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Preparation of copper–indium sulfide thin films by single-source OMCVD: mass-spectral investigation of decomposition path of the organometallic sources

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In order to prepare high-quality $CuInS_2$ thin films vapor phase decomposition patterns of three copper–indium binuclear complexes,

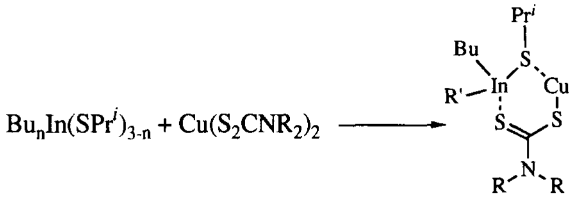
$Bu_2In[S(i\text{-}Pr)]Cu(S_2CNBu_2)$ (1a)
$BuIn[(i\text{-}Pr)]Cu(S_2CNBu_2)$ (1b)
and
$Bu_2In[S(i\text{-}Pr)]Cu[S_2CN(i\text{-}Pr)_2]$ (1c)

as candidates for source materials were investigated using EI MS. The complex 1c showed series of intensive peaks due to the fragmentation of M^+. For 1a, only a fragmentation pattern starting from $BuIn(S_2CNBu_2)_2$ was detectable. This should suggest that 1a decomposed into $BuIn(S_2CNBu_2)_2$ and copper sulfide before vaporization. In addition an ambiguous feature could be observed for 1b, viz. two fragmentation paths. Consequently, we judge that 1c is a suitable source complex to prepare $CuInS_2$ *thin* films via a single-source OMCVD process. Thus chalcopyrite $CuInS_2$ thin films were successfully prepared via single-source OMCVD using 1c as a source complex, with $T_{substrate}$ 400 °C, T_{source} 80 °C, base pressure 0.7 Torr and carrier (nitrogen) flow rate 0.8 L min^{-1}. Fragmentation of two copper dithiocarbmates, $Cu(S_2CNBu_2)_2$ and $Cu[S_2CN(i\text{-}Pr)_2]_2$, and two butylindium thiolates, $Bu_2InS(i\text{-}Pr)$ and $BuIn[S(i\text{-}Pr)]_2$, as components of 1 is additionally discussed.

Keywords: Organoindium thiolates, copper dithiocarbamates, single-source OMCVD, copper–indium sulfide, mass spectra, fragmentation, solar cell, copper sulfide, indium sulfide

INTRODUCTION

In previous papers,[1-3] we reported that the reaction of alkylindium thiolates with copper dithiocarbamates gives new binuclear complexes such as **1a** and **1b** shown in Scheme 1. This class of complexes offers considerable potential to open a new methodology, namely a single-source process, for the preparation of an important ternary semiconductor material, copper–indium sulfide ($CuInS_2$) thin film. Copper–indium sulfide is one of the I–III–VI_2 chalcopyrites and is a potential candidate for an absorber layer in high-performance terrestrial solar cells.[4] It is difficult, however, to maintain the accurate stoichiometry of $CuInS_2$ films using conventional preparation procedures such as multi-source CVD,[5] spray pyrolysis,[6] evaporation[7] or sputtering.[8] Although **1a** and **1b** give $CuInS_2$ powders and thin films under static pyrolysis conditions, they give only copper-deficient phases such as In_2S_3 and $CuIn_5S_8$[9] during vapor-phase decomposition. Thus, we have thoroughly re-examined the decomposition path(s) of these binary complexes, together with



1

1a; R=Bu, n=2: **1b**; R=Bu, n=1: **1c**; R=Pr^i, n=2

Scheme 1

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those of copper dithiocarbamates and butylindium thiolates, investigating their fragmentation patterns in the vapor phase using electron impact mass spectroscopy (EI MS). The results obtained enabled the successful preparation of $CuInS_2$ thin films via a single-source OMCVD process using the new single source complex $Bu_2In[S\text{-}(i\text{-}Pr)]Cu[S_2CN(i\text{-}Pr)]$ (**1c**).

EXPERIMENTAL

General

Mass spectra (electron impact (EI), 70 eV, positive) were obtained with a JEOL JMS-DX303 instrument with a JEOL JMA-DA5000 data-processing system (Faculty of Engineering, Osaka University). The ionization chamber pressure was maintained at 10^{-6} Torr and the samples were introduced directly into the chamber by vaporizing at 100 °C. The range of masses scanned and the period were 35–700 masses and 1.0 s, respectively. Data acquisition was carried out from the third through the 30th scans. All the fragment peaks displayed in Figs 1–7 possessed isotopic splitting pattern(s) coincident with those calculated.

