Journal of the Korean Ceramic Society
Vol. 45, No. 1, pp. 30~35, 2008.

Photo-electronic Properties of Cd(Cu)S/CdS Thin Films and Diodes Prepared by CBD

Doo-Hee Cho†, Kyong-Am Kim, and Gi-Bong Song

Transparent Electronics Research Team, Electronic and Telecommunication Research Institute, Daejeon 305-600, Korea
(Received November 13, 2007; Accepted December 26, 2007)

ABSTRACT

In this paper, CdS/Cd(Cu)S thin films and diodes were manufactured via a chemical bath deposition (CBD) process, and the effects of NH_4Cl and TEA(triethylamine) on the properties of the films were examined. The addition of NH_4Cl significantly increased the thickness of the CdS and Cd(Cu)S films, however, the addition of TEA decreased the thickness in both cases slightly. The addition of NH_4Cl along with TEA increased the film thickness more effectively compared to the addition of only NH_4Cl. The thickness of the CdS film prepared from an aqueous solution of 0.007 M $CdSO_4$, 1.3 M NH_4OH, 0.03 M $SC(NH_2)_2$, 0.0001 M TEA and 0.03 M NH_4Cl was 310 nm. Dark resistivity of the CdS film was 1.2×10^3 Ωcm and the photo resistivity with 500 W/cm^2 irradiation of white light was 20 Ωcm. The Cd(Cu)S/CdS thin film diodes prepared by CBD showed good rectifying characteristics.

Key words : CdS, Chemical bath deposition, Diode, Thin film

1. Introduction

CdS is a photo-sensitive II-VI compound semiconductor material in which electron-hole pairs are generated by light irradiation.[1] This material has an energy band gap of 2.4 eV at room temperature.[2] CdS can be applied to electro-optic devices such as photo-sensors, photoconducting cells, transducers, laser materials, and non-linear integrated optical devices.[3] CdS thin films are frequently applied to various diode devices that have homo or hetero pn-junctions such as Cu(InGa)Se_2 solar cells, CdS/CdTe solar cells, photoelectrochemical cells, light emission diodes and bio-sensors.[4-7] However, the formation of p-type CdS is considered to be very difficult due to the self-compensation effect that occurs among the sulfur vacancies and acceptors in CdS.[8,9] Therefore, most CdS cells are fabricated with a heterojunction such as CdS/Cu_2S and CdS/CdTe.[9] Cu-doped CdS (Cd(Cu)S) films show p-type characteristics, and photovoltaic cells and light emission diodes have been manufactured using CdS/Cd(Cu)S homojunctions.[6,10] CdS films can be deposited by thermal evaporation, sputtering or chemical bath deposition (CBD) techniques. Among these deposition techniques, CBD is a relatively simple and inexpensive process that can produce uniform and adherent films on a large area substrate.[11] Thin films are deposited at a lower temperature with the CBD process, allowing the deposition of the film on flexible plastic substrates which is unstable at high temperatures.[12] CBD techniques using solutions as a deposition medium can also be applied to thin film deposition on non-planar substrates, moreover, the equipment used with CBD processes is simple and much less costly compared to vacuum systems.[13] CBD does not use expensive and toxic organometallic precursors as used in a vapor phase deposition methods, implying that it is environmentally less harmful.[14] However, the creation of thick CdS films using the CBD process is difficult[15]; thus, CBD is used generally to the process of thin films that are less than 100 nm thick. For electronic devices using pn-junction such as light emitting diodes and PV cells, a relatively thick film (~1 μm) is required. The present study outlines the addition of NH_4Cl and TEA effects on the thickness of the CdS and Cd(Cu)S thin films as well as on the electro-optical properties and the characteristics of Cd(Cu)S/CdS thin film diodes prepared by the CBD process.

