

Preparation and characterization of copper indium selenide powders and films

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Abstract A simple, less-hazardous and low cost co-deposition method for preparing $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ nanopowders was explored using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, InCl_3 and Se as the starting materials, and sodium borohydride (NaBH_4) as the reductant in deionized water. $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ films were prepared by pulling the indium tin oxide (ITO) coated glass substrates from $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ suspension. The suspension was prepared by dispersing the $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ nanopowders in the solution of dodecyl benzene sulphonate acid sodium salt. Morphology and structure of $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ nanopowders and films were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. The photo-absorption property was tested by UV-visible spectrometry. And the photoluminescence (PL) spectra were measured by fluorescence spectrophotometer.

Keywords Semiconductors · Nanopowders · Films · Co-deposition · Suspension

1 Introduction

CuInSe_2 (CIS) is a semiconducting I–III–VI₂ compound with chalcopyrite structure. It is a promising material for the fabrication of thin film solar cells due to its high absorption coefficient (10^5 cm^{-1}), direct band-gap energy ($E_g = 1.05 \text{ eV}$) and excellent thermal stability in air [1–7]. CIS can be made either n- or p-type under different

preparation conditions, so that homo- and heterojunctions can be fabricated. The homo- and heterojunctions have electrical properties that are suitable for photovoltaic devices. During the last decade, the efficiency of solar cells based on optimized CIS thin films has been reached up to 18% [8]. Many methods, such as RF-sputtering [9, 10], magnetron sputtering [11], single-source [12–14], multi-source vacuum evaporation [15], flash evaporation [10, 16, 17], quasi-flash evaporation [18], molecular beam epitaxy (MBE) [19], chemical spray [20], and electrodeposition [21, 22] have been explored to prepare polycrystalline CIS films.

In the present work, we report on the synthesis of $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ nanopowders by co-deposition method and $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ films prepared from $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ suspension, which, to our best knowledge, have not been reported yet.

2 Experiment

Se powders (99.95%) and other chemicals with analytical pure were used. Two 100-ml beakers both were filled with 40 ml deionized water. Put 0.02 mol Se powders into one of the beakers, and put NaBH_4 with 15 mol% excessive into the beaker to fully reduce the Se powders. Put 0.01 mol copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), 0.01 mol indium trichloride (InCl_3) into another beaker. Put both the beakers onto heaters ($\sim 50 \text{ }^\circ\text{C}$) and stirred by magnetic stirring. Se powders were reduced to Se^{2-} by NaBH_4 in deionized water. And then put the solutions of CuCl_2 and InCl_3 into the Se^{2-} solution with stirring, and dark product was quickly produced. Powder X-ray diffraction (XRD) analysis of the product after drying in vacuum shows that the product is $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$, rather than CIS. A certain amount of the $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ powder was ultrasonically

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dispersed into the 40 ml solution of dodecyl benzene sulphonic acid sodium salt with concentration of 0.01 mol/l to produce 0.1 mol/l $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ suspension. The indium tin oxide (ITO) coated glasses were first washed by deionized water for several times, dipped the ITO coated glasses into isopropyl alcohol for about 3 min, then put the glasses into deionized water and heated at about 50 °C for about 10 min, and finally dried in an oven. The polycrystalline $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ film was successfully prepared on the ITO coated glass substrate as follows: Pull the glass substrate from the $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ suspension and dried the substrate at 80 °C for 5 min. Repeated this process about ten times, and then the substrate was sealed and maintained at 200 °C for 2 h in Ar atmosphere. After cooling to room temperature naturally, $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ film on the substrate was fabricated. X-ray powder diffraction patterns of the products were obtained with D8 advance X-ray diffractometer with $\text{CuK}\alpha$ radiation. Transmission electron microscopy (TEM) images of the powders were taken with a JEM-1203 transmission electron microscope. The films were observed by scanning electron microscopy (JEOL JSM-5510LV). The photoabsorption property was tested by UV-Vis spectroscopy. The PL measurement was conducted on a fluorescence spectrophotometer (LS-55) excited by a 229-nm line at room temperature.