IR, ^1H and ^{13}C NMR spectra of **1** were recorded on a Hitachi 260-30 spectrophotometer and on a Hitachi R90H FT spectrometer, respectively. Thermal analysis was performed with a Seiko TG/DTA 20 type analyzer (ascending heating rate 10 °C min^{-1}, under nitrogen flow) equipped with an SSC570 thermal controller. Further analyses of the pyrolysates were carried out using a Rigaku Rotaflex powder X-ray diffractometer (XRD), a Shimadzu ESCA 650B (XPS), and a Rigaku System 3270 X-ray fluorescence analyzer.

Materials and procedure

Copper dithiocarbamate complexes,[2,10] butylindium thiolates,[11] and the copper–indium binuclear complexes[1,3] used in this paper were prepared by methods reported previously.

Vapor phase deposition of the thin films of copper sulfide, indium sulfide and copper–indium sulfide on a Si(111) substrate was performed in a cold-walled horizontal reactor under reduced pressure as described previously.[12] Generally, these source complexes were placed in a bubbler and heated to 80 °C during deposition, to transport the precursor effectively in a stream of nitrogen carrier gas to the reactor. Static decomposition studies were carried out using a hot-walled 40 mm (o.d.) quartz tube, as reported earlier.[1,3]

RESULTS AND DISCUSSION

Pyrolysates obtained from $Cu(S_2CNBu_2)_2$, butylindium thiolates and **1** under static and vapor-phase conditions are summarized in Table 1. All

Table 1 Correlation between precursors and pyrolysates (sulfide thin films)

Source material	Temperature (°C)	Method[a, b]	Product[c]	Ref.
$Cu(S_2CNBu_2)_2$	320	Static	Cu_2S	10
	400	CVD	Cu_2S	This study
$Bu_2In[S(i\text{-}Pr)]$	280	Static	InS	13
	>250	CVD	InS	14
$BuIn[S(i\text{-}Pr)]_2$	340	Static	In_2S_3	13
	400	CVD	In_2S_3	12
$Bu_2In[S(i\text{-}Pr)]Cu(S_2CNBu_2)$ (**1a**)	300–350	Static	$CuInS_2$	3
	400	CVD	In_2S_3	This study
$BuIn[S(i\text{-}Pr)]_2Cu(S_2CNBu_2)$ (**1b**)	350	Static	$CuInS_2$	This study
	400	CVD	$CuIn_5S_8$	9
$Bu_2In[S(i\text{-}Pr)]Cu[S_2CN(i\text{-}Pr)]$ (**1c**)	310	Static	$CuInS_2$	This study
	400	CVD	$CuInS_2$	This study

[a] Static; the corresponding sulfide thin films on Si(111) or on glass substrates were prepared by printing/pyrolysis in a quartz tube. Usually a *p*-xylene solution of the source materials was used. [b] CVD; the sulfide thin films were prepared by the CVD process as described in the Experimental section. [c] Products were determined by XRD and XPS analyses.

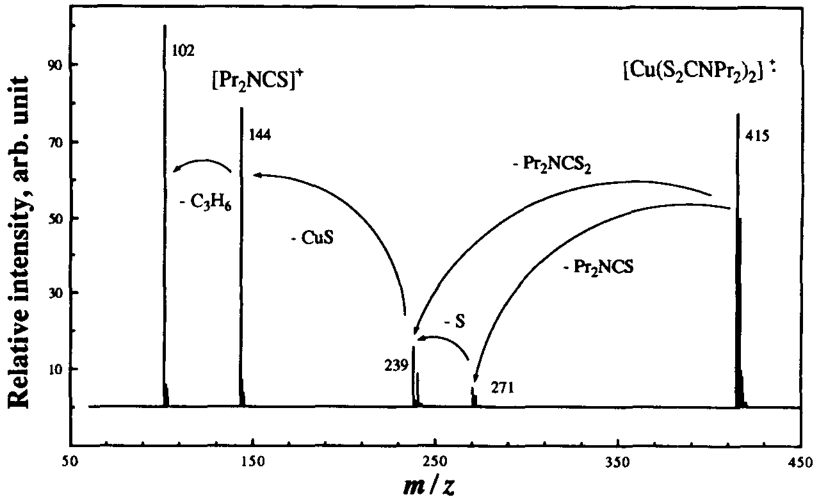


Figure 1 Fragmentation pattern of $Cu[S_2CN(i\text{-}Pr)_2]_2$.

