Scientia Iranica, Vol. 15, No. 3, pp 360–365

SCIENTIA IRANICA

Optical and Structural Properties of Copper Doped CdS Thin Films Prepared by Pulsed Laser Deposition

S.M. Mahdavi*, A. Irajizad[1], A. Azarian[1] and R.M. Tilaki[1]

This paper presents the study of the structural and optical properties of copper doped cadmium sulfide thin films prepared by pulsed Nd:YAG laser. The copper concentration in the targets was varied from 0.05% to 5% in weight and they were heated at a temperature of 500°C in air for one hour. It was observed that annealing un-doped and doped thin films at temperatures above 160°C leads to an abrupt increase in the optical transmission, changing from dark brownish to transparent yellowish. For annealed samples at 300°C, increasing Cu concentration from 0.0% to 2%, leads to an increase in the optical transmission up to 80%, at a wavelength of about 700 nm. XRD patterns showed the hexagonal phase of cadmium sulfide and a number of CdO peaks relating to the partial oxidation of cadmium. The XPS spectra of the annealed samples indicate an accumulation of Cu at the surface. Therefore, Cu impurity can enhance CdS oxidation and the size of the crystallites. The highest value of the photo-current for the samples is related to the lowest Cu concentration, i.e: 0.05%.

INTRODUCTION

Cadmium sulfide is an n-type semiconductor that has been used extensively in many applications, including photo resistance sensors, low cost solar cells for energy conversion, light emitting diodes, laser materials, optical waveguides and nonlinear optical devices [1-4]. Different techniques have been used to fabricate cadmium sulfide thin films, such as vacuum evaporation, chemical bath deposition, sputtering, spray pyrolysis and recently pulsed laser deposition [5]. Pulsed laser deposition is recognized as an important technique for the fabrication of multi-component thin films, due to flexibility and the stoichiometric deposition of the materials [6,7].

Copper impurity changes the type of CdS semiconductor from n to p [8-11]. The Cu:CdS thin films have many applications, such as high efficiency photovoltaic cells (over 8.5%) [12] and light emitters [13]. Moreover, the doping of copper changes the bandgap energy of CdS and also improves its photoelectrical properties [14]. Recently, a few reports have been published on the properties of Cu:CdS layers; for example, the studying of Cu:CdS/CdS homo junction and its rectifying [15]. Different methods have been used to dope the CdS films by Cu, such as the thermal annealing of a Cu/CdS bi-layer [1]. The aim of the present work is to add a few percent of Cu in CdS targets and study the effect of copper on the optical, structural and photo-conducting properties of the thin films prepared by a pulsed laser deposition.

EXPERIMENTAL

A pulsed Nd:YAG laser, with a fundamental harmonic of 1064 nm, a 10 Hz repetition rate of 130 mJ/pulse energy and 10 ns duration, was used for the laser ablation of Cu:CdS targets. The area of the spot size was 1 mm^2. Cadmium sulfide and copper powder were mixed together thoroughly, then pressed into pellets and annealed at 300°C and 500°C in air. The copper concentration was varied from 0.05% to 5% in weight in the target. The film depositions were carried out in a vacuum chamber with a base pressure of 10^{-5} torr. The laser beam was focused at an incident angle of 40° onto the surface of the target. Samples were kept at a distance of 20 cm. To avoid the texturing effect and to get film uniformity, the targets were rotated at 20 rpm.

*. *Corresponding Author, Department of Physics, Sharif University of Technology, P.O. Box 11155-9161, Tehran, I.R. Iran. E-mail: mahdavi@sharif.edu*

1. *Department of Physics, Sharif University of Technology, P.O. Box 11155-9161, Tehran, I.R. Iran.*

Therefore, ablation takes place at different points of the target. Hence, the concentration of copper in the spot size of the target is more likely the copper concentration in the powder.

Scanning Electron Microscopy (SEM) and Energy Dispersive X ray Spectroscopy (EDX) techniques were used to observe surface morphology and film composition. The film thickness was also determined by the Rutherford Backscattering Spectroscopy (RBS) experiment. To do such a measurement, a 2 MeV He^+ beam was used and the detector was placed at a scattering angle of 165°. The surface of the samples was investigated by X-ray Photoemission Spectroscopy (XPS), using a CHA analyzer and a dual Mg and Al anode X-ray source. In order to study the crystalline structure of the deposited films, an X-Ray Diffraction (XRD) measurement was carried out using Cu K_a radiation ($\lambda = 1.5418\mathring{A}$).