3 Results and discussion

Figure 1 shows the typical XRD patterns of the powders and films prepared. The XRD pattern for the powders only shows two broad peaks, indicating the crystallinity of the powders is not so good. The crystallinity of the films is

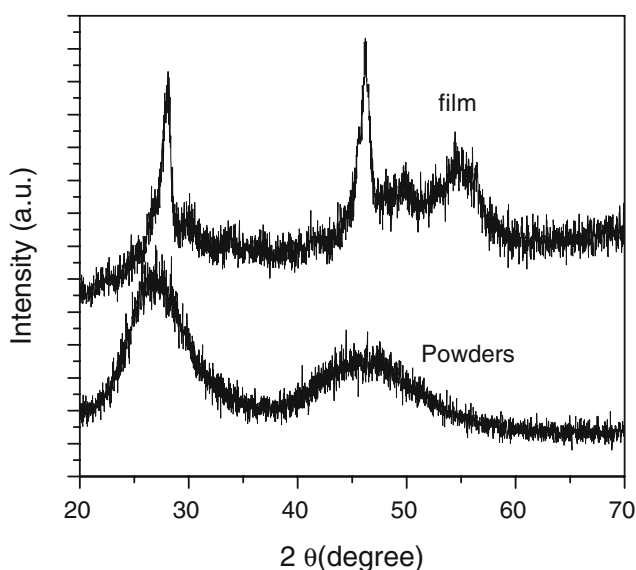
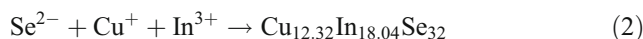
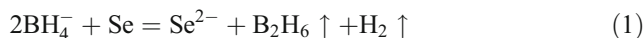


Fig. 1 XRD patterns for the $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ powders and $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ film

better than that of the powders. The peaks of the powders and films correspond to the reported data for $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ (JCPDS card file, no. 79-1809). The composition of the products is deviated from the CuInSe_2 as we expected (the reason for this will be explained in the following text). The grain size of the $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ powders calculated by Scherrer's equation based on the XRD line width is 11 nm.

Figure 2 shows TEM image of $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ powders which are mainly spherical particles with grain size about 8–15 nm, in agreement with the result calculated from the Scherrer's equation.

It is known from the redox potentials ($E_{\text{Se}^0/\text{Se}^{2-}}^0 = -0.924\text{V}$, $E_{\text{H}_2\text{O}/\text{BH}_4^-}^0 = -1.24\text{V}$) that Se in the deionized water can be reduced into Se^{2-} by NaBH_4 . In our experiment, CuCl_2 was used as the starting material, and the valence of Cu is +2, while in the product, $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$, the valence of Cu is +1. Therefore, we deduce that some of the Cu^{2+} was reduced into Cu^+ by the remaining NaBH_4 in the solution, and finally $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ formed. The reaction process is proposed as follows: the Se powders were reduced into Se^{2-} by NaBH_4 , and the Se^{2-} directly reacted with Cu^+ and In^{3+} into $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ at room temperature. The formation mechanism can be expressed as follows:



In terms of large-scale applications, one of the most promising preparation techniques was based on two-step deposition of Cu and In metals followed by selenization of the precursor using H_2Se [23–26] or Se vapors [27–29]. This process is quite simple and does not need expensive apparatus, such as MBE or metal organic chemical vapor deposition (MOCVD). However, H_2Se gas is very toxic and hazardous; the time-weighted average threshold limit value (TLV-TWA) of H_2Se is 0.05 ppm and it is usually stored in high-pressure ($\sim 20 \text{ gf/cm}^2$) cylinders. Compared with this method, our method has a few advantages: the raw materials are easier to store and cheaper, the powders can be synthesized at room temperature, the average grain size of the powders is smaller, and the most important thing is that no toxic materials are used.

The UV-vis absorption spectrum of the $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ powders is shown as in Fig. 3. The absorbance is excellent in the range of UV and visual light. The absorbance in the range of 200 to 400 nm is much better than that in the range of 400 to 1,100 nm. This phenomenon may be attributed to the size effect of the nanopowders.

SEM image of the $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ film (Fig. 4) shows a uniform surface. The surface of the film is quite smooth. The thickness of the films is estimated to be about 1.5 μm .

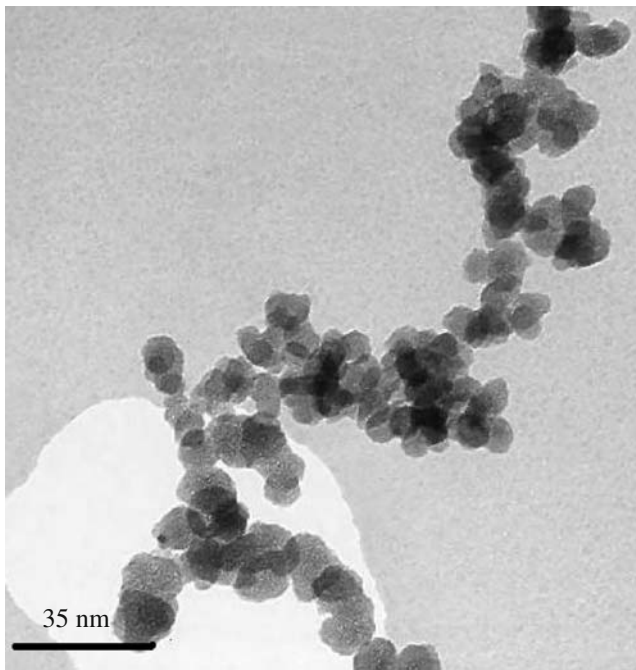


Fig. 2 TEM image of the $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ powders

