

Optical and morphological studies of copper doped cadmium selenide thin films.

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Abstract: Copper doped cadmium selenide thin films with variable composition 0.01-1 mol% have been grown on non-conducting glass substrate by dip coating technique. The effect of doping has been investigated. X-ray diffraction optical absorption microscopy techniques were used to characterize the films. The X-ray diffraction study indicates all the films were crystalline in hexagonal structure. Examination of absorption spectra suggests direct kind of band gap, the magnitude of which varies non-linearly as copper content in the film increases. The grain size increases up to 0.1 mol% and afterwards decreases.

IndexTerms: Thin films, X-ray diffraction, doping

I. INTRODUCTION

The electronic and optical properties of semiconductors are strongly influenced by the doping process, which provides the basis for tailoring the desired carrier concentration and, consequently, the absorption, emission and transport properties as well. When the density of n-type or p-type doping becomes sufficiently high, the impurity merges with conduction and valence band and causes the formation of band tail and band gap shrinkage. In photoelectrochemical cells, one of the reasons for the loss in conversion efficiency is due to higher resistivity of the photoelectrode material. An efficient way is to decrease the resistivity, lowering the band gap and to improve the properties of semiconducting material is to dope with a suitable impurity called dopant. This enhances properties in number of host lattice¹⁻⁹. Cadmium Selenide is a semi-conducting material taken into concern as a necessary compound for the progress of diverse optoelectronic gadgets¹⁰⁻¹⁴.

A very attractive method for producing thin films, by large area deposition at low cost, is the chemical method. The method requires the presence of chalcogen ions and complexed metal ions. Complexation provides small metal cation concentration to produce the controlled homogeneous precipitation of the thin films on the solid substrate. Thin film formation by chemical method proceeds through various reaction steps at the substrate surface. First step is the nucleation-taking place on the substrate surface. An impurity already deposited on the substrate or adsorbed cation or anion or impurities on substrate surface in contact with reaction mixture can act as nucleation centers. Once the layer of material is formed, further growth takes place by adsorbing more and more ions from the solution giving a continuous film. The film growth takes place either by an ion-by-ion condensation or by adsorption of colloidal particles on substrate surface.

Pawar¹⁵ et al electrodeposited cadmium selenide and Fe doped cadmium selenide thin films. The doping concentration of Fe is optimized by using (photo) electrochemical characterization technique. The deposition mechanism and Fe incorporation are studied by cyclic voltammetry. The photoelectrochemical study shows that Fe doped thin films are more photosensitive than that of undoped thin films. The X-ray diffraction analysis shows that the films are polycrystalline with hexagonal crystal structure. The complete surface morphology has been changed after doping.

In the proposed research work, doped and undoped binary or ternary thin films of group II-VI will be prepared by employing a dip method.¹⁶ It is a modified chemical bath deposition method. This method requires the complexed metal ions and chalcogen ions.

II. MATERIALS AND METHODS

Every chemical applied in preparation have been analytical level. Ammonia, selenium powder, cadmium sulfate, sodium sulphite and trichloroacetic acid were utilized.

Sodium selenosulphate (0.2 M) became applied selenide ion resource for synthesise of cadmium selenide samples. The mixture became ready by heating 3.0g selenium fine particles accompanied by 9.0 g Na_2SO_3 in 100mL two fold purified water for 8 hour on 353 K. Mixtures became cool, filter to take out solid residue and put in storage inflask.¹⁷

For manufacture of CdSe samples, 10 mL of (0.2 M) cadmium sulphate octahydrate have been in use in 100 mL glass vessel, and after that it be chelated by means of trichloroacetic acid. 15 mL (5N) ammonia became mixed this reactive solution. Afterward 10 mL (0.2 M) sodium selenosulphate is further mixed in vessel. 30 mL distilled water become mixed in the bath

By using pH meter, pH of reactants was measured. It was observed to be 10.20. The glass vessel becomes placed in the ice. The solution was stirred strongly prior to dipping non conducting as well as conducting substrates, which were mounted upright somewhat slanting in reaction mixture. Temperature of reactive solution became formerly allowable to rise to 298 K extremely gradually. Once four hour was completed, templates have been distant. The deposited glass substrate was dried in nature.