the variants from which **1** can be prepared viz. $Bu_2InS(i\text{-}Pr)$ and $BuInS(i\text{-}Pr)$ gave the same pyrolysates both in the static and CVD pyrolyses. This means that these compounds possess sufficient volatility and act as real precursors in the CVD process. However, the pyrolysates from **1a** and **1b** in the CVD process were different from those obtained under static conditions. This phenomenon suggests that **1a** and **1b** are transformed into certain non-volatile substances before vaporization in the CVD process, especially within the bubbler. Therefore we attempted to identify the decomposition path of these source complexes together with their components using mass spectroscopy.

Copper dithiocarbamate complexes

Static pyrolysis of copper dithiocarbamates in a crucible or on a substrate led to the formation of cuprous sulfide powders[2] and thin films,[10] respectively. Vapor phase decomposition in the CVD system similarly gave tetragonal cuprous sulfide (chalcocite) thin films; $T_{substrate} = 400\ ^\circ C$, $T_{source} = 200\ ^\circ C$, carrier flow rate $= 0.2\ L\ min^{-1}$, base pressure $= 0.2$ Torr, growth rate $= 0.8\ \mu m\ h^{-1}$.

The fragmentation patterns of two copper dithiocarbamates were investigated here. Both cupric dithiocarbamates displayed similar fragmentation patterns, as shown in Figs 1 and 2. Thus, it can be seen that they successively lost dithiocarbamate

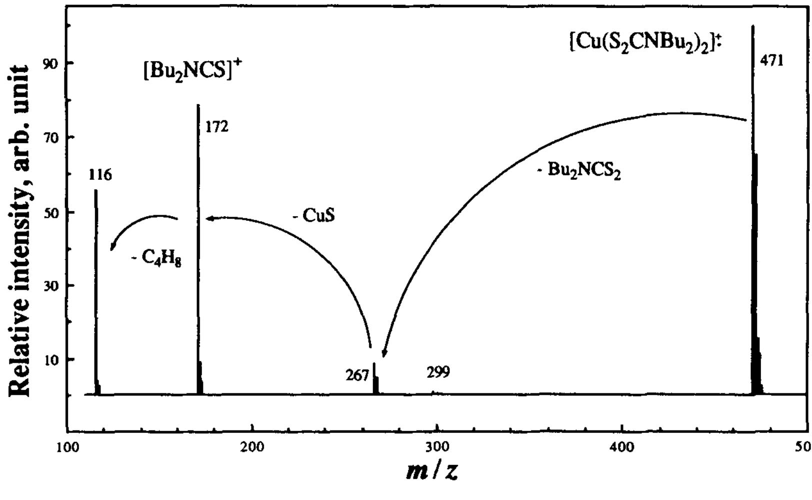


Figure 2 Fragmentation pattern of $Cu(S_2CNBu_2)_2$.

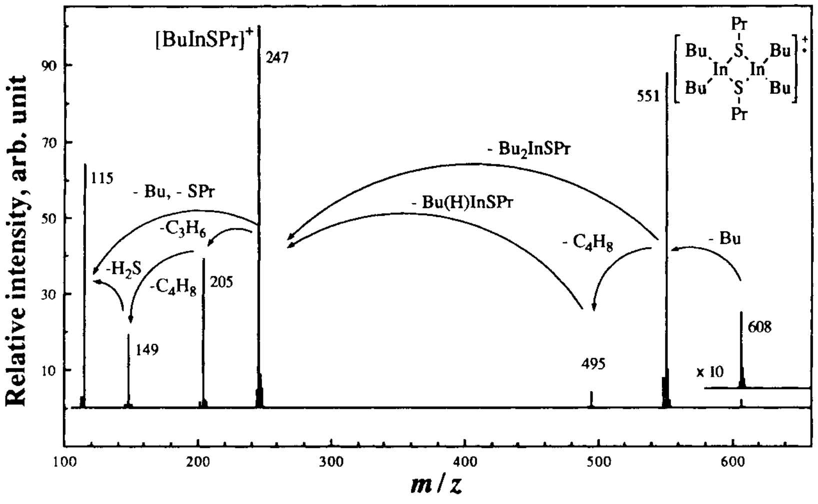


Figure 3 Fragmentation pattern of $Bu_2InS(i\text{-}Pr)$.

and thiocarbamoyl moieties to give cupric sulfide. Similarly, in the static pyrolysis, these copper dithiocarbamates gave primarily cupric sulfide, followed by partial loss of sulfur to give cuprous sulfide.[10] although many research groups have reported on the decomposition mechanisms of copper dithiocarbamates, the results reported often appear confusing because different pyrolysates and different routes were reported by different research groups.[2, 15] Based on the data in Table 1 we believe that copper dithiocarbamates should conclusively give cuprous sulfide as a pyrolysate both in the static and vapor-phase pyrolysis.