Optical properties are important for sensor and photovoltaic applications. Therefore, samples were characterized by a UV/VIS Jasco spectrophotometer. The band gap energy of the samples was calculated from their optical transmission spectra.

In order to study the effects of Cu impurity on thin film photoconductivity, CdS thin films were illuminated by a tungsten lamp with an intensity of 5×10^{-3} Wcm^{-2}. Two copper electrodes were evaporated on top of the surface of the films. The photo/dark resistance of the films was determined by applying a constant voltage of 20 V to the electrodes.

RESULTS AND DISCUSSION

Films formed by laser ablation techniques are usually affected by the splashing of large particles from the target and are enhanced if the targets are made from pressed micron sized powder. Therefore, the targets were annealed at 500°C in air, to obtain higher mechanical quality and lower splashing, compared with those that were annealed at lower temperatures. The target was also annealed in a nitrogen environment at a temperature of about 500°C, but lost its size and weight, showing the sublimation of CdS. For annealed targets in air, it has been known that annealing leads to the formation of a very thin layer of CdO at the surface and this layer protects the target from sublimation [16]. To remove the CdO layer, the rotating target surfaces were ablated for a few minutes before exposing the substrates to the ablated species. All films have similar deposition conditions (number of incident pulses, their energy and duration time). The results showed that the target annealing temperature affects the sample's optical transparency. The color of the deposited films, prepared from annealed targets at 500°C in air, are black or dark brownish, whereas those formed from annealed targets at 300°C are transparent yellowish, which are the same in color as films formed by the thermal evaporation of CdS powder or films formed by the chemical bath deposition method [17]. Doping the targets with a low percentage of Cu did not have much effect on the color of the deposited samples. The annealing of un-doped and doped dark films at temperatures above 160°C leads to an abrupt increase in transmission, as shown in Figure 1. Annealing samples at 500°C reduces the optical transmission. The electrical conductivity measurements showed that all as deposited films have high electrical resistance. The electrical conductivity of the films as a function of the annealing temperature showed similar behavior, i.e. it increases as the annealing temperature is increased, as expected.

Doping the samples by Cu concentration up to 2% enhances the optical transmission. Figure 2 presents the spectra of the annealed samples at 300°C with 0.0% to 5% impurity. It is observed that 80-90% optical transmission of CdS films can be achieved by 2% Cu doping, that is about 2 times more than similar deposited film without Cu impurity. Higher Cu concentration in the target results in lower optical transmission.

The energy gap of the samples was calculated using their transmission curves and the following formula, where the films reflectance was ignored:

$$\alpha = (-1/d)\ln(I/I_0) = A(h\nu - E_g)^{1/2}. \quad (1)$$

Here, I_0 and I are the intensity of the incident and the transmitted light on/from the sample, respectively. Moreover, d is the thickness of the layer, $h\nu$ the energy of the incident light and E_g the band gap of the sample. A typical graph of $(\alpha h\nu)^2$ versus $h\nu$ (eV) of the sample with 0.5% Cu in the target is shown in Figure 3. The results showed a small decrease in E_g, from 2.4 ± 0.05

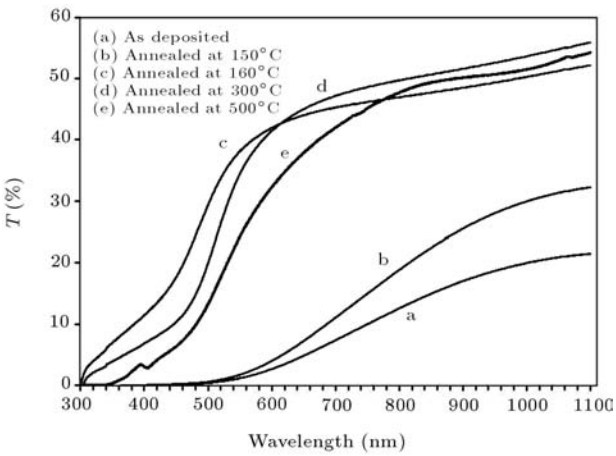

Figure 1. Optical transmission of the deposited and annealed CdS thin films at different temperatures.