III. RESULT AND DISCUSSION

Copper doped cadmium selenium existing in hexagonal and cubic phase the. X-ray refraction (XRD) spectra of copper doped cdse samples coated on amorphous materials are indicated in fig.1. JCPDS information of cdse and cu selenide was utilized to determine the phase of the sample the XRD pattern suggest polycrystalline nature of sample. The study of spectrum indicate that all the film samples have hexagonal phase¹⁸⁻¹⁹ Each copper dopant sample demonstrate (002) as main peak. (101), (110), (112) (202) peaks have been observed. It is a conformity with formerly report.²⁰ For sample having dopant amount greater than 0.01mol%, observe intense diffraction peak at $2\theta = 44.590$ corresponding to (022) planes of cubic structure of copper selenide. While sample having dopant quantity larger than 0.05 mol%, another peak at $2\theta = 64.980$ corresponding to (004) plane of cubic structure of copper selenide obtained. For 1.0 mol% copper doped in cadmium selenide sample futher new peak of cubic copper selenide was found at $2\theta = 52.920$ corresponding to (113) plane. Other possible structures of copper selenide were not observed. For sample, up to 0.1mol% copper dopant the peak height as well as polycrystalline nature improves. Greater than 0.1mol% quantity of copper, the peak height and polycrystalline natures decreases.

The optical parameters of copper inserted cadmium selenide thin samples were computed in the wavelength changes from 400-800 nm. The acquire absorbance became utilized to estimate absorptivity, optical energy as well as nature of transition. Variation of absorbance with wavelength of representative copper doped films is shown in Fig.2.

Absorptivity of all doped sample is greater than undoped cadmium selenide. The copper dopant samples signify exceptionally absorptive character. For shorter wavelength the magnitude of absorptivity is high and decreases later for higher wavelength. For 0.01 mol% copper doped sample, magnitude of absorptivity became $2.50 \times 10^4 \text{ cm}^{-1}$ at 400nm and $2.33 \times 10^3 \text{ cm}^{-1}$ at 800nm. For 1.0mol% copper doped sample, absorptivity became $2.96 \times 10^4 \text{ cm}^{-1}$ at 400nm and $5.19 \times 10^3 \text{ cm}^{-1}$ at 800 nm. The absorptivity enhances up to 0.1mol% of dopant and later reduces. Important absorption that related to electron stimulations of valence to conduction band, may be applied to compute character in addition to magnitude of band energy. Optical energy has been computed utilizing Tauc's relation.²¹