Figure 5 shows that the PL spectrum of the film excited at 229 nm. There are three band emissions: the purple emission at 384 nm (3.23 eV), the blue emission at 469 nm (2.65 eV) and the red emission at 687 nm (1.81 eV). The emission at 458 nm (3.76 eV) is the double excitation wavelength. The PL intensity of the three band emissions is weak as shown in Fig. 5, indicating that this material is not suitable to be used as PL material. In point of PL mechanism of the $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ film, it may be

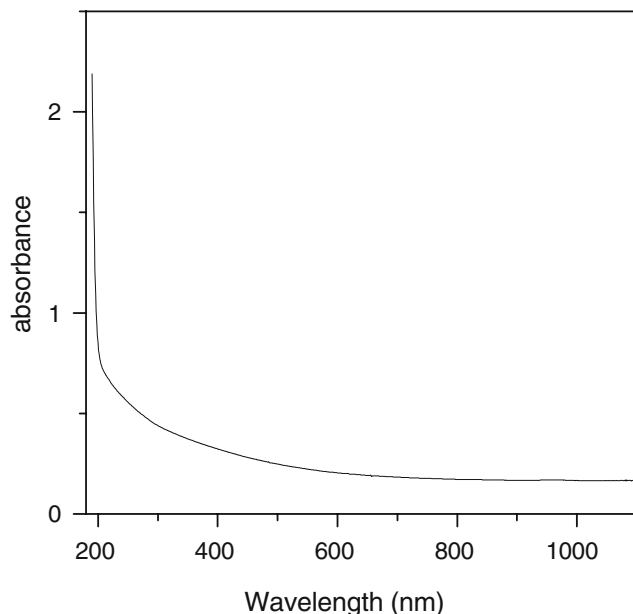


Fig. 3 Wavelength dependence of absorbance of the $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ powders

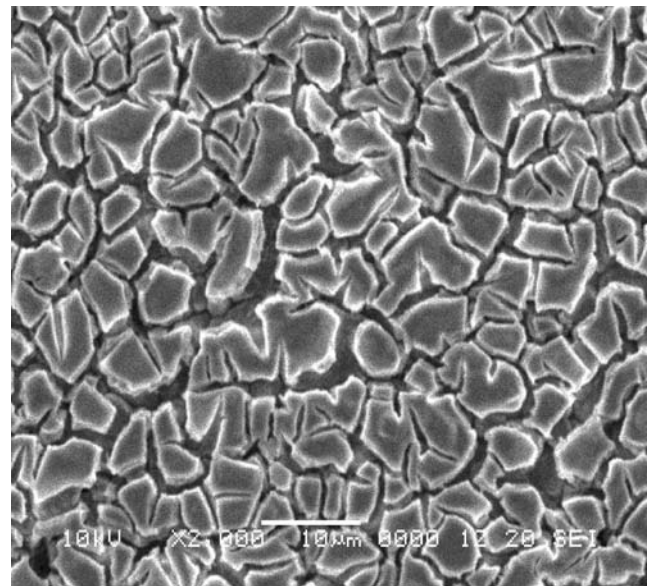


Fig. 4 SEM image of the $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ film

originated from the recombination of an electron on a donor formed by Se vacancies and a hole on an acceptor formed by Cu or In vacancies. The holes and electrons recombined via a self-trapped excitation to emit photons, hence purple, blue and red emissions appear.

4 Conclusions

A new less-hazardous and low cost method for preparation of $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ powders and films was developed.

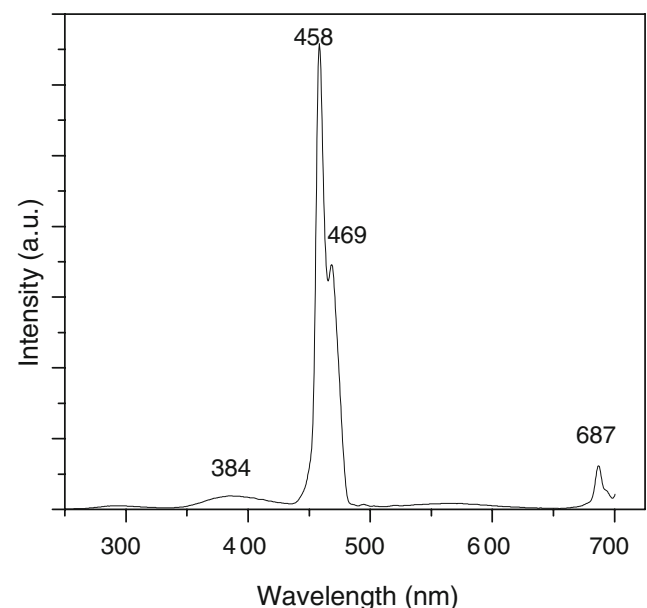


Fig. 5 Photoluminescence spectrum of the $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ film under excitation at 229 nm