2. Experimental Procedure

CdS and Cd(Cu)S thin films were deposited with the experimental set-up that consisted of a water bath, a reaction reservoir, Teflon jigs and covers, and a magnetic stirrer. The experimental set-up is schematically shown in Fig. 1. Borosilicate glass plates served as substrates for CBD after cleaning with the following steps: 1) washing with DI water, 2) ultrasonic cleaning in acetone, 3) ultrasonic cleaning in iso-propyl alcohol, and 4) ultrasonic cleaning in DI water. The substrate size was 20×20 mm^2 and the substrate was held with a Teflon jig. The substrate was immersed in 300 ml of aqueous solution containing $CdSO_4$, $CuSO_4$, $SC(NH_2)_2$, NH_4OH, NH_4Cl, and TEA. The solution was heated up to 60~70°C before the substrate was im-

†Corresponding author : Doo-Hee Cho
E-mail : chodh@etri.re.kr
Tel : +82-42-860-6035 Fax : +82-42-860-5202

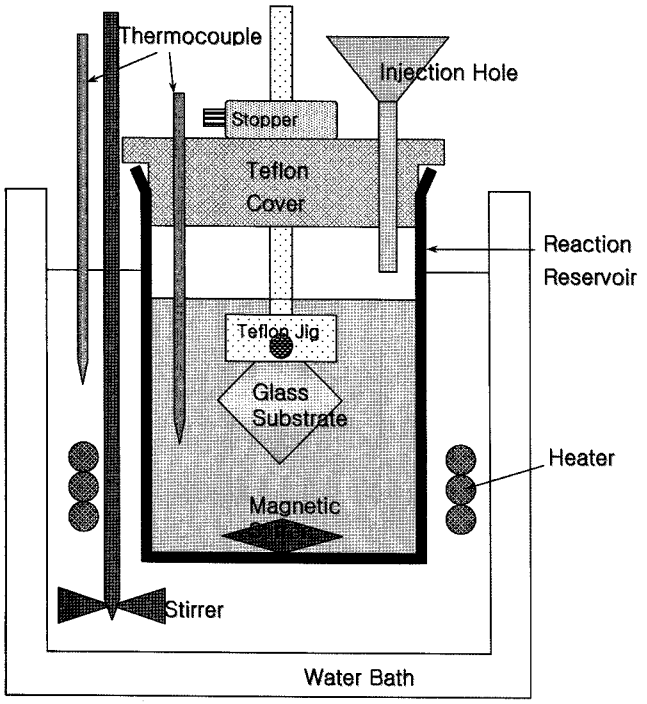


Fig. 1. Schematic diagram of the CBD set-up.

mersed. It was stirred during the CBD process by a Teflon-coated magnetic stirrer at 50 rpm. The thin-film coated samples were cleaned in DI water using an ultrasonic cleaner for 30 seconds and were then dried in air at 120°C using a convection oven. X-ray diffraction (XRD) spectra of the films were recorded with a Rigaku RU-200BH diffractometer using CuKα radiation. A Cd(Cu)S/CdS diode was prepared in the following process: 1) An ITO coated glass plate was cleaned following the same process used to clean the glass substrate; 2) a photoresist mask for the diode pattern was formed on the ITO layer in a photolithography process; 3) a Cd(Cu)S thin film was formed by the CBD process; 4) ultrasonic cleaning was done in DI water; 5) a CdS film was formed on the Cd(Cu)S film by the CBD process; 6) ultrasonic cleaning in DI water and drying in air at 120°C were conducted; 7) the photoresist mask was lifted off in an organic solvent using an ultrasonic cleaner, 8) this was washed with DI water and was dried; 9) a photoresist mask for an upper electrode region was formed in a photolithography process; 10) a metal electrode layer was formed by a thermal evaporation process; 11) the photoresist mask was lifted off in an organic solvent using an ultrasonic cleaner, and 12) this was washed with DI water and dried at 120°C. The I-V characteristics of the thin film diode device were measured with a Hewlett-Packard 4145B semiconductor analyzer.

3. Results and Discussion

The CdS and Cd(Cu)S film thickness depending on the added content of NH_4Cl is shown in Fig. 2. The solution compositions were 0.005 M of $CdSO_4$, 0.05 M of $SC(NH_2)_2$,

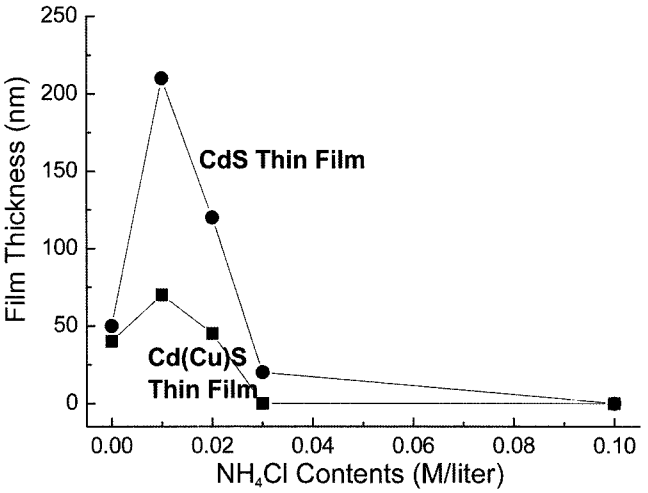


Fig. 2. Thickness dependence of CdS and Cd(Cu)S thin films on the NH_4Cl content in the case of an addition of NH_4Cl by itself.

