Thermal-assisted chemical bath deposition and optical property of CuS films

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CuS films were fabricated by a chemical bath deposition process in an aqueous solution of cupric acetate, thiourea, and sodium ethylenediamine tetraacetate (EDTA-2Na) at different temperatures. The films were characterized by X-ray diffraction, atomic force microscopy, UV-vis spectrophotometry and luminescent spectrophotometry. The effects of deposition temperature and reaction time on the thickness, transmittance and band gap, and luminescence of the films were investigated. The deposition rate first increased with increase of temperature up to 75 ℃ and then was decreased at 100 ℃. The band gap of the films ranged from 2.41-2.72 eV that decreased with increased deposition temperature and deposition time, except for the films deposited at 100 ℃ which band gap first decreased and then increased with the time. We believe this simple chemical bath deposition technique can be further extended to the rapid fabrication of other semiconductor films

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1. Introduction

Copper sulfides (Cu_xS, x = 1–2) are significant binary compounds that attract much attention due to their wide range of applications in optical and electrical devices, such as photo thermal conversion, electroconductive electrodes, microwave shielding coatings, solar control coatings, dye-sensitized solar cells, potential nanometer-scale switch, cathode materials in lithium rechargeable batteries and some chemical sensors [1-6]. Additionally, it has recently been reported that CuS can transform into a superconductor below the 1.6 K because of its metallic conduction property [7].

Even though physical techniques are very suitable for synthesizing uniform and high quality films, they are also very expensive and consume large amounts of energy. Additionally, they inevitably destroy the film morphology at high temperatures above 500 ℃ [8]. On the other hand, chemical methods are economical and suitable for maintaining desired structures. Thus, to prepare CuS thin films with desired shapes and structures, many different chemical methods have been developed: the liquid–liquid interface reaction [9], chemical vapor deposition (CVD) [10], chemical vapor reaction (CVR) [11], electrochemical method [12], successive ionic layer adsorption and reaction (SILAR) [13], atomic layer deposition (ALD) [14], spray-ion layer gas reaction (ILGAR) [15], etc. Among them, chemical bath deposition (CBD) [16–18] tends to be a better mean to deposit CuS films with particular shape, orientation and thickness because of the advantages of having a variety of substrates (insulators, semiconductors and metals) for deposition, a large surface area, simplicity, and lower cost. However, chemical bath deposition takes a significant amount of time to achieve the appropriate film thickness. To enhance the deposition efficiency, microwave assistance has been introduced to the chemical bath deposition [19]. Currently, chemical bath deposition is generally carried out at room temperature, but higher temperatures can accelerate molecular motion and so enhance the deposition efficiency of the film.

In this paper, we present (i) a time-saving route for fabricating uniform CuS films with a simple chemical bath composition at the temperature higher than room temperature; (ii) the effects of deposition temperature and deposition time on the thickness and the optical property of the deposited films.

2. Experiment method

2.1. Fabrication of the film

The starting materials used were all analytic grade chemicals without any further processing. The bath solution was composed of 0.01 mole cupric acetate ($Cu(CH_3COO)_2.H_2O$), 0.015 mole thiourea ($SC(NH_2)_2$), 80 ml deionized water and 0.01 mole disodium ethylenediamine tetraacetate (EDTA-2Na, $C_{10}H_{14}N_2Na_2O_3$). The solution was homogenized by magnetic stirring in a beaker at room temperature for 0.5 h. In same time, commercial glass slides used as substrates were cleaned in acetone and methanol ultrasonically for

0.5 h and then rinsed with deionic water. Subsequently, the three solutions were separately heated from room temperature to 50 ℃, 75 ℃, 100 ℃ in furnace and maintained for 10 min, after which, three cleaned glass substrates were put vertically into each of the three solutions. After 0.5 h, 1.0 h, and 1.5 h of deposition, the films were successively taken out from the solutions, and rinsed with deionized water to remove the residual bath solution and loosely adhered CuS particles on the films and then naturally dried in air.

