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COMMUNICATION

Thermal decomposition of butylindium thiolates and preparation of indium sulfide powders

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Thermal properties of organoindium thiolates were investigated by means of thermogravimetric (TG) and differential thermal (DT) analysis. Dibutylindium propylthiolates ($Bu^n_2InSPr^n$, $Bu^n_2InSPr^i$, $Bu^i_2InSPr^n$ and $Bu^i_2InSPr^i$) decomposed up to 280°C along with an exothermic DT peak and gave indium(I) sulfide (InS) powders. Although the arylthiolate Bu^n_2InSPh also afforded InS powders, it decomposed at a slightly higher temperature. In contrast, the dithiolate and the dithiocarbamate complexes $[Bu^nIn(SPr^i)_2$ and In $(S_2CNBu_2)_3]$ gave indium(III) sulfide (In_2S_3) powders.

Keywords: Organoindium thiolates, thermal decomposition, indium sulfide powders, optoelectronic materials, vapor deposition.

INTRODUCTION

Recently, there has been much interest given to the optoelectronic properties of indium sulfides (InS[1] and In_2S_3[2]). Both of them possess a medium band gap energy (*ca* 2.0 eV) and are strongly expected to become useful photoconducting materials. In addition, indium sulfides are also important as a component of ternary charcogenides such as $CuInS_2$.[3] In this paper, we describe the preparation of indium sulfide powders via the thermal decomposition of several organoindium thiolates. Based on investigations of the thermal properties of the organoindium thiolates, the thermolysis of the butylindium thiolates to indium sulfide powders was optimized. Further, we propose that organoindium thiolates are suitable precursors for indium sulfide powders and also for their thin films.

EXPERIMENTAL

Analysis

Thermal analysis (TG and DTA) was performed by a Seiko-TG/DTA 20. Analyses of the pyrolyates by powder X-ray diffraction and X-ray fluorescence analysis were carried out by means of a Rigaku Rota Flex X-ray diffractometer, and a Rigaku D6C X-ray fluorescence analyzer, respectively.

Materials

Butylindium thiolates were prepared by the direct substitution of tributylindium with the corresponding thiols in ether and were purified by several distillations under reduced pressure.[4] Indium tris(dibutyldithiocarbamate) was synthesized by the reaction of indium(III) oxide (In_2O_3) with dibutyldithiocarbamic acid (HS_2CNBu_2) which was generated from dibutylamine and CS_2 *in situ* and recrystallized from acetonitrile–methanol.[5]

RESULTS AND DISCUSSION

Thermal analysis (TG and DTA) of the organoindium thiolates was investigated under nitrogen gas flow conditions and the results are summarized in Table 1. Four dibutylindium propylthiolates and butylindium bis(isopropylthiolate) showed similar TG and DTA curves: the main decomposition processes were exothermic and the weight loss ended between 269 and 370°C. Such exothermic peaks indicate that the

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Table 1 Thermal analysis of butylindium thiolates and their pyrolysis products[a]

Compound	TG (°C) Weight loss Initial	TG (°C) Weight loss Final	TG (°C) Weight loss (%) (Calc.)[b]	DTA (°C) Exo	DTA (°C) Endo	Product
$Bu_2^nInSPr^n$	140	282	75 (52)	274		InS
$Bu_2^nInSPr^i$	148	277	72 (52)	265		InS
$Bu^nIn(SPr^n)_2$	87	336	49 (49)	250		In_2S_3
Bu_2^nInSPh	160	360	52 (52)	320	160	InS
$Bu_2^iInSPr^n$	123	277	75 (52)	242		InS
$Bu_2^iInSPr^i$	97	269	55 (52)	264		InS
$In(BU_2CNS_2)_3$	260	370	77 (78)	–	177, 330	In_2S_3

[a] Thermal analysis was carried out as follows: nitrogen flow, 10°C min^{-1}, room temperature to 400°C. Pyrolysates were identified by X-ray diffraction patterns comparing with JCPDS cards: InS, No. 19–588; In_2S_3: No. 25–390. [b] Calculated percentage to give the pyrolysate weights obtained are shown in parentheses.

