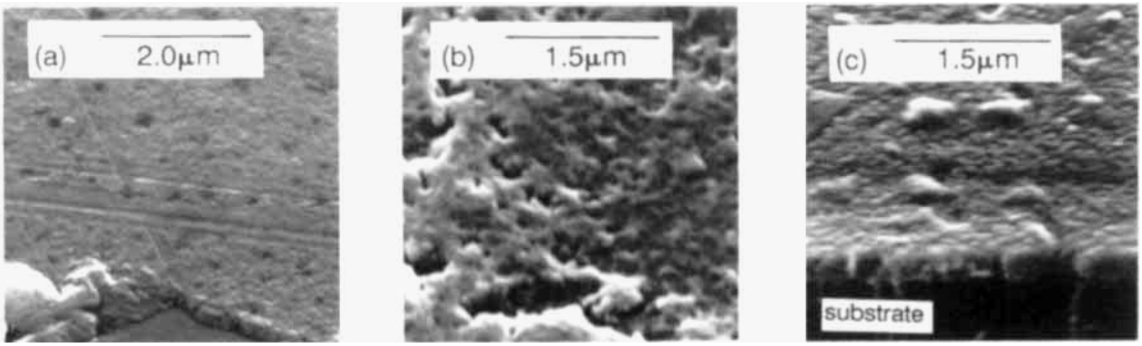

Figure 2 Photomicrographs of (a) indium sulfide and (b, c) zinc sulfide thin films obtained from BuIn(SiPr)$_2$, EtZnSiPr and EtZnSiPr–Zn(S$_2$CNnBu$_2$)$_2$ at 300 °C, respectively.

above-mentioned organometallic precursors and the results obtained are summarized in Table 1.

Amorphous β-In$_2$S$_3$ thin films 1000–2000 Å (100–200 nm) thick were obtained at pyrolysis temperatures of 300 and 400 °C. Values of the optical band gap energy of these indium sulfide thin films were estimated at 2.1–2.2 eV, which coincided with those of β-In$_2$S$_3$ single crystals (1.98 eV)[8] and thin films prepared by spray pyrolysis (2.20 eV).[9] Their surface morphology was observed by SEM and a typical photomicrograph is shown in Fig. 2(a). It was found that these films possessed a smooth surface and consisted of small crystallites, ca 250 Å (25 nm) in diameter.

In contrast, XRD, patterns shown in Fig. 3 indicate that the pyrolysate from EtZnSiPr is polycrystalline β-ZnS; however, these ZnS films were contaminated by significant amounts of zinc oxide (ZnO). Thus the partial oxidation of ZnS layers deposited initially in part resulted in a lower band gap energy value of 3.2–3.4 eV, which was significantly lower than that of β-ZnS (3.6 eV)[10] and slightly higher than that of ZnO (3.2 eV).[10] Especially, a transparent and conducting ZnO film was obtained at 500 °C; average resistivity was 3×10^{-1} Ω cm, and average visible transmittance was about 90%. Similar sulfide–oxide conversion was reported for solution pyrolysis of sulfur-deficient systems such as Bu$_2$InSiPr, which proceeded by trace amounts of oxygen contained in argon (purity 99.99%).[3] In contrast, pyrolysis carried out below 300 °C gave ZnS films without oxidation but with significant contamination by organic moieties.

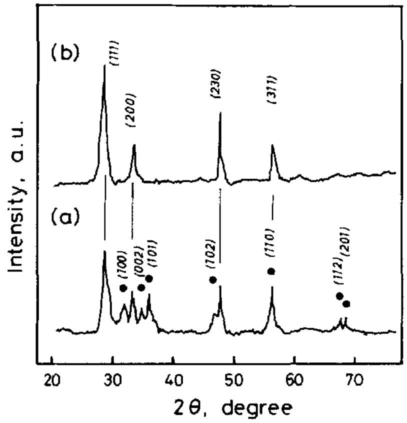

Figure 3 Typical XRD patterns of ZnS thin films obtained from the pyrolysis of (a) EtZnSiPr and (b) EtZniPr–Zn(S$_2$CNnBu$_2$)$_2$ (2 : 1 molar ratio) in chloroform on Si(111) at 300°C for 1 h. All Miller indices were cited from JCPDS no. 5-566 for ZnS and no. 5-664 for ZnO. ●, Peaks resulting from ZnO.

To avoid the undesirable oxidation, precursors having larger sulfur contents such as zinc dithiocarbamate complexes were examined but the solution pyrolysis of sole zinc dithiocarbamates gave only powders deposited over the substrates. Eventually, it was found that the combination of EtZnSiPr and Zn(S$_2$CNnBu$_2$)$_2$ (2 : 1 molar ratio) gave polycrystalline β-ZnS films without oxidation even at 300 °C. The ZnS films thus obtained showed a larger band gap energy of 3.55 eV and the average particle size was 500 Å (50 nm). The effective formation of ZnS layers by the addition of the dithiocarbamate complex resulted from the formation of bridged binuclear complexes as in the butylindium alkylthiolate and copper dithiocarbamate system for deposition of CuInS$_2$.[2c, 11]

In conclusion, it is found that thin films of In$_2$S$_3$ and ZnS which were valuable for electroluminescence (EL) devices, terrestrial solar cell windows and photocatalysts[12] could be easily prepared by solution pyrolysis of the corresponding organometallic thiolates.

REFERENCES

1. For review, see Chopra, K L and Kaur, I *Thin Film Device Applications*, Plenum, New York, 1987

2 (a) Nomura, R, Kanaya, K and Matsuda, H *Bull. Chem. Soc. Jpn*, 1989, 62: 939; (b) Nomura, R, Inazawa, S'-J, Matsuda, H and Saeki, S *Polyhedron*, 1987, 6: 507; (c) Nomura, R, Fujii, S, Kanaya, K and Matsuda, H *Polyhedron* 1990, 9: 361

3 Nomura, R, Moritake, A, Kanaya, K and Matsuda, H *Thin Solid Films*, 1988, 167: L27

4 Nomura, R, Kanaya, K and Matsuda, H *Chem. Lett.* 1988: 1849

5 Nomura, R, Inazawa, S'-J, Kanaya, K and Matsuda, H *Polyhedron* 1988, 8: 763

6 Coats, G E and Ridley, D *J. Chem. Soc.*, 1965: 1870

7 Nomura, R, Inazawa, S'-J, Kanaya, K and Matsuda, H *Appl. Organomet. Chem.*, 1989, 3: 195

8 Bube, R H and McCarroll, W H *J. Phys. Chem. Solids*, 1959, 10: 333

9 Kim, W-T and Kim, C-D *J. Appl. Phys.*, 1986, 60: 2631

10 Bencit, C *Selected Constants Related to Semiconductors*, Pergamon Press, Oxford, 1961

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

12 (a) Fischer, A G In: *Luminescence of Inorganic Solids*, Goldberg, P (ed), Academic Press, New York, 1966, Chapter 10; (b) Karanjai, M K and Dasgputa, D *Thin Solid Films*, 1987, 155: 309; (c) Yanagida, S, Mizuhashi, K and Pac, C *J. Am. Chem. Soc.*, 1986, 108: 647