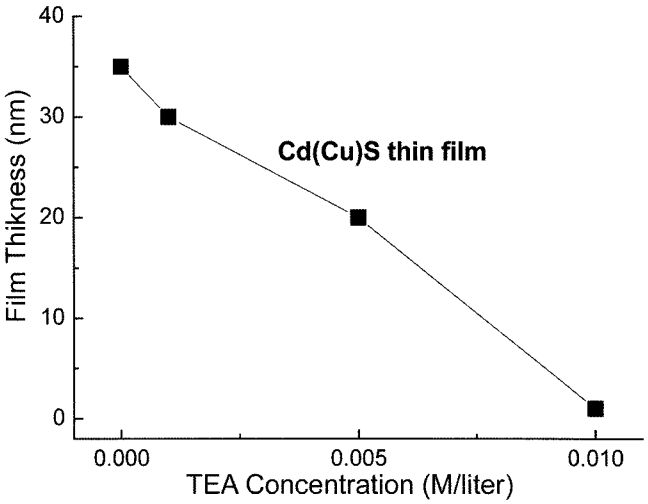


Fig. 3. Thickness dependence of Cd(Cu)S thin films on the TEA content, with a lone addition of TEA.

1.3 M of NH_4OH and 0~0.1 M of NH_4Cl (comp. A) for CdS film deposition, and 0.005 M of $CdSO_4$, 0.0001 M of $CuSO_4$, 0.05 M of $SC(NH_2)_2$, 1.3 M of NH_4OH and 0~0.1 M of NH_4Cl (comp. B) for Cd(Cu)S film deposition. A small addition of NH_4Cl significantly enhanced the thickness of the CdS and Cd(Cu)S thin films, however, a disproportionate amount of NH_4Cl added to the solution decreased the thickness of the film. An addition of TEA decreased the film thickness slightly, as shown in Fig. 3. The compositions of the solutions were identical to the composition shown above for the Cd(Cu)S film, except that NH_4Cl was substituted with TEA. The change in the CdS and Cd(Cu)S film thickness depending on NH_4Cl in the case of the addition of NH_4Cl in conjunction with TEA is shown in Fig. 4. The addition of NH_4Cl in conjunction with TEA enhanced the film thickness more significantly. The peak concentration of NH_4Cl was 0.01 M when NH_4Cl was added alone and 0.03 M when NH_4Cl was added along with TEA in the case of the CdS film formation.

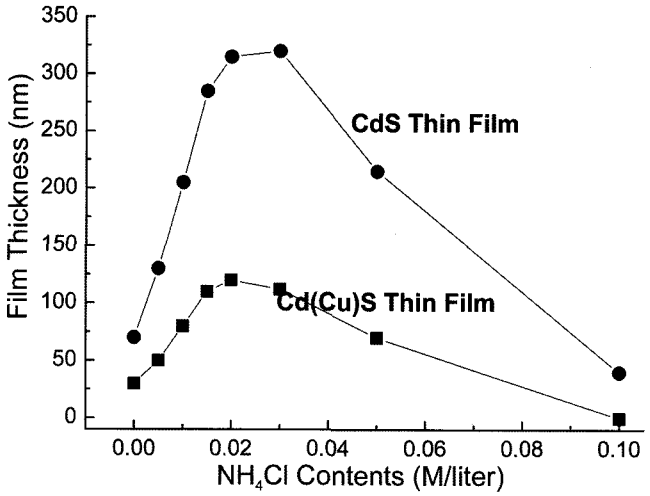


Fig. 4. Thickness dependence of CdS and Cd(Cu)S thin films on the NH_4Cl content, with a combined addition of NH_4Cl and TEA.