2.2. Characterization of the films

The structural phase of the deposited CuS films were identified at room temperature using an X-ray diffractometer (XRD, CuK$_{\alpha1}$, λ=0.15406 nm, Model No: D/Max-2200PC, Rigaku, Japan). The morphology and texture of the films were analyzed using atomic force microscopy (AFM, Model No: SPI3800N, Japan). The light transparent of the films were determined with a UV-vis spectrophotometer (Model No: 752N, China). The photoluminescence of the powders was measured on a luminescent spectrophotometer (Model no: F-4600, Hitachi, Japan).

3. Results and discussion

Fig. 1 shows the XRD patterns of the CuS films. The main phase of the films was identified as hexagonal covellite CuS (PDF#05-0464). The chemical process for the CuS film formation can be given by:

$$\text{EDTA-2Na}^{+}+\text{Cu}^{2+} = \text{EDTA-Cu}+2\text{Na}^{+} \tag{1}$$

$$\text{SC(NH}_2)_2+2\text{H}_2\text{O} = 2\text{NH}_4^{+}+\text{CO}_2+\text{S}^{2-} \tag{2}$$

$$\text{EDTA-Cu}+2\text{H}_2\text{O} = \text{EDTA}+\text{Cu}^{2+}+2\text{H}_2\text{O} \tag{3}$$

$$\text{Cu}^{2+}+\text{S}^{2-} = \text{CuS} \tag{4}$$

CuS has a very small solubility constant (Ksp=1.27× 10-36) and so is easily formed from the Cu^{2+} and S^{2-} ions in the aqueous solution. However, the Cu^{2+} can be chelated with EDTA, so the release rate of Cu^{2+} from the chelate compound EDTA-Cu could control the formation rate of the CuS. By optimization at 50 ℃, the molar ratio of EDTA-2Na: Cu^{2+}=1.0 was most effective to the deposition rate. The deposition temperature can accelerate the release rates of Cu^{2+} and S^{2-} from the EDTA-Cu and $SC(NH_2)_2$., and so affect the deposition of the film.

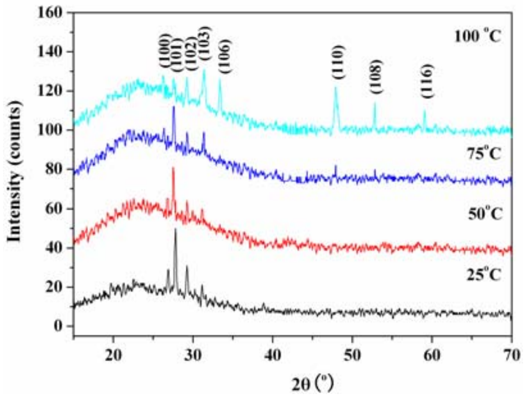

Fig. 1. XRD patterns of the CuS films deposited at different temperature for 1.5 h.

Fig. 2 shows AFM micrographs of the CuS films deposited at 50 ℃. The films were composed of uniform particles. With increasing deposition time, the average particle size increased and particle morphology tended to be rodlike. Fig. 3 shows The AFM micrographs of the CuS films deposited at 75 ℃ indicated that the film also showed increased average size and obvious tendency to rodlike particle morphology with increasing deposition time compared to the film deposited at 50 ℃. Fig. 4 shows The AFM micrographs of the CuS films deposited at 100 ℃ indicated that the average particle size had not obvious variation but the morphology was first rodlike and then changed to tetragonal and granular with increasing deposition time. The thickness of the films determined from AFM analysis are shown in Fig. 5. They were in range of 350-790 nm and varied with deposition time and deposition temperature. At room temperature (25 ℃), the thickness of the film deposited for 1.5 h was only ~62 nm. The CuS films with thickness of ~465 nm deposited by Xin et al [19] were achieved at room temperature for 8 h and at microwave heating for 40 min, and can not be further increased due to the equilibrium of two competing processes taking place in the deposition solution. The thermal assistant in 50-100 ℃ obviously accelerated deposition of the film. Fig. 5 indicated that the deposition rate appeared maximal at deposition temperature of 75 ℃. At lower temperature of 50 ℃, the release of Cu^{2+} anion from the EDTA-Cu was slower, and thus the deposition rate was lower. At higher temperature of 100 ℃, excessive Cu^{2+} anions in the solution inversely led to the too fast formation of CuS particle and undesirably large particles that was difficult to be tightly adhered on the film and so resulted in slower deposition rate of the film.

