The preparation of Cu(In,Al)S$_2$ films by direct reduction and sulfuration of the oxide precursors

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We report the preparation of Cu(In,Al)S$_2$ (CIAS) films by direct reduction and sulfuration of the oxide precursors, and propose that this is a promising approach for application in solar cells. The CIAS films with a single chalcopyrite phase clearly show a "sandwich" structure. Typical near-stoichiometric slightly S-poor films with two energy band gaps ($E_{g1} = 1.0$ eV, $E_{g2} = 1.4$ eV) are also obtained, which shows that the sulfuration process is incomplete and that the E_g can be increased by alloying aluminum and sulfur.
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CuInSe$_2$ (CIS) and related compounds are suitable materials for absorber layers in high-efficiency thin-film solar cells [1–3]. The E_g of CIS can be increased to match the solar spectrum for higher efficiency by alloying group III or VI elements. Significant work has been reported on the effect of the increased E_g by addition of gallium to CIS to create Cu(In,Ga)Se$_2$ (CIGS) films and devices [4,5]. Currently, the highest conversion efficiency obtained for CIGS solar cells is 19.9% [4]. The E_g of CIGS can be varied from 1.0 to 1.7 eV. However, with E_g greater than 1.3 eV the efficiency of CIGS devices is limited by degradation of the electronic properties of the CIGS layer, leading to a decrease in the junction quality factor [6,7].

Cu(In,Al)Se$_2$ (CIASe) covers a wide E_g range from 1.04 to 2.67 eV; this material is much cheaper and requires smaller alloy concentrations than the gallium alloys to achieve a comparable band gap [8–10]. It has therefore been considered as an alternative to wider band gap CIGS solar cells. CIASe laboratory-scale device efficiency has reached as high 16.9% using a co-evaporation process [11]. Other sputtering methods have also been reported for depositing CIASe films [10,12]. However, vacuum approaches suffer from drawbacks, including complexity, high production costs and difficulty in scaling up—these are the main problems facing commercialization of thin-film solar cells.

In this regard, significant work has been reported on the development of the low-cost non-vacuum coating techniques for CIGS deposition [13–15]. However, the preparation of CIASe films by non-vacuum methods have rarely been reported in the literature. Meanwhile, the substitution of selenium by sulfur is recommended for safety reasons: selenization is much more toxic and complicated compared to sulfuration. Hence, an attempt has been made to prepare CIAS films using this potential low-cost non-vacuum method. First, particles of CuO, Al$_2$O$_3$ and In$_2$O$_3$ are synthesized by a simple liquid-phase chemical method. Next, the oxide precursor films are deposited by spin-coating the slurry of oxide particles and reduced to CIA alloy films. Finally, the CIAS films are produced via a sulfuration process. To the best of our knowledge there have been no previous reports of the preparation of the CIAS films by a non-vacuum method of this type. The structure and optical properties of the CIAS films are also investigated.

The CIAS films were prepared by direct reduction and sulfuration of the oxide precursors. First, particles of CuO, Al$_2$O$_3$ and In$_2$O$_3$ were synthesized by a liquid-phase chemical method. In a typical synthesis, solutions A, B and C were prepared by dissolving the required amount of CuSO$_4$·5H$_2$O, NaOH and Na$_2$CO$_3$ in deionized water, respectively. Then solution B and solution C were added into solution A under stirring. After precipitation, washing and filtration, the powder

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was heated to 350 °C for 1 h and then centrifuged and washed several times with deionized water. Using the same route, $In_2(SO_4)_3$ solution D and NaOH solution E were mixed under stirring. After precipitation, washing and filtration, the powder was heated to 700 °C for 2 h and then centrifuged and washed several times with deionized water. Then solution F, including the required amount of Na_2CO_3, was added into solution G including the required amount of $AlCl_3$ under stirring. After precipitation, washing and filtration, the powder was heated to 500 °C for 2 h and then centrifuged and washed several times with deionized water. Second, the requisite amounts of CuO, Al_2O_3 and In_2O_3 particles, a suitable thickening agent (ethyl cellulose) and dispersant (polyethylene glycol) were selected to formulate the slurry with suitable viscosity. The precursor layers were deposited by spin-coating the precursor slurry. The sample was heated to remove solvent and burn the organic additive. The precursor films were then reduced to CIA alloy films under a H_2/Ar atmosphere. Finally, the pretreated films were sulfurized in a two-zone furnace with a quasi-closed quartz crucible under a vacuum furnace of 3×10^{-2} Pa. In order to avoid oxidation, we argon washed the chamber three times. The sulfuration process was performed at 500 °C for 1 h with sulfur vapor evaporated at 300 °C.