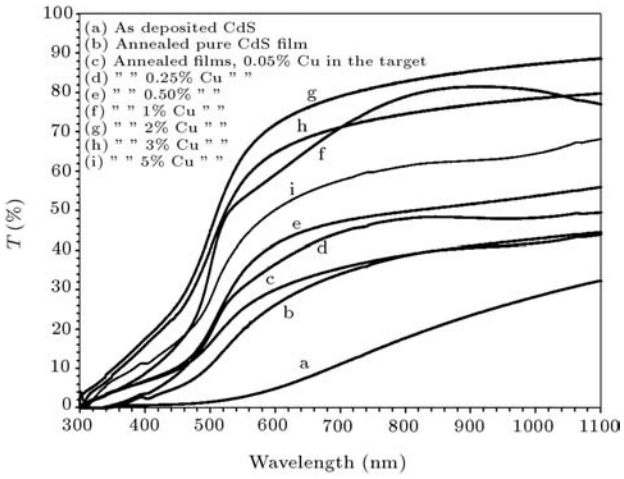

Figure 2. Optical transmission of the deposited and annealed CdS samples at 300°C with different percent of Cu impurity.

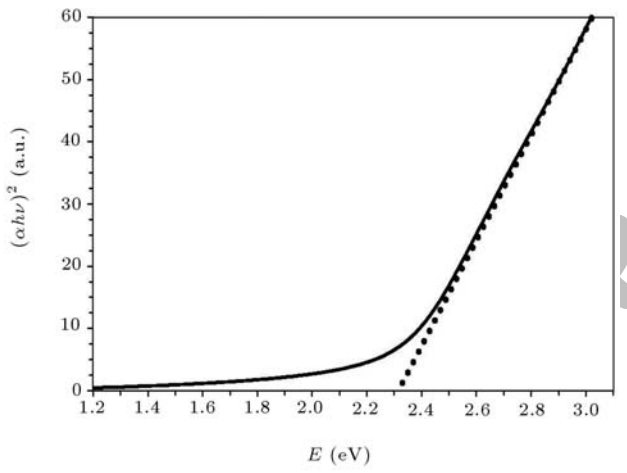

Figure 3. A typical graph of $(\alpha h\nu)^2$ versus $h\nu$ (eV) of the sample with 0.5% Cu in the target.

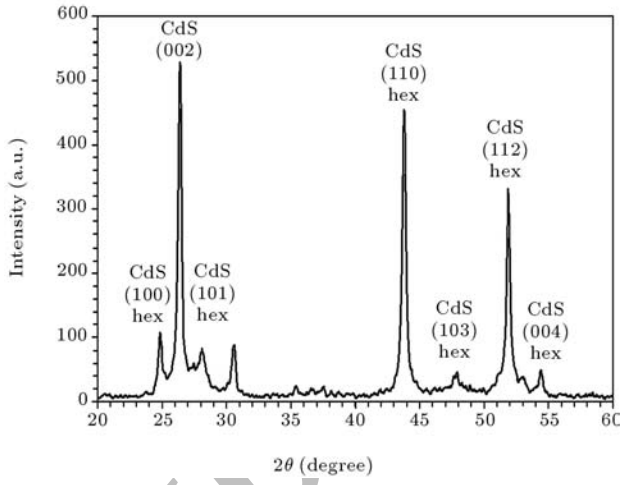

Figure 4. XRD pattern of CdS target annealed at 500°C in air.