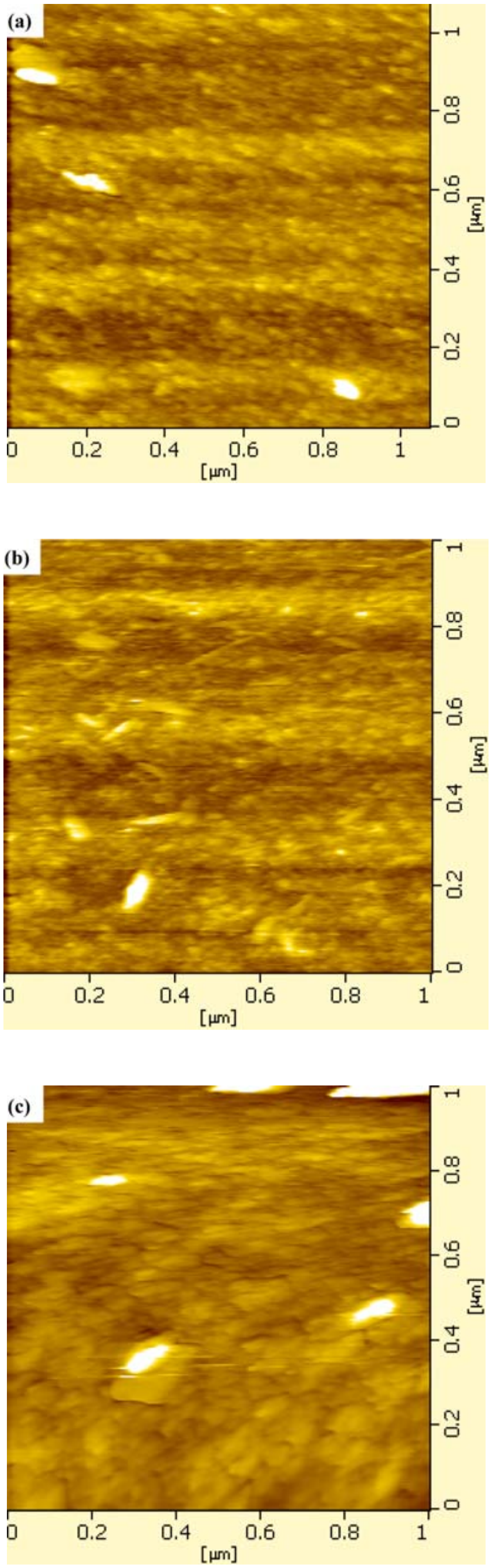

Fig. 2. AFM micrographs of the CuS films deposited at 50 ℃ for (a) 0.5 h, (b)1.0 h, and (c) 1.5 h.