The phase composition and the crystal structure of the films were determined by X-ray diffraction (XRD, D/Max-rA). The morphology of the films was observed by field emission scanning electron microscopy (FES-EM, JEOL-JSM-6700F). The composition of CIAS films was measured by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The optical absorption spectrum was recorded on a UV–vis 365-type spectrophotometer in the range 300–1500 nm.

Figure 1a–c shows the XRD patterns of the CuO, Al_2O_3 and In_2O_3 particles produced by the liquid-phase chemical method, respectively. It is found that all the oxide precursors, including CuO, Al_2O_3 and In_2O_3, have a single-phase structure, and no peaks are f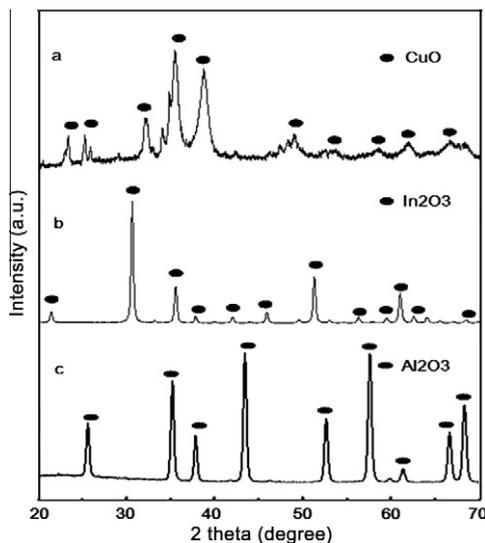ound from any other phases. Many other techniques have been used to synthesize the oxide precursors, such as ball milling technology, combustion method and solid-state reaction [15,16]. However, these methods are usually time-consuming, more complicated and tend to produce impurities. In our study, highly pure oxide precursors can be obtained by this simple, low-cost, liquid-phase chemical method, which is very suitable for large-scale commercial manufacturing.

Figure 2a and b shows the XRD patterns of CIA alloy films and CIAS films, respectively. After spin-coating, pretreatment and reduction, it can be observed that the CIA alloy films show predominantly Cu_9In_4, $Cu_{11}In_9$ and AlCu phases (Fig. 2a). As shown in Figure 2b, the CIAS films with a single chalcopyrite structure have the preferred (1 1 2) orientation after sulfuration of the CIA alloy films. The other prominent peaks observed correspond to the (2 0 4)/(2 2 0) and (1 1 6)/(3 1 2) phases. In addition to these commonly observed orientations, weak orientations such as (1 0 3), (2 1 1) and (0 0 8) are also observed in the XRD pattern, distinguishing the chalcopyrite phase from the sphalerite phase. All peaks observed on the patterns agree well with the diffraction lines in the single-phase chalcopyrite structure of CIAS, and no peaks are found from any other phases.

Planar and cross-sectional SEM micrographs of CIAS films are shown in Figure 3a and b, respectively. It can be seen that the CIAS films are composed of closely packed particles interspersed with voids after sulfuration. The porous nature of particle-derived films has been previously observed [17]. The SEM image clearly shows three layers: the glass substrate, an intermediate small-grained layer, and a top large-grained layer. The sulfuration process results in the growth of CIAS particles up to micron levels in grain size only in the upper parts of the layer with remaining small nanoparticles in the intermediate parts. This "sandwich" structure has also been reported by other groups [17,18], and can be resolved by increasing the sulfuration time or by increasing the sulfur vapor pressure.