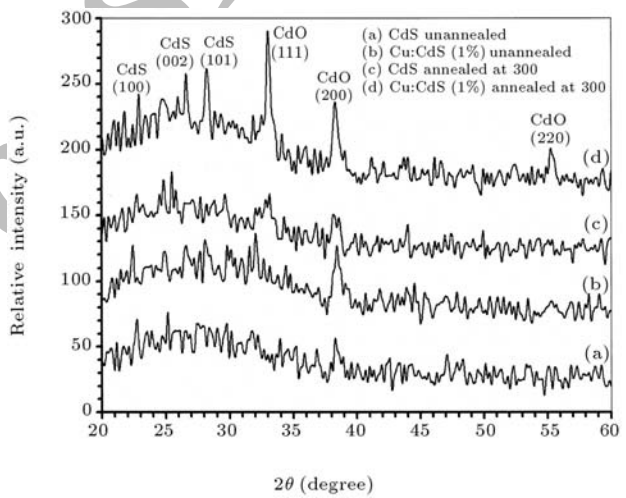

Figure 5. XRD pattern of deposited and annealed CdS thin films with and without Cu impurity.

eV for un-doped annealed samples to about 2.35 ± 0.05 eV for doped samples.

In order to determine the crystalline structure of the target and films and, also, the effect of Cu impurity on the film structure, XRD experiments were performed. Figure 4 shows the XRD spectra of the pressed CdS powder that was annealed at 500°C in air for one hour. It demonstrates a hexagonal phase that is similar with the data obtained from the CdS powder.

The XRD pattern of CdS and 1% Cu:CdS samples, which were deposited under similar conditions, are shown in Figure 5. As shown, the undoped as deposited or annealed samples (*a*&*c*), have an amorphous structure with a few very weak peaks related to CdS. However, those related to doped films (*b*&*d*) show peaks with relatively higher intensity. It is known that the annealing process can increase the size of the grains. In addition, Cu, as an impurity, can help the formation of larger crystallites. It was observed that increasing the Cu impurity enhances CdO, compared with CdS peaks in the samples. Figure 6 shows the XRD pattern of similar CdS films with a Cu concentration of about 1, 0.5 and 0.25% in weight in their targets. Intense peaks at $2\theta = 33°$and $2\theta = 38.3°$are related to the (111) and (200) planes of the CdO cubic structure. Cadmium and copper can be oxidized in the ablated plume by a small amount of residual oxygen and, also, more oxidation can be resulted during the annealing process. The crystalline nature improvement of the films has an important effect on the enhancement of the optical transmission, as observed in Figure 2. The crystal size was determined from the XRD spectrum using the Scherer formula:

$$D = 0.9\lambda/\beta \cos\theta, \qquad (2)$$

where D is crystal size, λ is the wavelength of the

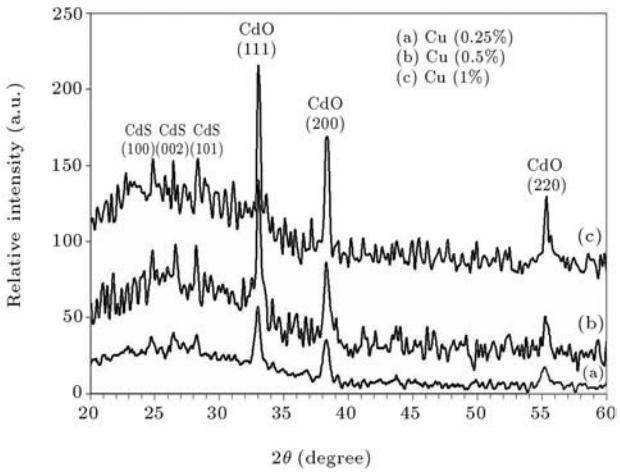

Figure 6. XRD pattern of doped with different Cu concentration and undoped CdS thin films. All samples were annealed in air at 300°C for 1 hour.

X-ray, β is Full Width at Half Maximum (FWHM) and θ is Bragg's angle. The crystal size of CdS was calculated from (101) peak samples, while the crystal size of CdO was obtained from the (111) plane of the cubic phase of cadmium oxide. By increasing the copper concentration, the grain size of cadmium sulfide is increased from 240 ± 20 Å for 0.05% Cu: CdS films to 440 ± 20 Å for annealed samples with 1% Cu in its target, whereas the CdO average crystal size for annealed 1% Cu: CdS films is about 673 ± 20 Å.