For the formation of the Cd(Cu)S film, the NH_4Cl peak concentration was 0.01 M for the single NH_4Cl addition and 0.03 M for the addition of NH_4Cl with TEA. The combined addition of NH_4Cl and TEA was more effective for the CdS and Cd(Cu)S thin film depositions by CBD process compared to the separated addition, as shown in Figs. 2 and 4. The thickness of the CdS film prepared from the aqueous solution of 0.005 M $CdSO_4$, 1.3 M NH_4OH, 0.05 M $SC(NH_2)_2$, 0.0001 M TEA and 0.03 M NH_4Cl (comp. C) was 320 nm, and that of the Cd(Cu)S film from the aqueous solution of 0.005 M $CdSO_4$, 0.0001 $CuSO_4$, 1.3 M NH_3, 0.05 M $SC(NH_2)_2$, 0.0001 M TEA and 0.03 M NH_4Cl (comp. D) was 120 nm. The TEA and NH_4Cl combined addition not only increased the film thickness but also shifted the peak position to the higher concentration side.

The reaction mechanism that occurs in the CBD reaction for the CdS film formation consists of the following steps: 1) Equilibrium between the complexing agent and water, 2) Formation/dissociation of ionic metal-ligand complexes, 3) Hydrolysis of the sulfur source, and 4) Formation of the solid.[14,16-18] Generally, hydrolysis of the sulfur source is a critical step as it provides the desired non-metal species that pull the metal cations out of the solution to form solid films. The kinetics of this step is highly sensitive to the pH and temperature of the solution.[14,19] However, in practice, the important issue is whether the solid forms as a film on the substrate or as colloidal particles in the solution. Whether the film deposition proceeds by ion-by-ion growth on the substrate or by a colloidal and cluster mechanism is also important in the film formation. The formation of metal-ligand complexes, which would occur immediately in the normally alkaline solutions in step 2, allows control over the rate of the formation of solid metal hydroxides which competes with the formation of the sulfide solid in step 4.[14,20] In addition, the abundance of NH^{4+} ions suppresses the formation of metal hydroxide; hence, NH_4OH is widely used as a complexing agent.[15] However, in the ion-by ion mechanism, metal complexes are initially formed on surface of the substrates and then decomposed into the sulfide solid in a high-pH solution.[21,22] This mechanism is a sluggish process that allows precipitation of many Cd^{2+} ions into the colloidal particles in the solution.[14,15] An excessive addition NH_4OH is the cause of the increase in the pH, and thick

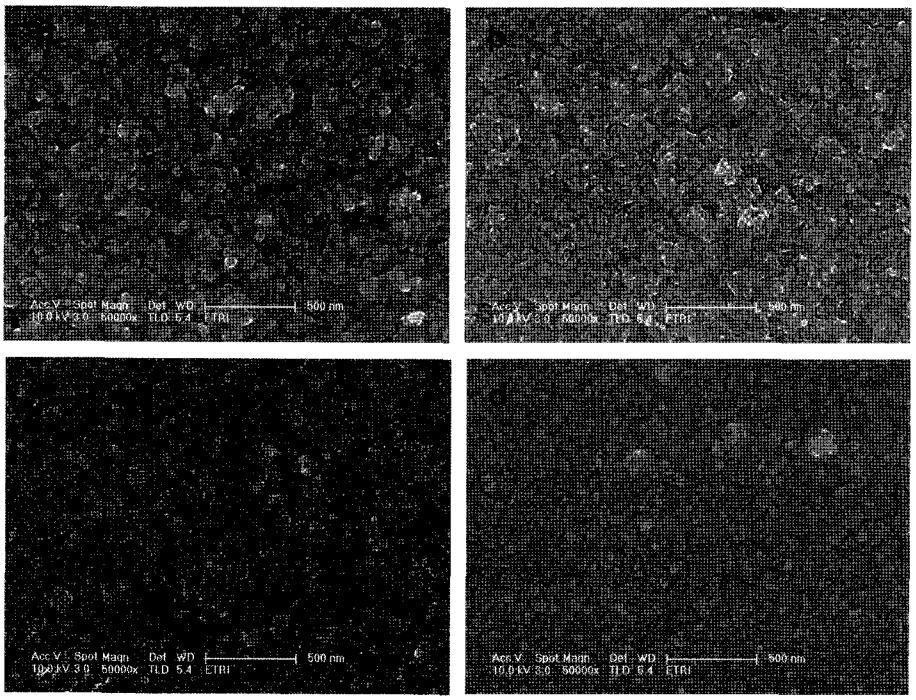


Fig. 5. SEM photographs of CdS thin films formed with solutions of a) comp. A and b) comp. C, and Cd(Cu)S thin films with c) comp. B and d) comp. D.

films cannot be obtained in the CBD process for CdS film formation due to the aforementioned reasons. The NH_4Cl addition is considered to be effective to increase the CdS film thickness for low NH_4Cl contents. However, an excessive addition of NH_4Cl raises the concentration of Cl^- ions. These ions are thought to inhibit the CdS solid formation and reduce the thickness of the film.

