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Heterogeneous reaction route to $CuInS_2$ thin films

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High quality thin films of $CuInS_2$ have been deposited on a copper coated silicon substrate using vapors obtained from $(Et_3NH)[In(SC(O)Ph)_4]$.

$CuInS_2$, a ternary I–III–VI_2 material with chalcopyrite like structure, has a high absorption co-efficient and its band gap ($\sim$1.5 eV) is suitable for solar energy absorption. Hence thin films of $CuInS_2$ have been regarded as a potential candidates for photovoltaic applications.[1,2] Thin films of $CuInS_2$ have been obtained using various techniques including evaporation, sputtering, spray pyrolysis, multi-source and single source precursor CVD.[3–12] Thiolate, thiocarbamate and thiocarboxylate ligands have been used to extensively synthesize single source precursors for various metal sulfide materials.[13–16] Hampden-Smith and his coworkers have reported that thin films of β-In_2S_3 could be obtained through aerosol assisted chemical vapor deposition from thf solutions of the compound $[HL][In(SC(O)Me)_4]$ (L = 3,5-dimethylpyridine) over a silicon substrate.[17] Here in this paper, we report an unprecedented method to produce thin films of $CuInS_2$ by employing a copper coated silicon substrate and a precursor compound $(Et_3NH)[In(SC(O)Ph)_4]\cdot H_2O$ (**1**).

Compound **1** was synthesized by reacting $InCl_3$, NaSC(O)Ph and $(Et_3NH)(SC(O)Ph)$ in the ratio 1 : 3 : 1 in appropriate solvents.† The structure of **1** has been unequivocally characterized using various techniques including single crystal X-ray diffraction techniques.‡ The structure of **1** is illustrated in Fig 1. The compound crystallized in a chiral space group $P2_12_12_1$, is similar to the structure reported for the anhydrous compound.[18] The N–H proton of the Et_3NH^+ group is involved in N–H···O bonding to the lattice water. The In–S distances are normal and In(1) has distorted tetrahedral symmetry as revealed by the S–In–S angles.

Thermal decomposition and pyrolysis studies show that the compound decomposes to In_2S_3 in mainly two steps. The first involves the removal of the lattice water (42–94 °C) followed by decomposition of the compound (130–400 °C). X-Ray powder diffraction measurement on the residue obtained from thermolysis of the compound, at 300 °C and under a dynamic vacuum of 0.5 Torr, indicated pure tetragonal In_2S_3 (JCPDS No. 25–390).

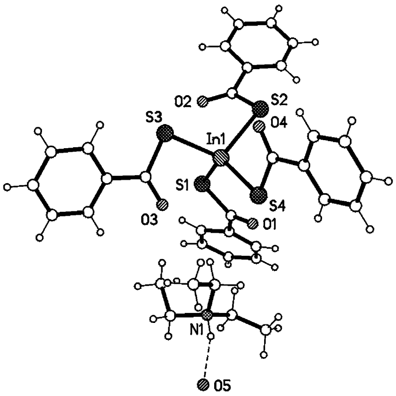

Fig. 1 Structure of **1**. Selected bond distances (Å) and angles (°): In(1)–S(1) 2.470(2), In(1)–S(2) 2.481(2), In(1)–S(3) 2.475(1), In(1)–S(4) 2.465(2); S(1)–In(1)–S(2) 104.29(7), S(1)–In(1)–S(3) 104.70(6), S(1)–In(1)–S(4) 117.99(6), S(2)–In(1)–S(3) 110.97(5), S(2)–In(1)–S(4) 103.81(5), S(3)–In(1)–S(4) 114.65(6). H-bond parameters: O···H 1.97 Å, O···N 2.860(8) Å; N–H···O 164°.