To study the effect of copper concentration on surface morphology and film composition, SEM, EDX and XPS experiments were performed. The SEM micrograph of the results indicated nano-size grains and micron size splashed particles. With regard to the limitation of the SEM resolution, it was observed that adding Cu impurity to the targets increased the size of the grains in the droplets and their background layer, as presented in Figure 7.

The atomic number ratio of Cd/S was obtained from the EDX experiment. For all the deposited samples, this ratio is about 1.4, whereas, for films that were annealed in air, it was more than 1.4. This ratio was about 1 for the targets. Increasing Cu in the targets or annealing temperatures resulted in higher Cd/S ratios. For example, this ratio was about 4 for annealed samples at 300°C, which were prepared by targets containing 1% Cu. The lower concentration of sulfur in films is due to the escape of S from the laser plume and faster S evaporation from the deposited layers. Therefore, the deposited films are rich in Cd. So, annealing samples in air partially oxidized the cadmium atoms and clusters. In fact, the higher electrical conductance of samples after annealing at temperatures up to 500°C, is due to the crystallization of the films and the formation of

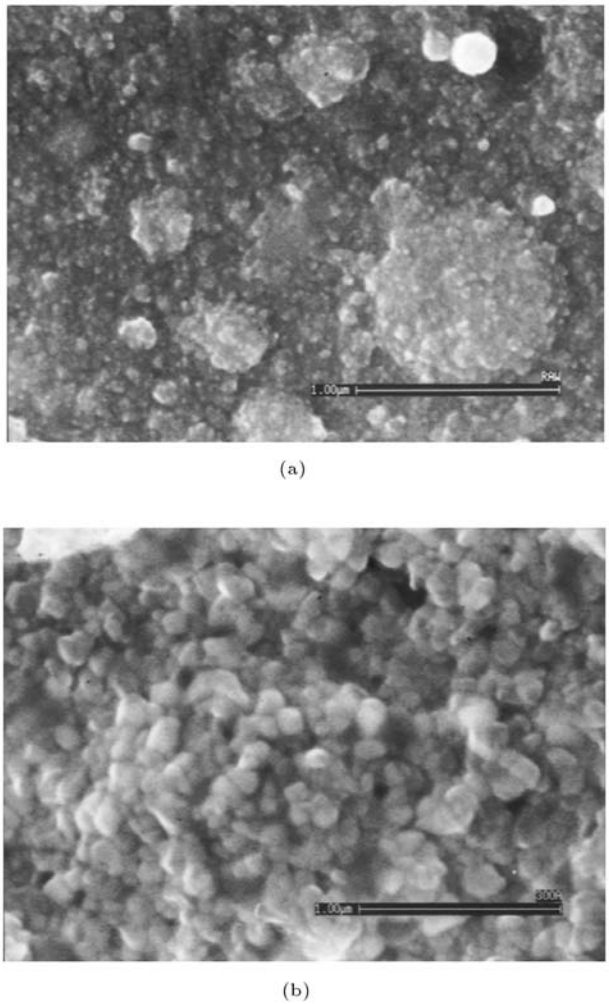

Figure 7. SEM images of a) Deposited doped thin film with 1% Cu in weight in its target and b) the thin film after annealing in air at 300°C.

conductive CdO. By annealing the samples at 600°C, a decrease in electrical conductance, optical transmission and photo-conductivity is resulted. This is likely to be the interface mixing of glass substrate and films.

The excess Cd in the films could adhere to the glass substrate to form CdO at the interface, therefore, laser ablated samples should present good adhesion to glass, compared with chemically deposited films.

The XPS data in Figure 8 shows the surface composition of the sample that was deposited from a target doped with 1% Cu, after being bombarded by Ar ions to remove the adsorbed species. It shows Cd, S, O, C and a small trace of Cu. A clear oxygen peak indicates the existence of CdO at the surface. After annealing the sample in the UHV condition, not only did the Cu peak intensity increase, but also a new Cu Auger peak appeared. These results indicate that Cu accumulates at the surface. The Cd/S ratio is about 1.4 for the sample before annealing, similar to EDX results. However, this ratio is about 1.2 at the surface after