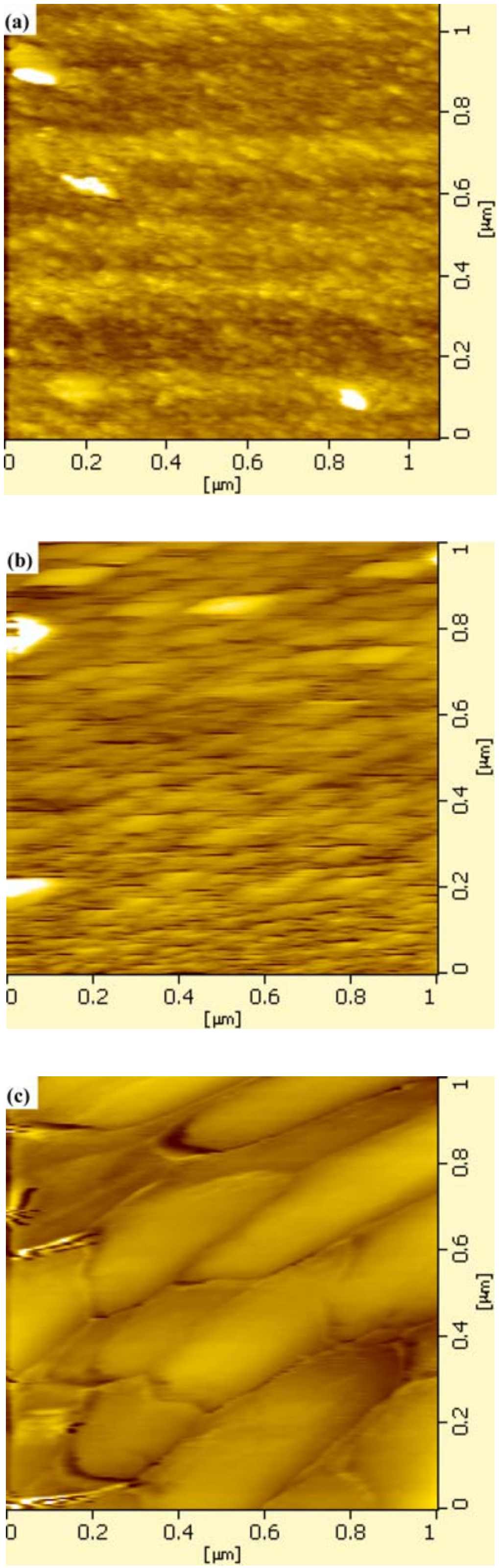

Fig. 3. AFM micrographs of the CuS films deposited at 75 ℃ for (a) 0.5 h, (b)1.0 h, and (c) 1.5 h.

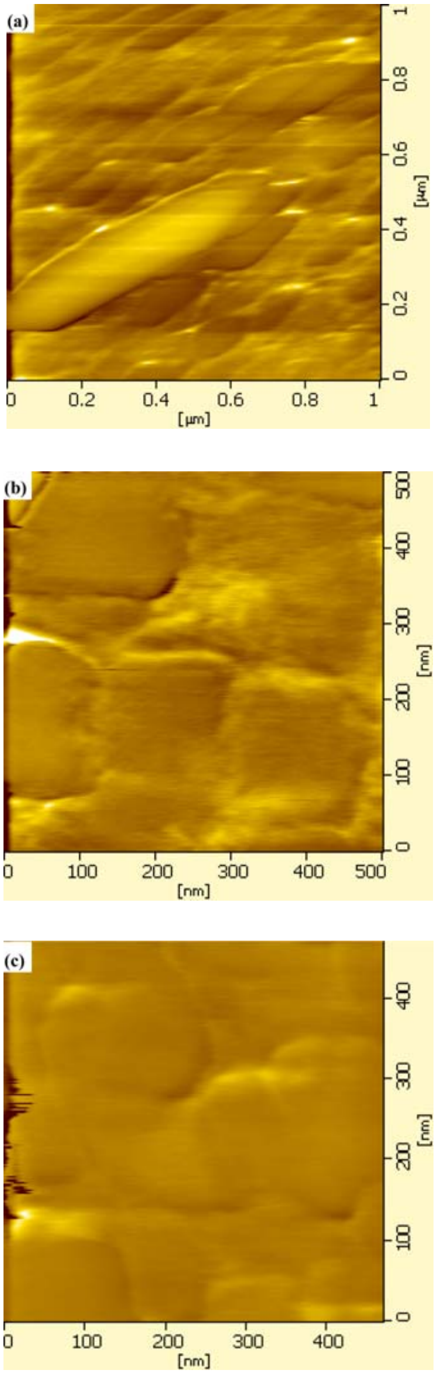

Fig. 4. AFM micrographs of the CuS films deposited at 100 ℃ for (a) 0.5 h, (b)1.0 h, and (c) 1.5 h.

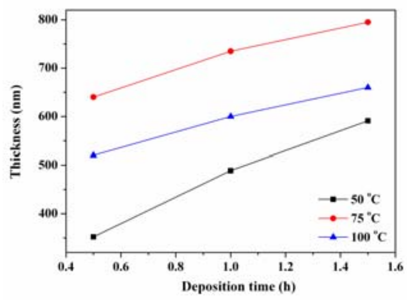

Fig. 5. Film thickness vs. deposition time.

Fig. 6 shows the transmittance spectra of the CuS films fabricated with different temperatures. The transparency of the films decreases with increasing the deposition time for each deposition temperatures. The films deposited at 75 ℃ showed the greatest decrease in transparency with deposition time, which was consistent with the increases of the film thicknesses as shown in Fig. 5.