Compound **1**, which resembles $[HL][In(SC(O)Me)_4]$ reported by Hampden-Smith and coworkers,[17] is expected to sublime at low pressure and hence was thought to be a suitable candidate to produce thin films of In_2S_3 using the CVD technique.§ CVD experiments conducted on Ni coated silicon substrates using the precursor **1** show the deposition of crystalline In_2S_3 thin films. The SEM in Fig. 2 shows an image of crystalline facets with good coverage attained after 10 min of growth time. The formation of stoichiometric In_2S_3 has been substantiated by XRD and XPS of the thin films. XPS show peaks at 444.9 and 161.9 eV corresponding to the In 3d and S 2p binding energies of In_2S_3. The grazing angle thin film XRD pattern of β-In_2S_3 is shown in Fig. 3(a). All of the peaks could be indexed to a body centred tetragonal lattice with cell constants $a = b = 7.555$ Å, $c = 32.053$ Å, which are close to the reported data for In_2S_3. Preferred orientation along the (109) plane could be observed.

However if copper-coated silicon was used as the substrate during growth using **1**, stoichiometric $CuInS_2$ was found to be deposited instead of In_2S_3. Fig. 4(a) shows the crystalline facets

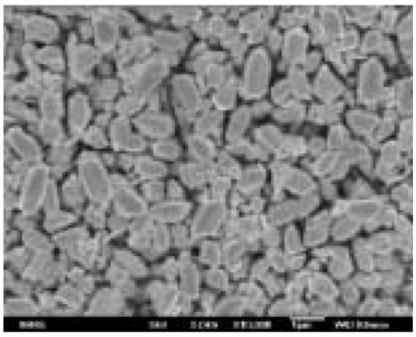

Fig. 2 SEM image of In_2S_3 film on a Ni–Si substrate.

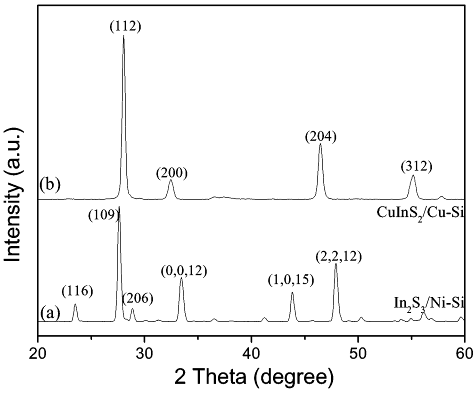

Fig. 3 Grazing angle X-ray diffraction of (a) In_2S_3 thin film on a Ni-Si substrate and (b) $CuInS_2$ thin film on a Cu–Si substrate.

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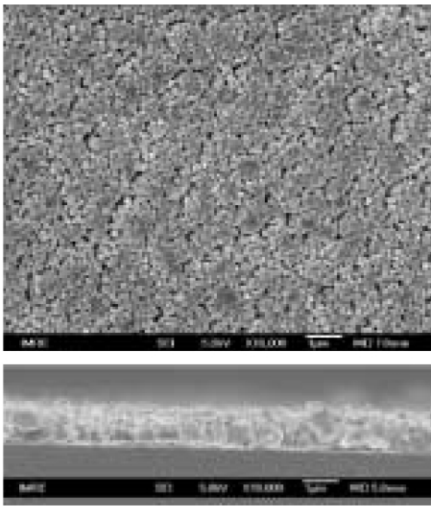

Fig. 4 SEM image of $CuInS_2$ thin films grown on a Cu–Si substrate: top view (top) and side view (bottom).

observed in SEM while the thickness of the film was measured to be ~1 μm (Fig. 4, side view). The grazing angle thin film XRD in Fig. 3(b) shows only the peaks characteristic of the $CuInS_2$ phase with no evidence of segregation of Cu_2S.

TEM diffraction of the $CuInS_2$ film observed along the [110] zone axis showing strong Bragg reflections at 004, 220, 112 which is typical of perfectly ordered chalcopyrite structure, as shown in Fig. 5. Rutherford backscattering measurements¶ show that the composition of the film is homogeneous within 1 μm and stoichiometric for $CuInS_2$ (Cu : In : S = 0.24 : 0.26 : 0.50). Therefore the result clearly indicates that the heterogeneous reaction of **1** with copper affords a more efficient route for the growth of stoichiometric, highly ordered $CuInS_2$ films.