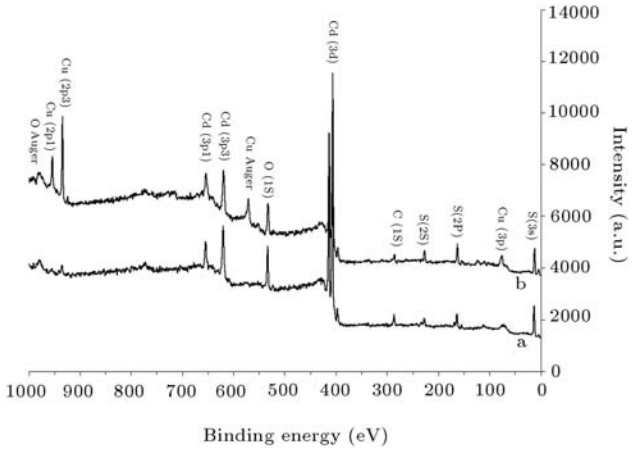

Figure 8. The XPS data from the film was deposited from a target doped with 1% Cu. a) as deposited and b) after annealing at 300°C in the UHV system.

heating in the UHV. The smaller value, in comparison with EDX results, is due to a higher S concentration at the surface in comparison with the bulk.

The effect of Cu impurity on film photoconducting was also studied. Figure 9 demonstrates the relative rise and decay curves for Cu: CdS annealed samples at 200°C films, with a) 1%, b) 0.5% and c) 0.05% Cu concentration in the targets. The highest value of the photocurrent is related to the lowest concentration of Cu, as reported by Amalnerkar [18]. If the required time to reach 63% of the final value is to be considered as the rise response time in the authors' samples, the values are about 35 to 70 sec.

CONCLUSION

The structural and optical properties of copper doped cadmium sulfide films, prepared by pulsed Nd:YAG laser from annealed pressed Cu: CdS powder, were studied. Annealing un-doped and doped films at 160°C and more leads to an abrupt increase in the optical transmission, changing from a dark color to transparent yellowish films. Increasing Cu concentration from 0.05% to 2% weight in the targets of the annealed samples at 300°C, results in higher optical transmission. The XRD pattern of the annealed films showed the hexagonal phase of the cadmium sulfide and a number of CdO peaks.

Cu impurity can enhance the crystal size of CdS and oxidize the Cd atoms during the annealing process in air. The band gap energy of the doped samples obtained from the optical transmission spectra are less than pure CdS films, without obvious dependency on Cu concentration up to 5%. The XPS spectra of the annealed samples indicate an accumulation of Cu at the surface. The highest value of the photocurrent for the samples is related to the lowest Cu concentration, i.e. 0.05%.

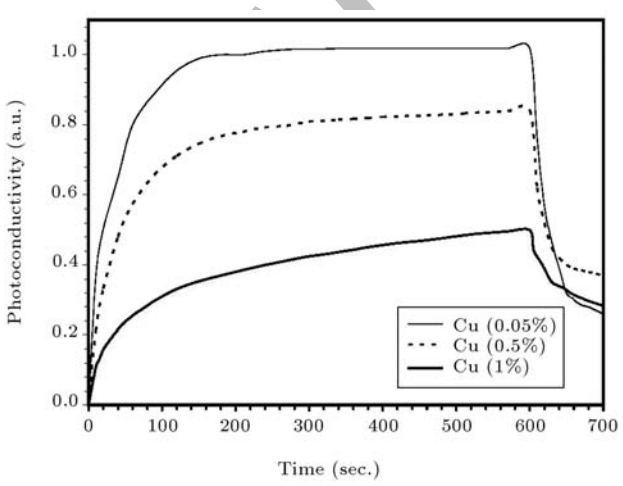

Figure 9. Relative rise and decay photoconductivity curves for Cu:CdS as deposited films at different Cu concentration in targets.

ACKNOWLEDGMENT

The support of this work by Sharif University of Technology and the Hi-Tech Center is gratefully acknowledged.