Butylindium thiolates

Although the butylindium thiolates, $Bu_2InS(i\text{-}Pr)$ and $BuIn[S(i\text{-}Pr)]_2$, exist as monomers in solution,[10] their mass fragmentation patterns (shown in Figs 3 and 4) suggest that they are dimeric in the vapor phase, like alkylgallium alkoxides[16] and alkylindium amides.[17] The formation of such dimers probably results in their low volatility and low growth rate when they are employed as source materials for OMCVD preparation of indium sulfide thin films.[12] The butylindium thiolate dimers decompose with successive release of butyl, propylthio and indium thiolate

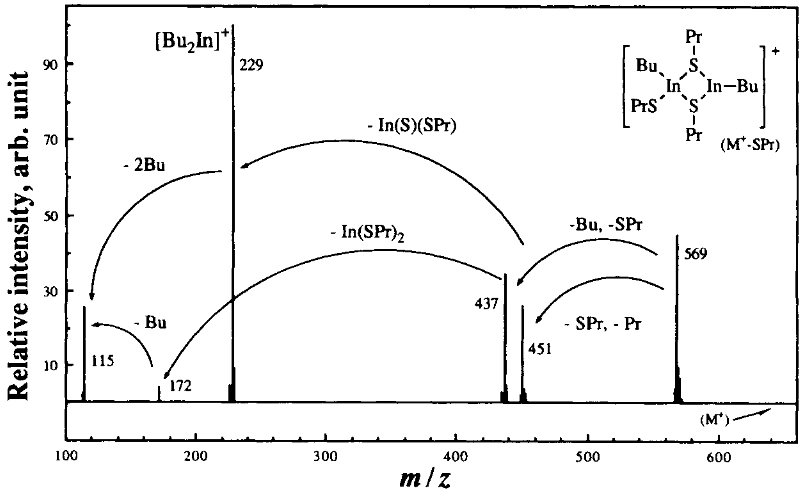


Figure 4 Fragmentation pattern of $BuIn[S(i\text{-}Pr)]_2$.

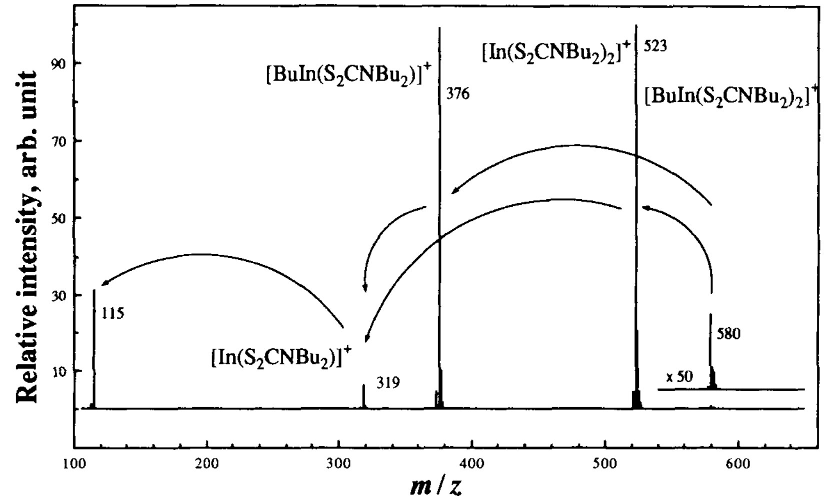


Figure 5 Fragmentation pattern of Bu[(i-Pr)S]$_2$In-Cu(S$_2$CNBu$_2$) (**1a**).

moieties, but we could not detect the formation of indium sulfide fragments directly. Thus the indium thiolate fragments may act as the main precursors for the indium sulfide formation. Consequently, the pyrolysates of butylindium thiolates in the vapor phase coincide with those formed under static pyrolysis conditions.