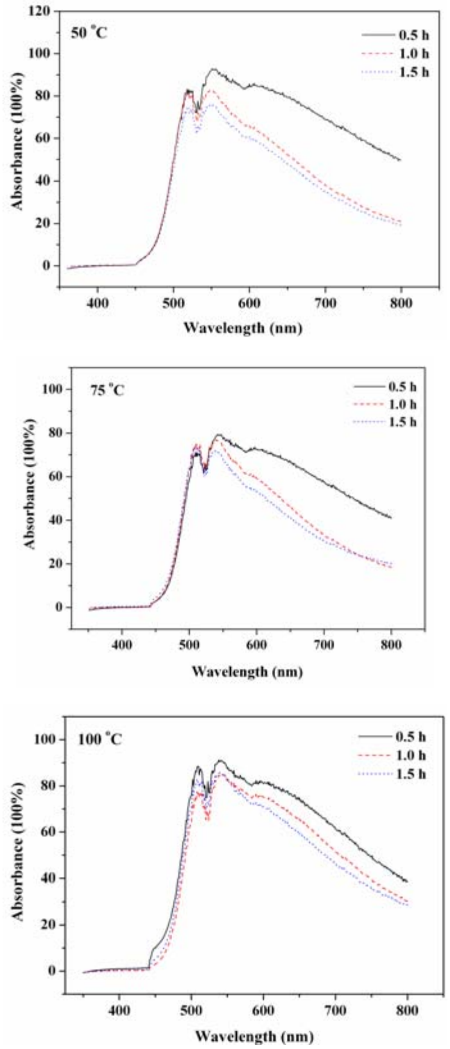

Fig. 6. Transmittance spectra of the CuS films.

CuS is considered as a direct band gap semiconductor, so the relationship between the adsorption coefficient (α) near the absorption edge and the optical band gap (Eg) for direct band transitions obeys the following formula [20]:

$$\left(\alpha h\nu\right)^2 = C\left(h\nu - E_g\right)$$

where $h\nu$ is photon energy and C is a constant. We assume

$$\alpha = \left(\frac{1}{d}\right)\left(\ln\frac{1}{T}\right)$$

where T is the transmittance and d is the film thickness. Fig. 7 shows the graphs of $(\alpha h\nu)^2$ vs. photon energy, $h\nu$, for the CuS thin films. The linear dependence of $(\alpha h\nu)^2$ on $h\nu$ at higher photon energies indicates that the CuS films are essentially direct-transition-type semiconductors. The straight-line portion of the curve, when extrapolated to zero, gives the optical band gap E_g. The E_g was in range of 2.41-2.72 eV which decreased with increasing deposition temperature and deposition time except for the films deposited at 100 ℃ that displayed increased bandgap when deposition time increased from 1.0 h to 1.5 h (Fig. 8). For comparison, Gadave and Lokhande [21] found an optical band gap of 2.40 eV for CBD deposited Cu_xS film from aqueous medium. Sartale and Lokhande [22] reported an optical band gap of 2.36 eV of SILAR deposited Cu_xS from nonaqueous medium. Puspitasari et al [18] reported an optical band gap of 2.8 eV for the CuS film prepared by a simple chemical method.