The film growth rate and mechanism are altered by the pH, temperature and chemical composition of the solution. Thus, additives such as NH_4Cl and TEA can change the thickness and microstructure of the film. Fig. 5 shows the microstructures of CdS and Cd(Cu)S films in the case of an addition of only NH_4Cl and a combined addition of NH_4Cl and TEA. The grain size of the CdS film is larger than that of the Cd(Cu)S film. On the other hand the CdS thin film showed diffraction peaks with a relatively high intensity, and the Cd(Cu)S thin film appears to be less crystalline as shown in Fig. 6 showing the X-ray diffraction spectra of the CdS and Cd(Cu)S thin films. Cu doping in the CdS film formation by CBD is considered to reduce the film thickness and suppress the growth of the crystalline phase. Therefore, the grain size and the thickness of the Cd(Cu)S films is decreased compared to CdS.[23,24] The grain size in the case of the combined addition of NH_4Cl and TEA was increased compared to the addition of NH_4Cl only. Pin holes were reduced and the films became denser with the combined TEA addition. It is thought that the combined addition of NH_4Cl and TEA in the solution suppresses the precipitation into colloidal particles and leads to the enhancement of the CdS grain growth rate in the film, which in turn increase the film thickness and density.

The CdS and Cd(Cu)S thin films prepared by CBD showed a high photo sensitivity. Dark resistivity of the CdS (comp. C) film was 3.8×10^3 Ωcm and the photo resistivity with 500 W/cm^2 irradiation of white light was 15 Ωcm. The dark resistivity of the Cd(Cu)S (comp. D) film was 1.8×10^6 Ωcm, while its photo resistivity was 23 Ωcm. The electrical resis-

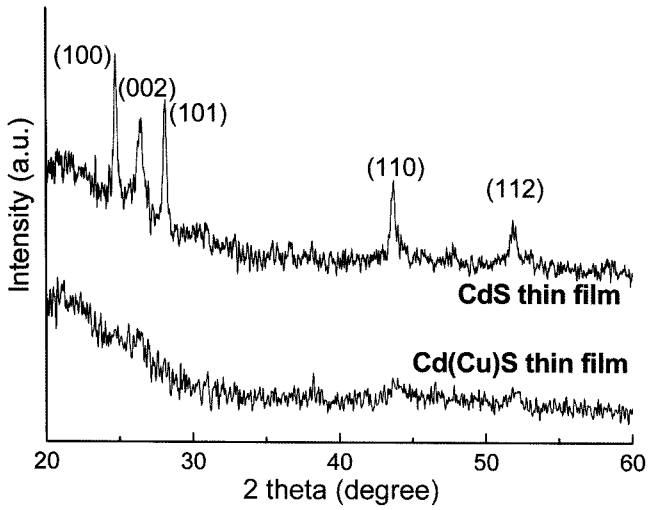


Fig. 6. XRD spectra of CdS (comp. C) and Cd(Cu)S (comp. D) thin films.