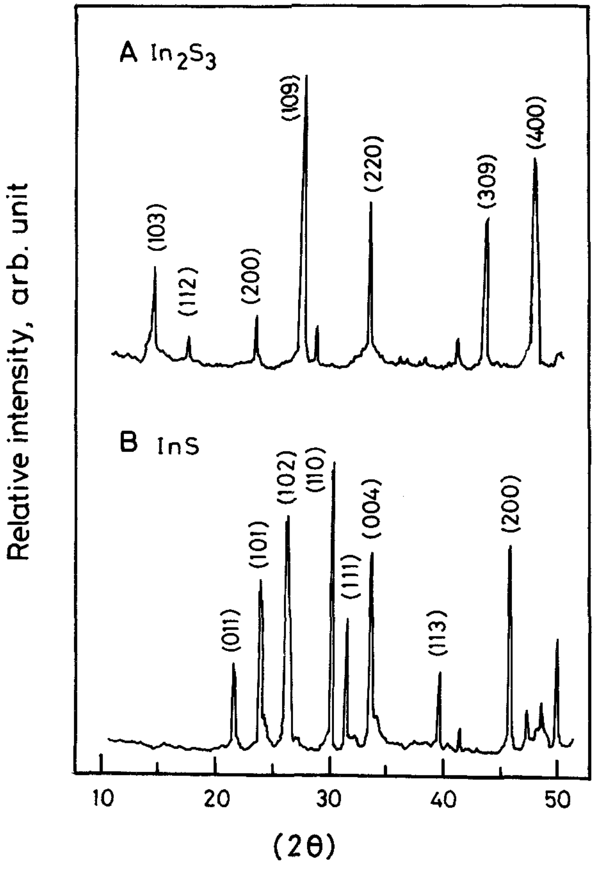

Figure 1 X-ray diffraction patterns of the pyrolysates. Pyrolysis conditions are as follows: pyrolysis temperature 300°C, atmosphere Ar, period 1 h, in a porcelain crucible (3 cm in diameter) set into a quartz tube (4 cm in diameter). (A) In_2S_3 powders obtained from $Bu^nIn(SPr^i)_2$. (B) InS powders obtained from $Bu^n_2In(SPr^i)$.

dissociation of indium—carbon (In—C) and carbon—sulfur (C—S) bonds is the main decomposition reaction, similar to the thermal decomposition of their oxygen analogues;[5] however, the exothermic peaks of the thiolates shifted to lower temperatures in the region of 150°C.

Controlled pyrolysis of these butylindium thiolates under an argon atmosphere at 300°C for 1 h gave indium sulfide powders which were confirmed by means of powder X-ray diffraction and X-ray fluorescence analysis. The composition of the products (S:In atomic ratio) was found to reflect well the compositions of the starting butylindium thiolates. Thus, four monothiolates afforded InS and the dithiolate gave In_2S_3. The typical powder X-ray diffraction patterns of the samples obtained at 300°C are presented in Fig. 1.

The pyrolysis was also attempted at 200, 400, and 500°C. The effect of the pyrolysis temperature on the ratio of sulfur to indium (S:In) in the pyrolysates was also investigated and the results osbtained for $Bu^nIn(SPr^i)_2$ and $Bu^i_2In(Pr^i)$ are shown in Fig. 2. The S:In ratios seemed to remain constant at 1.0 and 1.5 in the low-temperature area for the mono- and dithiolates, respectively. These S:In ratios agreed well with those of the corresponding indium sulfides. Low pyrolysis temperature (200°C), however, caused contamination by carbon residues (which were confirmed by infrared spectra) in the indium sulfide powders: thus, weak absorption peaks could be observed at 2800–3000 cm^{-1}. In addition, these samples possessed low crystallinity and showed very weak X-ray diffraction. Also, higher temperatures resulted in

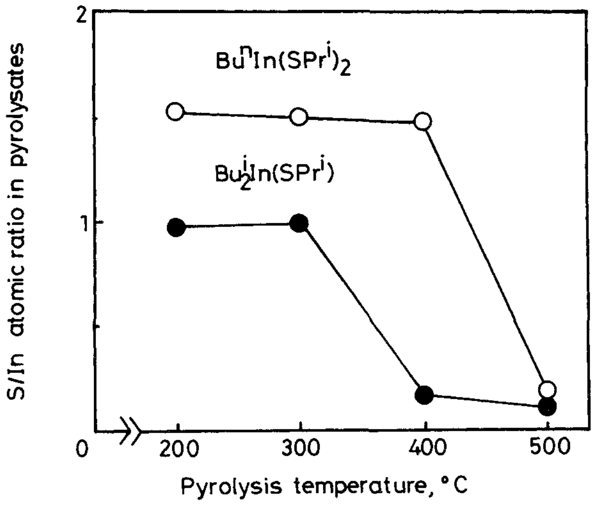

Figure 2 Correlation of pyrolysis temperature with S:In ratio in the pyrolysates. Pyrolysis was carried out under similar conditions to those indicated in Fig. 1. Ratios of S:In were obtained by means of X-ray fluorescence analysis.

oxidation of the indium sulfides to oxide (In_2O_3) and S:In ratios suddenly decreased. However, the dithiolate was found to be more stable to oxidation because of its higher turning point.

The butylindium thiolates described above, especially the alkylthiolates, are liquid at room temperature and can be purified by vacuum distillation.[4] In addition, they are soluble in several organic solvents. Thus, we feel these organoindium thiolates are suitable precursors to produce optoelectronic thin films via chemical processes such as printing, dip-dry methods and also organometallic chemical vapour deposition (OMCVD). We have attempted to employ these organoindium thiolates in the above-mentioned chemical thin film processes. In preliminary attempts, we find that $Bu^i_2In(SPr^i)$ could be applied in a printing method to give indium sulfide (InS) films on a glass substrate using its *p*-xylene solution at 250–300°C under an argon (Ar) atmosphere.

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