The starting materials are cheap and easy to be obtained, and the reaction conditions are mild. The quality of the film prepared from the $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ powders is good. The photoabsorption property of the powders analyzed by UV-visible spectrometry is excellent, while the PL property of the $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ film is not so good, implying that the $\text{Cu}_{12.32}\text{In}_{18.04}\text{Se}_{32}$ powders could be used to fabricate solar cells.

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References

1. J.A. Thornton, D.G. Cornog, R.B. Hall, S.P. Shea, J.D. Meakin, J. Vac. Sci. Technol. **A2**, 307 (1984)
2. T.L. Chu, S.C. Lin, J. Yue, J. Electrochem. Soc. **31**, 2182 (1984)
3. R. Trykozko, R. Bacewicz, J. Filipowicz, Solar Cells **16**, 351 (1986)
4. J. Szot, U. Prinz, J. Appl. Phys. **66**, 6077 (1989)
5. D. Pottier, G. Maurin, J. Appl. Electrochem. **19**, 361 (1989)
6. J. Herrero, J. Ortega, Sol. Energy Mater. Solar Cells **19**, 53 (1990)
7. J.H. Schon, V. Alberts, E. Bucher, Thin Solid Films **301**, 115 (1997)
8. N. Nancheva, P. Docheva, N. Djourellov, M. Balcheva, Mater. Lett. **54**, 169 (2002)
9. R.R. Arya, R. Beaulieu, M. Kwietniak, J. Loferski, L.L. Kazmerski, J. Vac. Sci. Technol. **20**, 302 (1982)
10. N. Romeo, V. Canevari, G. Sberveglieri, A. Bosio, L. Zanotti, Solar Cells **16**, 155 (1986)
11. J.A. Thornton, T.C. Lommasson, H. Talieh, B.H. Tseng, Solar Cells **24**, 1 (1988)
12. L.L. Kazmerski, M.S. Ayyagari, F.R. White, G.A. Sanborn, J. Vac. Sci. Technol. **13**, 139 (1976)
13. V.K. Gandotra, K.V. Ferdinand, C. Jagadish, A. Kumar, P.C. Mathur, Phys. Status Solidi A **98**, 595 (1986)
14. M.M. EL-Nahas, H.S. Soliman, D.A. Hendi, K.H.A. Mady, J. Mater. Sci. **27**, 1484 (1992)
15. N.G. Dhere, M.C. Loureno, R.G. Dhere, L.L. Kazmerski, Solar Cells **16**, 369 (1986)
16. D. Sridevi, K.V. Reddy, Indian J. Pure Appl. Phys. **24**, 392 (1986)
17. H. Sakata, N. Nakao, Phys. Stat. Sol. A **161**, 379 (1997)
18. A. Ashida, Y. Hachiuma, N. Yamamoto, T. Ito, Y. Cho, J. Mater. Sci. Lett. **13**, 1181 (1994)
19. S.P. Grindle, A.H. Clark, S. Rezaie-Serej, E. Falconer, J. McNeily, L.L. Kazmerski, J. Appl. Phys. **51**, 5464 (1980)
20. Y.D. Tembhurkar, J.P. Hirde, Thin Solid Films **215**, 65 (1992)
21. R.N. Bhattacharya, K. Rajeshwar, Solar Cells **16**, 237 (1986)
22. C. Guilln, J. Herrero, J. Appl. Phys. **71**, 5479 (1992)
23. M. Terauchi, T. Negami, M. Nishitani, M. Ikeda, H. Wada, T. Wada, Solar Energy Mater. Solar Cells **35**, 121 (1994)
24. M. Marudachalam, H. Hichri, R. Klenk, R. Birkmire, W. Shafarman, J. Schultz, Appl. Phys. Lett. **67**, 3978 (1995)
25. V. Alberts, P. Molefe, Jpn. J. Appl. Phys. **39**, 1650 (2000)
26. K. Kushiya, Thin Solid Films **387**, 257 (2001)
27. K. Kushiya, A. Shimizu, A. Yamada, M. Konagai, Jpn. J. Appl. Phys. **34**, 54 (1995)
28. K. Reddy, I. Forbes, R. Miles, M. Carter, P. Dutta, Mater. Lett. **37**, 61 (2001)
29. S. Bandyopadhyaya, S. Roy, S. Chaudhuri, A. Pal, Vacuum **62**, 61 (2001)