The composition of the CIAS films is determined by EDS. The ratio of Cu/(In + Al)/S = 23.34:(26.56 + 4.69):45.41 is close in composition to 1/1/2 and Al/(In + Al) = 0.15, which is consistent with that in the raw materials and shows a slightly S-poor film. This sulfuration process is clearly incomplete due to the lack of the reaction force of the sulfur vapor; this can be solved by increasing the sulfuration time or by increas-
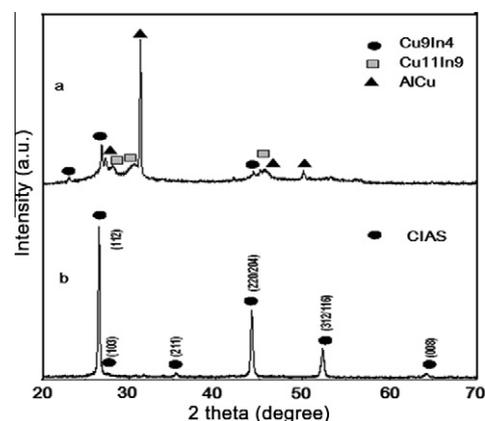

Figure 1. XRD pattern of oxide particles: (a) CuO, (b) In_2O_3 and (c) Al_2O_3.

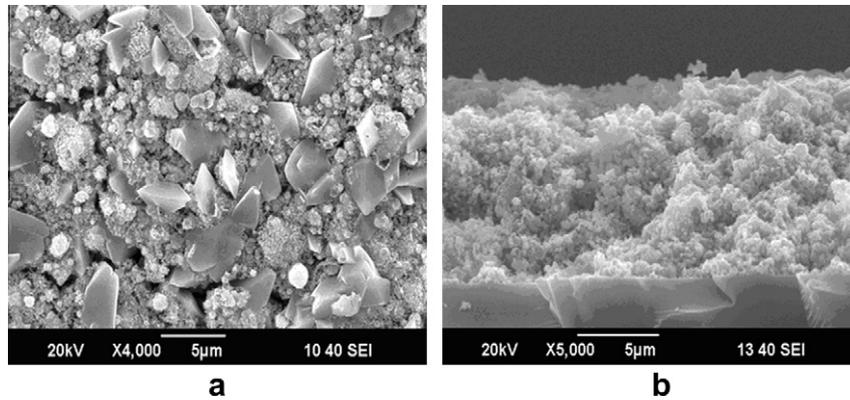**Figure 2.** XRD pattern of (a) CIA alloy films and (b) CIAS films.

Figure 3. Planar (a) and cross-sectional (b) SEM micrographs of CIAS films.

ing the sulfur vapor pressure. This phenomenon is perfectly in accordance with the results of the SEM analysis. Finally, a typical near-stoichiometric slightly S-poor CIAS film is obtained in our research.

The optical absorption spectra were recorded on a UV–vis 365-type spectrophotometer in the range 300–1500 nm. Figure 4 shows the photon energy dependence of the absorption coefficient for CIAS films. An absorption coefficient exceeding 10^5 cm^{-1} is obtained by absorption spectroscopy measurement. As is widely known, CIAS films are direct-gap semiconductors with the valence-band maximum and conduction-band minimum at $k = 0$. Hence, an E_{g1} of about 1.0 eV and an E_{g2} of about 1.4 eV for CIAS films are obtained by absorption spectroscopy; these values are achieved by calculating the midpoint of the absorption edge wavelength $\lambda_1 = 1240$ nm and $\lambda_2 = 886$ nm, respectively. The two E_gs indicate that the sulfuration process is insufficient, which is also consistent with the prior results. The E_{g2} of about 1.4 eV is much greater than that of CIS films at room temperature (1.04 eV) [19,20]. Hence, the E_g can be increased to match the solar spectrum for higher efficiency by alloying aluminum and sulfur.

In summary, CIAS films with a single chalcopyrite phase structure preferred (1 1 2) orientation have been prepared by direct reduction and sulfuration of the oxide precursors. It is found that all the oxide precursors, including CuO, Al$_2$O$_3$ and In$_2$O$_3$, produced by a simple liquid-phase chemical method show a single-phase structure. The sulfuration process results in the
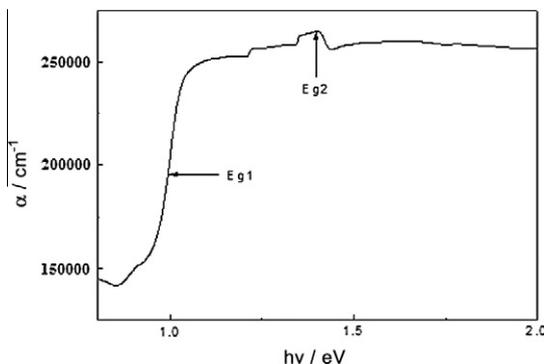
growth of CIAS particles up to micron levels in grain size only in the upper parts of the layer with remaining small nanoparticles in the intermediate parts. Typical near-stoichiometric slightly S-poor CIAS films with E_gs of about 1.0 eV and 1.4 eV are also obtained in our work, which indicates that the sulfuration process is incomplete and the E_g can be increased to match the solar spectrum for higher efficiency by alloying aluminum and sulfur. In brief, we have developed a simple, low-cost, non-vacuum process for fabrication of CIAS films, which indicates a promising approach for the large-scale industrial manufacture of solar cells.

