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Preparation of Copper-Indium-Sulfide Thin Films by Solution Pyrolysis of Organometallic Sources

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Thin films of copper-indium-sulfide ($CuInS_2$) were prepared by solution pyrolysis technique using a solution of diisobutylindium propylthiolate-copper bis(dibutyldithiocarbamate) in *p*-xylene at 250-350 °C. $CuInS_2$ films obtained were characterized by SEM, XRD, and X-ray microanalysis and optical gap of about 1.43 eV was measured.

Ternary chalcopyrites such as copper indium chalcogenide ($CuInS_2$ and $CuInSe_2$) are most promising optoelectronic materials.[1)] Meanwhile, thin films of $CuInS_2$ have been deposited by several techniques: vacuum evaporation,[2)] spray pyrolysis,[3)] chemical vapor deposition (CVD),[4)] sputtering,[5)] chemical transport,[6)] chemical bath deposition,[7)] and liquid phase epitaxy.[8)] Among these thin film techniques, spray pyrolysis has gained momentum in recent years owing to its successful use in the preparation of large-area photovoltaics and solar cells.[3)] However, spray pyrolysis generally contains a difficulty in the control of copper-to-indium and metal-to-sulfur ratios and a considerable low yield of the films. Thus, we attempted to produce $CuInS_2$ films by a solution pyrolysis (printing) method using organometallic sources such as diisobutylindium propylthiolate-copper bis(dibutyldithiocarbamate) ($Bu^i{}_2InSPr^n$-$Cu(Bu^n{}_2dtc)_2$) aiming to develop a more effective process.

Thermal analysis data showed that an equimolar mixture of $Bu^i{}_2InSPr^n$ [9)] and $Cu(Bu^n{}_2dtc)_2$[10)] decomposed up to 320 °C to afford chalcopyrite $CuInS_2$ powders. Thus, we attempted to prepare $CuInS_2$ films on a glass substrate using a *p*-xylene solution of $Bu^i{}_2InSPr^n$ and $Cu(Bu^n{}_2dtc)_2$ (concentration, 5 wt-% each) at 250-500 °C for 1 h under Ar atmosphere.[11)] Film compositions were determined by means of X-ray fluorescence analysis and the results obtained are shown in Fig. 1. Both ratios of In/Cu and S/Cu decreased with temperature and stoichiometric composition seemed to be achieved at 300-350 °C. Observation by XRD (Cu K_α) showed a mono phase consisting of chalcopyrite structure as shown in Fig. 2, however, the specimen obtained at 350 °C contained other phase(s).

These results indicated that $CuInS_2$ films was conveniently prepared by the solution pyrolysis of organometallic sources even at 350 °C. Further, SEM micrographs showed that the films were polycrystalline and that the grain size was in the range of 50-100 nm as shown in Fig. 3. The grain size was slight smaller than those obtained by chemical transport[6b)] and sputtering,[5a)] but was similar to that by spray pyrolysis.[3d,e)] The films obtained were extremely adherent to the glass substrate and black in appearance. The absorption edge was measured by uv-visible spectroscopy and the optical band gap was estimated to 1.43 eV. In conclusion, it is found that the organoindium thiolate and copper dithiocarbamate complex is an effective source for preparation of $CuInS_2$ films.

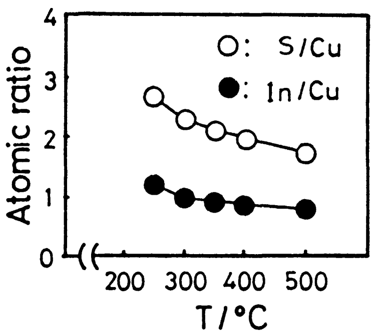

Fig. 1. Correlation between pyrolysis temperature and atomic ratios in as-deposited $CuInS_2$ films.

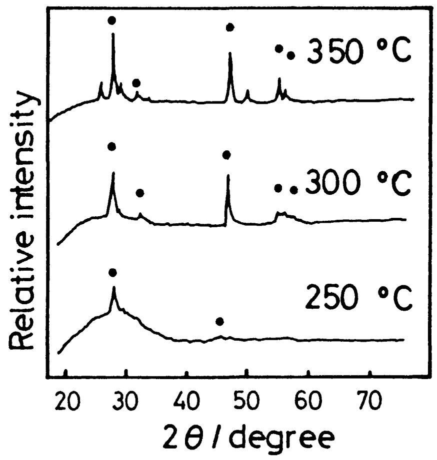

Fig. 2. X-Ray diffraction patterns of obtained $CuInS_2$ films. Dots indicate the peaks assignable to chalcopyrite $CuInS_2$ (JCPDS No. 32-339)

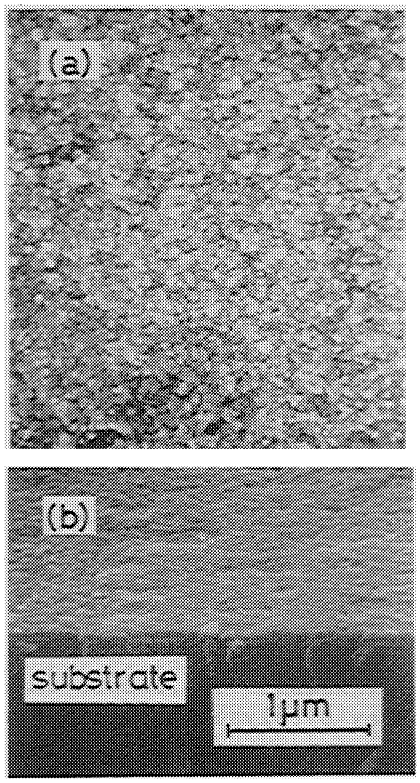

Fig. 3. SEM profiles of (a) surface and (b) cross section of the $CuInS_2$/glass specimen prepared at 300 °C.

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