Complexes 1a and 1b

In previous attempts to prepare CuInS$_2$ thin films under static conditions, by printing/pyrolysis,[3] we selected **1a** as a source because this compound really gave stoichiometric CuInS$_2$ in the static thermal decomposition in crucibles and possessed suitable solubility to form printing solutions. Further, CuInS$_2$ films obtained from **1a** were highly adhesive to the substrate, and did not crack. In vapor-phase pyrolysis using the above-mentioned CVD system, **1a** gives only In$_2$S$_3$ layers. The difference can be understood by a glance at the fragment pattern shown in Fig. 5. There seem to be no parent peaks and no fragment peaks directly due to **1a** in this fragment pattern. The presence of [BuIn(S$_2$CNBu$_2$)$_2$]$^+$ and [In(S$_2$CNBu$_2$)$_2$]$^+$ suggested that heating the complex for vaporization caused significant disproportionation of **1a** into butylindium dithiocarbamates and copper thiolates. The latter most likely form non-volatile aggregations or decompose further into copper sulfide which is also non-volatile

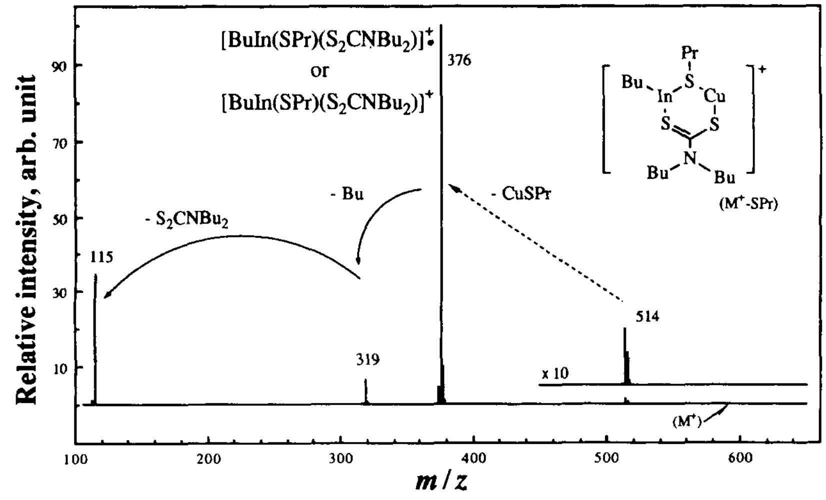
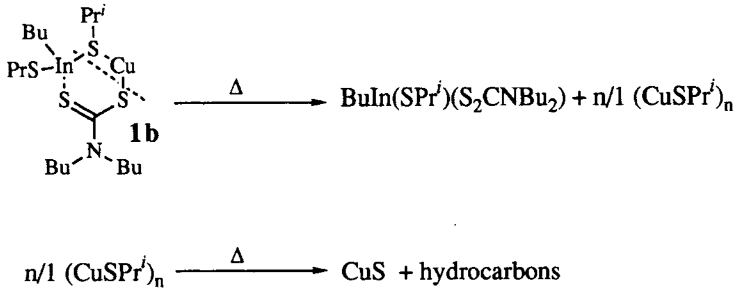


Figure 6 Fragmentation pattern of Bu$_2$[(i-Pr)S]In–Cu(S$_2$CNBu$_2$) (**1b**).



Scheme 2

under these conditions. Thus, the inherent low volatility of **1a** results in disproportionation and provides only indium species as a precursor.

The source complex was first modified by the introduction of the butylindium dithiolate component in place of the monothiolate with the idea of lowering the volatility of the indium species to balance the volatility of the copper species (**1b**) (complex **1b** also give CuInS$_2$ in static pyrolysis). This attempt partly succeeded, because the parent peak due to **1b** appeared and fragments including both indium and copper species were detectable in the MS as shown in Fig. 6. The peak appearing at $m/z = 376$ can be assigned to $[\mathrm{BuIn[S(i\text{-}Pr)](S_2CNBu_2)}]^+$ and is probably the parent peak derived from the disproportionation of **1b** (Scheme 2), because the peak appearing at $m/z = 514$, assigned to the fragment from **1b**, is too small. Indeed, vapor-phase pyrolysis of **1b** using the CVD system gave copper-deficient layers, i.e. the spinel CuIn$_5$S$_8$.[9]

New source complex

As a second modification, we attempted to prepare CuInS$_2$ thin films using **1c**, aiming at increasing the volatility of the copper species and the binuclear complex itself. Judging from the fragmentation pattern shown in Fig. 7, although we could not detect the M$^+$ peak, the height of the M$^+$ − Bu peak at $m/z = 486$ and that of the $(\mathrm{BuIn[(Si\text{-}Pr)][S_2CN(i\text{-}Pr)_2]})^+$ peak at $m/z = 348$ seemed comparable. This suggests that **1c** will vaporize without disproportionation and can supply equal amounts of indium and copper moieties to the CVD reactor under these conditions.