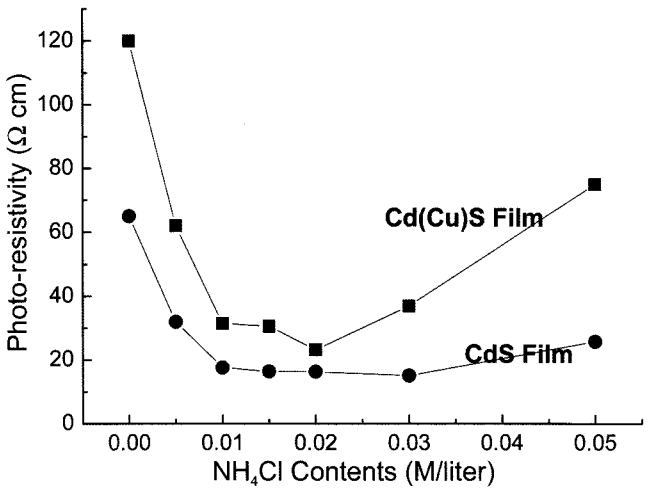
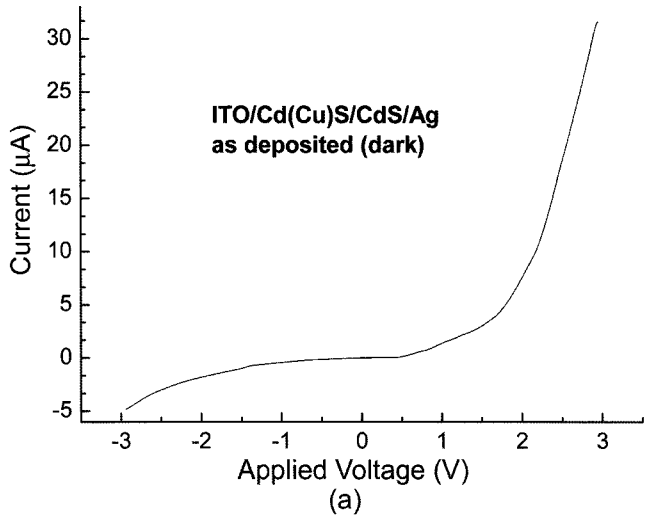


Fig. 7. Photo-resistivity dependence of CdS and Cd(Cu)S thin films on the NH_4Cl content.



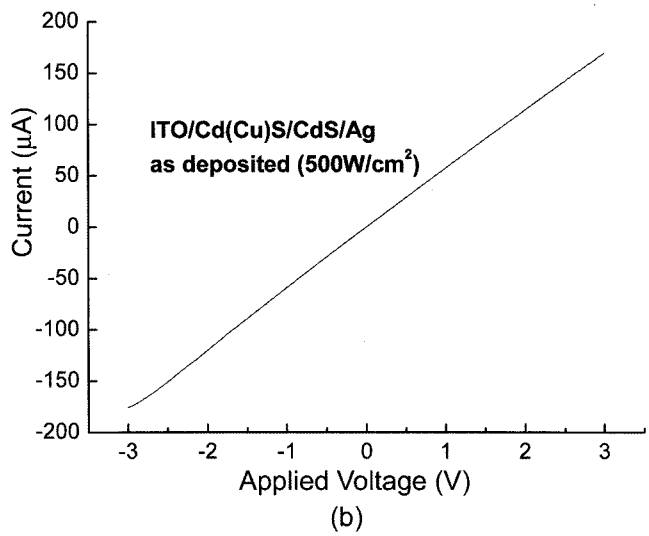


Fig. 8. I-V characteristic curve for ITO/Cd(Cu)S/CdS/Ag thin film diode as deposited.

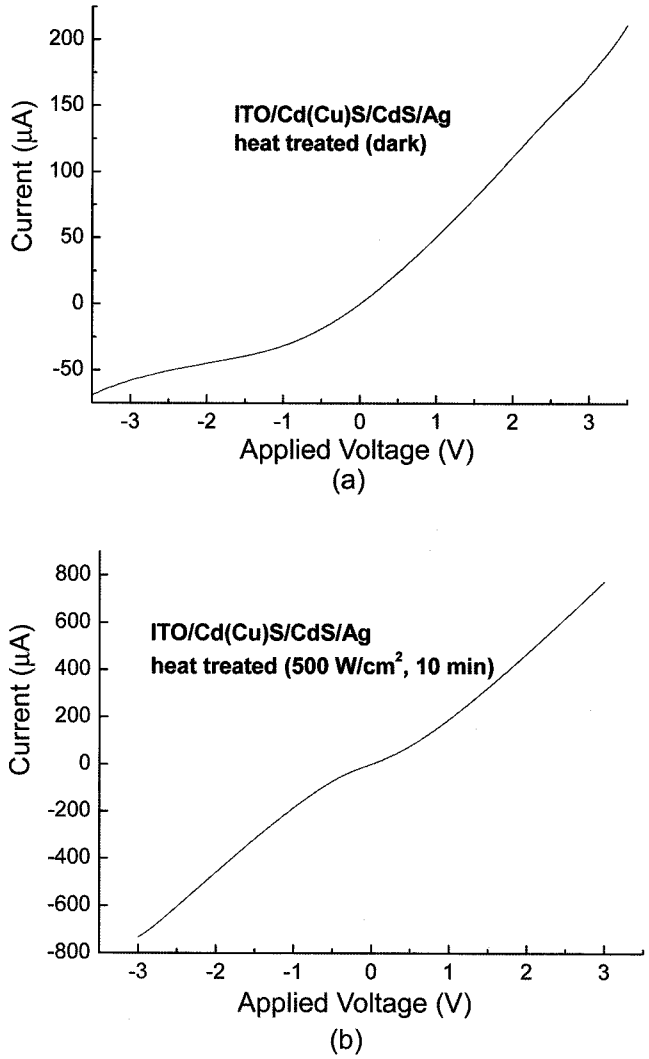


Fig. 9. I-V characteristic curve for ITO/Cd(Cu)S/CdS/Ag thin film diode after a heat treatment.