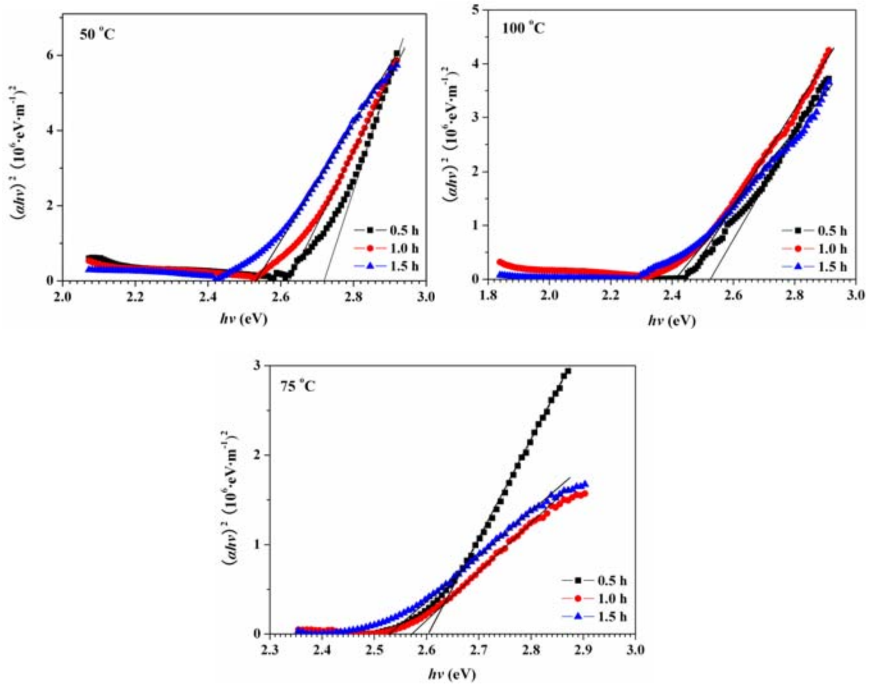

Fig. 7. Plots of $(\alpha h\nu)^2$ vs. $h\nu$ of the CuS films.

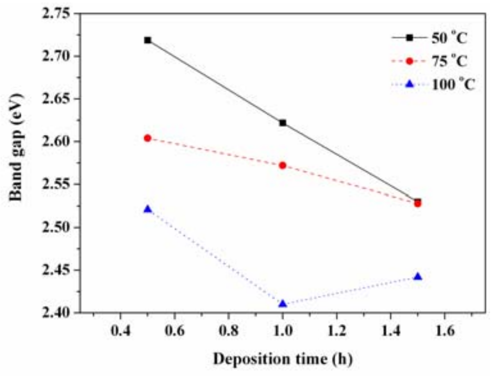

Fig. 8. Optical band gap of the films.

Fig. 9 shows the photoluminescence spectra of the CuS films deposited at different deposition temperaure. They were measured at monitor wavelength λ_{exc}=440 nm and excitation wavelength of λ_{em}=350 nm. The excitation peaks of the films deposited at 50 ℃, 75 ℃ and 100 ℃, were respectively centered at ~349.3−350.6 nm, ~335.9−337.7 nm and ~336.0−338.2 nm that decreased as increase in deposition time. The emission peaks of the films deposited at 50 ℃ were centered at ~443.9−445.2 nm that decreased with increasing the deposition time. The films deposited at 75 ℃ showed two emission peaks that were centered at ~411.6−413.2 nm and ~438.0−440.3 nm that decreased with increasing the deposition time. The films deposited at 100 ℃ showed two emission peaks that were centered at ~412.1−413.0 nm and ~438.0−440.3 nm that increased and then decreased with increasing the deposition time. These value are different from that of CuS nanorods (420, 450 and 462 nm [23], and 515 nm [24]) and nanoplates (339 nm [25]). According to them, various morphologies of CuS may be responsible for this different phenomenon of PL. The blue shifts of the films with variation of granolar to rodlike morphology is basically consistent with the results reported by Roy et al.[23].

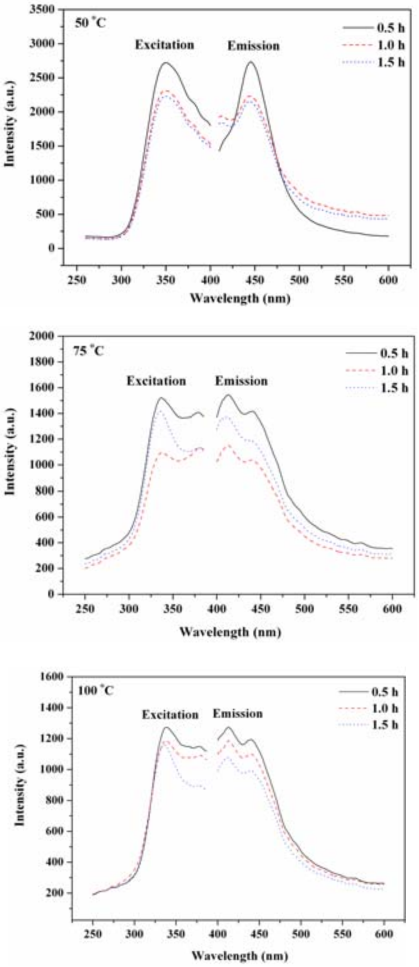

Fig. 9. Luminescence spectra of the films measured at λ_{exc}*=440 nm and* λ_{em}*=350 nm.*