Thus, we can obtain chalcopyrite CuInS$_2$ layers by OMCVD with $T_{\mathrm{substrate}} = 400\,°\mathrm{C}$ and $T_{\mathrm{source}} = 80\,°\mathrm{C}$ (base pressure 0.7 Torr and carrier flow rate 0.8 L min^{-1}). Figure 8 shows XRD patterns of CuInS$_2$ thin films thus obtained. Diffraction peaks due to chalcopyrite CuInS$_2$ were observed. Further XPS analysis suggested the formation of

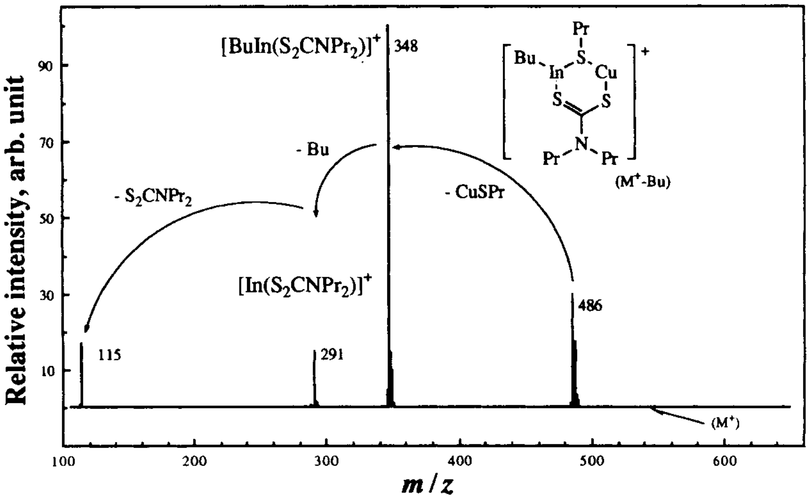


Figure 7 Fragmentation pattern of Bu$_2$[(i-Pr)S]In–Cu[S$_2$CN(i-Pr)$_2$] (**1c**).

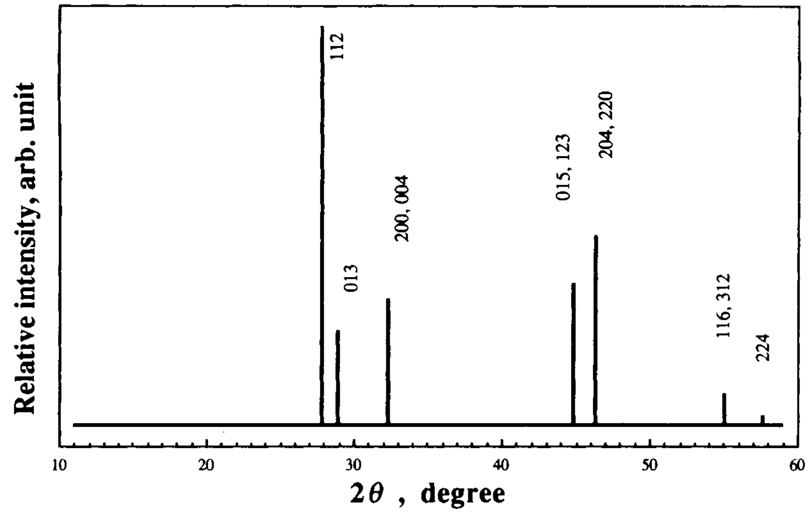


Figure 8 XRD patterns of $CuInS_2$ thin films obtained with $T_{substrate}$ at 400 °C and T_{source} 80 °C (base pressure = 0.7 Torr, carrier flow rate = 0.8 L min^{-1}, 4 h); *hkl* indices near the corresponding peaks are cited from[18]

stoichiometric $CuInS_2$ layers. Further detailed studies relating the vapor-phase growth of $CuInS_2$ layers are now in progress and the results obtained will be published in due course.

In conclusion, with the introduction of **1c** as a new source complex, it is now possible to prepare $CuInS_2$ thin films by a single-source OMCVD process. The complex **1c** remains stable during vapor transport between the bubbler and the reactor, without disproportionation, in contrast to **1a** and **1b**, which readily decompose into butylindium dithiocarbamates and copper sulfide before vaporization.

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