[1] J. Guillemoles, U. Rau, L. Kronik, H. Schock, D. Cahen, Adv. Mater. 11 (1999) 957.
[2] K. Ramanathan, M.A. Contreras, C.L. Perkins, S. Asher, F.S. Hasoon, J. Keane, D. Young, M. Romero, W. Metzger, R. Noufi, J. Ward, A. Duda, Prog. Photovoltaics: Res. Appl. 11 (2003) 225.
[3] Q.J. Guo, S.J. Kim, M. Kar, W.N. Shafarman, R.W. Birkmire, E.A. Stach, R. Agrawal, H.W. Hillhouse, Nano Lett. 8 (2008) 2982.
[4] I. Repins, M.A. Contreras, B. Egaas, C. DeHart, J. Scharf, C.L. Perkins, B. To, R. Noufi, Prog. Photovoltaics: Res. Appl. 16 (2008) 235.
[5] M.A. Contreras, B. Egaas, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Hasoon, R. Noufi, Prog. Photovoltaics: Res. Appl. 7 (1999) 311.
[6] W.N. Shafarman, R. Klenk, B.E. McCandless, J. Appl. Phys. 79 (1996) 7324.
[7] U. Rau, M. Schmidt, A. Jasenek, G. Hanna, H.W. Schock, Sol. Energy Mater. Sol. Cells 67 (2001) 137.
[8] P.D. Paulson, M.W. Haimbodi, S. Marsillac, R.W. Birkmire, W.N. Shafarman, J. Appl. Phys. 91 (2002) 10153.
[9] Y.B.K. Reddy, V.S. Raja, Sol. Energy Mater. Sol. Cells 90 (2006) 1656.
[10] D.C. Perng, J.W. Chen, C.J. Wu, Sol. Energy Mater. Sol. Cells 95 (2011) 257.
[11] S. Marsillac, P.D. Paulson, M.W. Haimbodi, R.W. Birkmire, W.N. Shafarman, Appl. Phys. Lett. 81 (2002) 1350.

Figure 4. The photon energy dependence of the absorption coefficient of CIAS films.

[12] D. Dwyer, I. Repins, H. Efstathiadis, P. Haldar, Sol. Energy Mater. Sol. Cells 94 (2010) 598.

[13] S.J. Ahn, K.H. Kim, K.H. Yoon, Colloids Surf. A 313 (2008) 171.

[14] M. Kaelin, D. Rudmann, A.N. Tiwari, Sol. Energy 77 (2004) 749.

[15] P.F. Luo, R.Z. Zuo, L.T. Chen, Sol. Energy Mater. Sol. Cells 94 (2010) 1146.

[16] B. Vidhya, S. Velumani, A.A. Jesus, M.A. Arturo, R. Asomoza, J.A. Chavez-Carvayar, Mater. Sci. Eng. B 174 (2010) 216.

[17] S. Ahn, K. Kim, K.H. Yoon, Curr. Appl. Phys. 8 (2008) 766.

[18] L.S. Douglas, J.C. Calvin, A.F. Rebecca, W. Holm, K. James, J.M. Richard, M.J. Kim, A.P. Philip, N. Rommel, S.G. David, J. Electron. Mater. 27 (1998) 433.

[19] P.F. Luo, P.H. Yu, R.Z. Zuo, J. Jin, Y.K. Ding, J.D. Song, Y.T. Chen, Physica B 405 (2010) 3294.

[20] H.S. Soliman, M.M. Elnahas, O. Jamjoum, Kh.A. Mady, J. Mater. Sci. 23 (1988) 4071.