tivity was significantly decreased by the irradiation with white light. The difference between dark and photo resistivity of the Cd(Cu)S film was larger than that of CdS. The photo resistivity changes in the CdS and Cd(Cu)S films with NH_4Cl contents are shown in Fig. 7. The photo resistivity of the CdS and Cd(Cu)S film decreased with NH_4Cl content up to the thickness peak position and then increased. The film resistivity showed a trend that was opposite to that of the film thickness, showing a decrease with the growth of the film thickness. On the other hand, the grain size increased and the film microstructure became denser as the film thickness increased, as seen in the Figs. 4 and 5. Therefore, it is thought that the larger grain size and denser microstructure enhanced the electrical conductivity of the film.

We have manufactured an ITO/Cd(Cu)S/CdS/Ag thin film diode with CBD process following to the manufacturing steps mentioned in experimental procedure. Fig. 8 shows I-V characteristics of the thin film diode sample. As shown in Fig. 8, it showed relatively good rectifying properties in the dark, however, the rectifying characteristics disappeared and current density was extensively increased under 500 W/cm^2 white light irradiation. It behaved like an ohmic resistance device under white light illumination. Fig. 9 shows I-V characteristics of the thin film diode sample after heat treatment at 450°C for 30 min. The rectifying characteristics were deteriorated after heat treatment. It is considered that Cu^{2+} ions diffused into CdS layer during the heat treatment and pn junction between CdS and Cd(Cu)S layer was partially broken down.

4. Conclusion

Thick and dense n-type CdS thin films and p-type Cd(Cu)S thin films along with Cd(Cu)S/CdS thin film diodes were prepared using the CBD process. A small addition of NH_4Cl was found to increase the thickness of the CdS and Cd(Cu)S thin films remarkably, and the addition of NH_4Cl along with TEA enhanced the film thickness even more significantly. The film thickness, grain size and film density were increased and pin holes were reduced in the cases of the combined addition of TEA and NH_4Cl compared to the addition of NH_4Cl alone. The CdS and Cd(Cu)S thin films prepared via CBD process showed a high photo sensitivity. The photo resistivity decreased as the film thickness increased, which was most likely due to the growth of the grain size and the film density. Additionally, a Cd(Cu)S/CdS thin film diode manufactured by the CBD process showed good rectifying characteristics.

Acknowledgments

This work was supported by IT R&D program of MIC/IITA [2006-S079-02, Smart window with transparent electronic devices].

REFERENCES

1. V. Lantto and V. Golovanov, "A Comparison of Conductance Behaviour Between SnO_2 and CdS Gas-sensitive Films," *Sens. Actuators*, **B 24-25** 614-18 (1995).
2. H. Metin and R. Esen, "Annealing Studies on CBD Grown CdS thin Films," *J. Cryst. Growth*, **258** 141-48 (2003).
3. K. Senthil, D. Mangalaraj, and Sa.K. Narayandass, "Structural and Optical Properties of CdS thin Films," *Appl. Surf. Sci.*, **169-170** 476-79 (2001).
4. M.A. Martinez, C. Guillen, M.T. Gutierrez, and J. Herrero, "Optimization of CdS-TCO Bilayers for Their Application as Windows in Photovoltaic Solar Cells," *Sol. Energy Mat. Sol. Cells*, **43** 297-310 (1996).
5. G. Milczarek; A. Kasuya, S. Mamykin, T. Arai, K. Shinoda, and K. Tohji, "Optimization of a Two-compartment Photoelectrochemical Cell for Solar Hydrogen Production," *Int. J. Hydrogen Energy*, **28** 919-26 (2003).
6. T. Abe, J. Sato, S. Ohashi, M. Watanabe, and Y. Kashiwaba, "Light Emission of a CdS(Cu)/CdS Thin-Film Diode," *Phys. Stat. Sol. (b)*, **229** 1015-19 (2002).
7. J. Travas-Sejdic, H. Peng, R.P. Cooney, G.A. Bowmaker,