4. Conclusion

The CuS semiconductor films were fabricated on a glass substrate in a simple chemical bath solution containing EDTA-2Na as the chelating agent. Thermal assistance was used to accelerate deposition. The effect of deposition temperature on the deposition efficiency and optical properties of the films were investigated. It was found that the thermal assistance in range of 50-100 ℃ obviously accelerated deposition of the film and the maximum deposition rate appeared at 75 ℃, at which the film thickness reached ~790 nm in 1.5 h. The optical band gap of the films was in range of 2.41-2.72 eV which decreased with increasing deposition temperature and deposition time except for the films deposited at 100 ℃ that displayed increased bandgap when deposition time increased from 1.0 h to 1.5 h.

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References

[1] I. Grozdanov, M. Najdoski, J. Solid State Chem. **114**, 469 (1995).
[2] L. Huang, P. K. Nair, M. T. S. Nair, R. A. Zingaro, E. A. Meyers, J. Electrochem. Soc. **141**, 2536 (1994).
[3] H. Lee, S. W. Yoon, E. J. Kim, J. Park, Nano Lett. **7**, 778 (2007).
[4] T. Sakamoto, H. Sunamura, H. Kawaura, T. Hasegawa, T. Nakayama, M. Aono, Appl. Phys. Lett. **82**, 3032 (2003).
[5] J. S. Chung, H. J. Sohn, J. Power Sources **108**, 226 (2002).
[6] A. A. Sagade, R. Sharma, Sens. Actuators B **133**, 135 (2008).
[7] K. Tezuka, W. C. Sheets, R. Kurihara, Y. J. Shan, H. Imoto, T. J. Marks, K. R. Poeppelmeier, Solid State Sci. **9**, 95 (2007).
[8] A. Bauger, J. C. Mutin, J. C. Niepce, J. Mater. Sci. **18**, 3041 (1983).
[9] C. N. R. Rao, K. P. Kalyanikutty, Acc. Chem. Res. **41**, 489 (2008).
[10] M. Kemmler, M. Lazell, P. O. Brien, D. J. Otway, J.-H. Park, J. R. Walsh, J. Mater. Sci. Electron. **13**, 531 (2002).
[11] K. J. Wang, G. D. Li, J. X. Li, Q. Wang, J. S. Chen, Cryst. Growth Des. **7**, 2265 (2007).
[12] T. Kuzuya, K. Itoh, M. Ichidate, T. Wakamatsu, Y. Fukunaka, K. Sumiyama, Electrochem. Acta **53**, 213 (2007).
[13] H. M. Pathan, J. D. Desai, C. D. Lokhande, Appl. Surf. Sci. **202**, 47 (2002).
[14] J. Johansson, J. Kostamo, M. Karppinen, L. Niinistö, J. Mater. Chem. **12**, 1022 (2002).
[15] C. H. Fischer, H. J. Muffler, M. Bar, T. Kropp, A. Schonmann, S. Fiechter, G. Barbar, M. C. Lux-Steiner, J. Phys. Chem. B **107**, 7516 (2003).
[16] K. D. Yuan, J. J. Wu, M. L. Liu, L. L. Zhang, F. F. Xu, L. D. Chen, F. Q. Huang, Appl. Phys. Lett. **93**, 132106 (2008).
[17] P. K. Nair, V. M. Garcia, O. Gomez-Daza, M. T. S. Nair, Semicond. Sci. Technol. **16**, 855 (2001).
[18] I. Puspitasari, T. P. Gujar, K. D. Jung, O. S. Joo, Mater. Sci. Eng. **B 140**, 199 (2007).
[19] Mudi Xin, Kunwei Li, Hao Wang, Appl. Surf. Sci. **256**, 1436 (2009).
[20] N. Serpone, D. Lawless, R. Khairutdinov, J. Phys. Chem. **99**, 16646 (1995).
[21] K. M. Gadave, C. D. Lokhande, Thin Solid Films **229**, 1 (1993).
[22] S. D. Sartale, C. D. Lokhande, Mater. Chem. Phys. **65**, 63 (2000).

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