REFERENCES

1. Kashiwaba, Y., Sato, J. and Abe, T. "Emission of lights of various colors from p-CdS:Cu/n-CdS thin-film diodes", *Appl. Surface Science*, **212-213**, pp 162-165 (2003).
2. Bacaksiz, E., Novruzov, V., Karel, H., Yanmaz, E., Altunbas, M., Kopya, A.I. "Light–assisted depostion of Cds thin films" *J. Phys. D: Appl. Phys.*, **34**, pp 3109-3112 (2001).
3. Ullrich, B., Bagnall, D.M., Sakai, H. and Segawa, Y. "Photoluminescence and lasing of thin CdS films on glass formed by pulsed-laser deposition" *Journal of Luminescence*, **87-89**, pp 1162-1164 (2000).
4. Senthil, K., Mangalarj, D., Narayandass, S.K. "Structural and optical properties of CdS thin film", *Applied Surface Science*, **169-170**, pp 476-479 (2001).
5. Ulrich, B., Tomm, J.W., Dushkina, N.M., Tomm, Y., Sakai, H. and Segawa, Y. "Photoelectric dichroism of oriented thin film CdS fabricated by pulse-laser depoition", *Solid State Communications*, **116**, pp 33-35 (2000).
6. Desserre, J. and Eloy, J.F. "Interaction of a pulsed laser beam with a complex target: application to the preparation of compounds in thin layers", *Thin Solid Films*, **29**, pp 29-41 (1975).
7. Doubowski, J.J., Williams, D.B., Sewell, P.B. and Norman, P. "Epitaxial growth of (100)CdTe on (100)GaAs induced by pulsed laser evaporation", *Appl. Phys. Lett.*, **46**(11), pp 1081-1083 (1985).

8. Kashiwaba, Y., Komatsu, T., Nishikawa, M., Ishikawa, Y., Segawa, K. and Hayasi, Y. "X-ray diffraction studies of p-CdS:Cu thin films", *Thin Solid Films*, **408**, pp 43-50 (2002).

9. Kashiwaba, Y., Isojima, K. and Ohta, K. "Improvement in the efficiency of Cu-doped CdS/non-doped CdS photovoltaic cells fabricated by an all-vacuum process" , *Solar Energy Materials & Solar Cells*, **75**, pp 253-259 (2003).

10. Abe, T., Kashiwaba, Y., Baba, M., Imai, J. and Sasaki, H. "XPS analysis of p–type Cu–doped CdS thin films", *Applied Surface Science*, **175-176**, pp 549-554 (2001).

11. Petre, D., Pintilie, I., Pentia, E. and Botila, T. "The influence of Cu doping on opto-electronic properties of chemically deposited CdS", *Materials Science and Engineering*, **B58**, pp 238-243 (1999).

12. Kashiwaba, Y., Isojima, K. and Ohta, K. "Improvement in the efficiency of Cu-doped CdS/non-doped CdS photovoltaic cells fabricated by an all-vacuum process", *Solar Energy Materials & Solar Cells*, **75**, pp 253-259 (2003).

13. Abe, T., Sato, J., Ohashi, S., Watanabe, M. and Kashiwaba, Y. "Light emission of a Cds(Cu)/CdS thin film diode", *Phys. Status Solidi*, **B229**, p 1015 (2002).

14. Petre, D., Pintilie, I., Pentia, E., Pintilie, I. and Botila, T. "The influence of Cu doping on opto–electronic properities of chemically deposited Cds", *Materials Science and Engineering*, **B58**, pp 238-243 (1999).

15. Kashiwaba, Y., Abe, H., Kirita, H., Ikeda, T. "Fabrication of Cu–doped CdS cell by an all-evaporation process and its photovoltaic properties", *Jpn. J. Appl. Phys.*, **29**, pp 1733-1738 (1990).

16. Nair, P.K., Daza, O.G. and Readigos, A.A.C. "Formation of conductive CdO layer on CdS thin films during air heating", *J. Campos and M.T.S. Nair, Semicond. Sci. Technol.*, **16**, pp 651-656 (2001).

17. Oliva, A.I., Solis-Canto, O., Castro-Rodriguez, R. and Quintana, P. "Formation of the band gap energy on CdS thin films growth by two different techniques", *Thin Solid Films*, **391**, pp 28-35 (2001).

18. Amalnerkar, D.P. "Photoconducting and allied properties of CdS thick films", *Materials Chemistry and Physics*, **60**, pp 1-20 (1999).