M.B. Cannell, and C. Soeller, "Amplification of a Conducting Polymer-based DNA Sensor Signal by CdS Nanoparticles," *Current Applied Physics*, **6** 562-66 (2006).
8. G. Mandel and Phys. Rev., "Self-compensation Limited Conductivity in Binary Semiconductors. I. Theory," **A 134** 1073-79 (1964).
9. Y. Kashiwaba, K. Isojima, and K. Ohta, "Improvement in the Efficiency of Cu-doped CdS/non-doped CdS Photovoltaic Cells Fabricated by an All-vacuum Process," *Sol. Energy Mat. Sol. Cells*, **75** 253-59 (2003).
10. H. Murai, T. Abe, J. Matsuda, H. Sato, S. Chiba, and Y. Kashiwaba, "Improvement in the Light Emission Characteristics of CdS:Cu/CdS Diodes," *Appl. Surf. Sci.*, **244** 351-54 (2005).
11. L. Wenyi, C. Xun, C. Qiulong, and Z. Zhibin, "Influence of Growth Process on the Structural, Optical and Electrical Properties of CBD-CdS Films," *Mater. Lett.*, **59** 1-5 (2005).
12. A. Cortes, H. Gomez, R.E. Marotti, G. Riveros, and E.A. Dalchiele, "Grain Size Dependence of the Bandgap in Chemical Bath Deposited CdS thin Films," *Sol. Energy Mat. Sol. Cells.*, **82** 21-34 (2004).
13. J.N. Ximello-Quiebras, G. Contreras-Puente, J. Aguilar-Hernandez, G. Santana-Rodriguez, and A. Arias-Carbajal Readigos, "Physical Properties of Chemical Bath Deposited CdS Thin Films," *Sol. Energy Mat. Sol. Cells*, **82** 263-68 (2004).
14. T.P. Niesen and M.R. De Guire, "Review: Deposition of Ceramic Thin Films at Low Temperatures from Aqueous Solutions," *J. Electroceramics.*, **6** 169-207 (2001).
15. I. Oladeji and L. Chow, "Optimization of Chemical Bath Deposited Cadmium Sulfide Thin Films," *J. Electrochem. Soc.*, **144** 2342-346 (1997).
16. C. Guillen, M.A. Martinez, and J. Herrero, "Accurate Control of Thin Film CdS Growth Process by Adjusting the Chemical Bath Deposition Parameters," *Thin Solid Films*, **335** 37-42 (1998).
17. N. R. Pavaskar, C. A. Menezes, and A. P. B. Sinha, "Photoconductive CdS Films by a Chemical Bath Deposition Process," *J. Electrochem. Soc.*, **124** 743-48 (1977).
18. M. Rami, E. Benamar, M. Fahoume, F. Chraibi, and A. Ennaoui, "Effect of the Cadmium Ion Source on the Structural and Optical Properties of Chemical Bath Deposited CdS thin Films," *Solid State Sci.*, **1** 179-88 (1999).
19. J.P. Enriquez and X. Mathew, "Influence of the Thickness on Structural, Optical and Electrical Properties of Chemical Bath Deposited CdS thin Films," *Sol. Energy Mat. Sol. Cells*, **76** 313-22 (2003).
20. C.J. Brinker and G.W.Scherer, "Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing," Academic Press Inc, San Diego, 1990.
21. M. Kostoglou, N. Andritsos, and A.J. Karabelas, "Progress Towards Modeling the CdS Chemical Bath Deposition Process," *Thin Solid Films*, **387** 115-17 (2001).
22. Y.J. Chang, C.L. Munsee, G.S. Herman, J.F. Wager, P. Mugdur, D.H. Lee, and C.H. Chang, "Growth, Characterization and Application of CdS Thin Films Deposited by Chemical Bath Deposition," *Surf. Interface Anal.*, **37** 398-405 (2005).
23. P. J. Sebastian and M. Ocampo, "Modification of Structural and Opto-electronic Properties of CdS Thin Films by Cu Doping," *J. Appl. Phys.*, **77** 4548-551 (1995).
24. P. J. Sebastian, "P-type CdS Thin Films Formed by in Situ Cu Doping in the Chemical Bath," *Appl. Phys. Lett.*, **62** 2956-958 (1993).