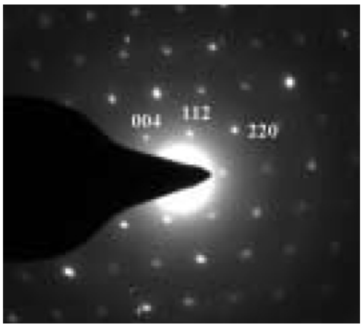

Fig. 5 Selected area diffraction pattern of $CuInS_2$ along the [110] zone axis.

It appears that the vapors of **1** or its decomposed fragments such as $[In(SC(O)Ph)_3]$ have reacted with the Cu metal to form the pure ternary sulfide films. This reaction is metal-specific because similar reaction conditions on nickel does not produce the ternary counterpart. It appears that the observed differences in the reactivity of Cu and Ni metals towards the vapors of **1** may be attributed to the difference in their redox properties.

The implications of this unprecedented heterogenous reaction are as follows. This new route may open the door for deposition of thin films where suitable precursor material is not available. The adherence of the thin films thus obtained may be better than those obtained by other methods. Further characterization and investigation on I–III–VI_2 systems are under progress.

Interestingly, $CuInSe_2$ thin films have been obtained by treating films of Cu–In alloy with H_2Se or other chalcogenating agents.[19] However, the reported procedure involves the usage of toxic substances (*e.g.* H_2Se) and leads to formation of various crystalline phases along with the formation of thin films of $CuInSe_2$ (*e.g.* In_6Se_7, $Cu_{2-x}Se$, InSe, $Cu_{11}In_9$).

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Notes and references

† A creamy white precipitate was formed when $InCl_3$ (0.20 g, 0.90 mmol) was allowed to react with NaSC(O)Ph, formed *in situ* by reacting NaOH (0.11 g, 2.70 mmol) and PhC(O)SH (319 μL, 2.70 mmol), in 30 mL of water. The solution was stirred for about 30 min and then $[Et_3NH]^+[PhC(O)S]^-$ in CH_2Cl_2 (15 mL) (prepared by reacting 106 μL of PhC(O)SH and 126 μL of NEt_3) was added. The yellow CH_2Cl_2 layer was separated and layered with light petroleum (bp 35–60 °C) to obtain a cream colored crystalline precipitate almost immediately. The compound was filtered off, washed with cold MeOH and Et_2O and dried under vacuum. Yield 0.62 g (89%). Anal. Calc. for $C_{34}H_{36}O_4S_4InN\cdot H_2O$: C, 52.10; H, 4.89; N, 1.79. Found: C, 51.78; H, 4.69; N, 2.28%. ^1H NMR ($CDCl_3$), δ 1.20 (t, 9H, CH_3CH_2, J 7.6 Hz), 3.22 (q, 6H, CH_3CH_2, J 10.9 Hz), 7.30–8.09 (m, 20H, C_6H_5). ^{13}C NMR ($CDCl_3$), δ 8.61 (CH_3CH_2), 46.84 (CH_3CH_2), 127.84 ($C^{2/3}$ of Ph), 128.68 ($C^{2/3}$ of Ph), 132.28 (C^4 of Ph), 139.41 (C^1 of Ph), 202.63 (PhCOS).

‡ Single crystals of the compound **1** were grown by slow diffusion of light petroleum (bp 35–60 °C) in to a $CHCl_3$ solution of the compound. *Crystal data* for **1**: orthorhombic, space group, $P2_12_12_1$; a = 12.9124(6), b = 12.9187(7), c = 21.561(1) Å, Z = 4, V = 3596.6(3) Å^3; D_c = 1.447 g cm^{-3}; $R1$ = 0.0434; $wR2$ = 0.1029, χ = −0.01(3). CCDC reference number 183392. See http://www.rsc.org/suppdata/cc/b2/b203156f/ for crystallographic data in CIF or other electronic format.

§ CVD was carried out by thermally evaporating the single source precursor **1** from a boron nitride cup in a vacuum reactor with a dynamic vacuum of 1×10^{-5} Torr. The boron nitride cup was maintained at 100 °C. The substrates were prepared by sputtering 1000 Å of nickel or copper films on silicon. The substrate temperature was maintained at 400 °C during growth.

¶ RBS meaurements were carried out using 2 MeV protons with Singletron accelerator at the Research Center for Nuclear Microscopy. The composition of the films were simulated using the SIMNRA code.

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