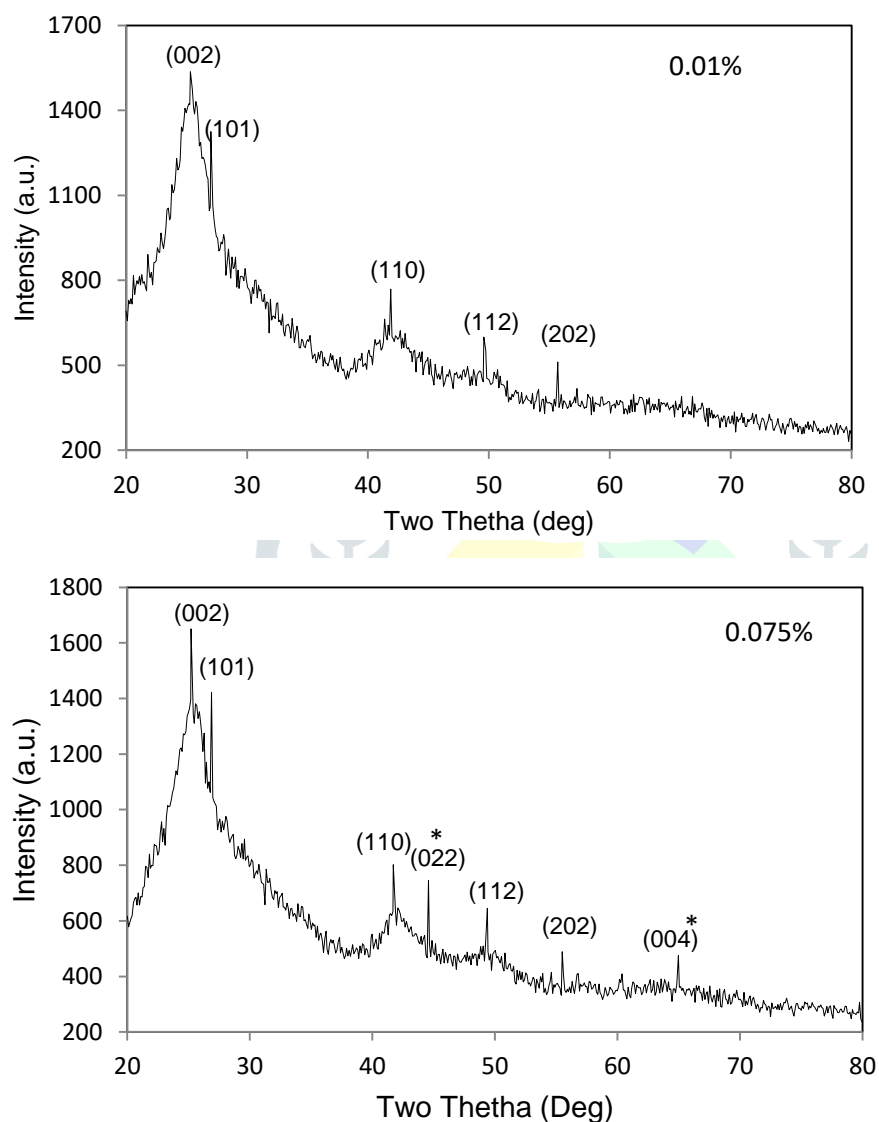
The optical gap has been computed through cut-off the linear region of charts drawn among $(\alpha h\nu)^2$ in opposition to photon energy on x- axis. Such charts are represented in Fig.3. The linear character of graph suggests the occurrence of direct transition. The optical gap of 0.01mol% copper doped cadmium selenide thin sample was found to be 2.02 eV, which is less than undoped cadmium selenide. It was originating that optical gap decay as quantity of copper upto 0.1 mol %. Greater than 0.1 mol% optical gap boost steadily. The optical gap of 1.0mol% copper doped cadmium selenide thin sample was found to be 2.10 eV which is equivalent with undoped cadmium selenide. The variation in optical energy was non-linear. The variation of band gaps for different films is due to the variation of crystallinity and or particle sizes. It is put forward that copper amount enhance, extra energy levels are establish in optical gap, through a resultant decrease in the optical energy related by means of direct transition. Analogous reduce in the optical energy is too observe for copper doped cadmium selenide nanoparticles synthesized via chemical method.²² The raise in optical energy after 0.1mol% is possibly due to reduce in crystalline character and diminish in particle dimension. To check the nature of transition, the chart of $\ln(\alpha h\nu)$ in opposition to $\ln(h\nu - E_g)$ was drawn. The slope of chart is approximately 0.5, indicating that samples indicate direct transitions.

The electron images of copper inserted CdSe samples were represented in figure. 4. Acquired samples were observed to be uniform. Material fully covered amorphous templates. As copper amount raise to 0.1 mol% granules dimension too enhances and later on

declined. For 0.01mol% copper dopant sample, the grain dimension became found out to be 65 nm. The grains are distributed randomly. For 0.075% dopant sample, the grains are densely packed. They fused with each other. Along with spherical grains some rods or needles are also obtained. Quantity of rods or needles increases with rise in copper amount. For 1.0 mol% copper dopant sample, the grain dimension was found out to be 62 nm. Micrograph shows mix type of morphology. It shows spherical, rods, needle, and ribbon like structure.

IV. CONCLUSION

Copper doped cadmium selenide thin films can be deposited by using dip coating method. The copper donor ions were found to dissolve substitutionally in the lattice of cadmium selenide up to a certain range of doping concentration. The films highly oriented in the hexagonal phase. The absorption study shows the presence of direct band gap. The band gap decreases from 2.02 to 1.73eV as the doping concentration increase from 0.01 to 0.1 mol%. Whereas for higher values of copper, band gap increases.



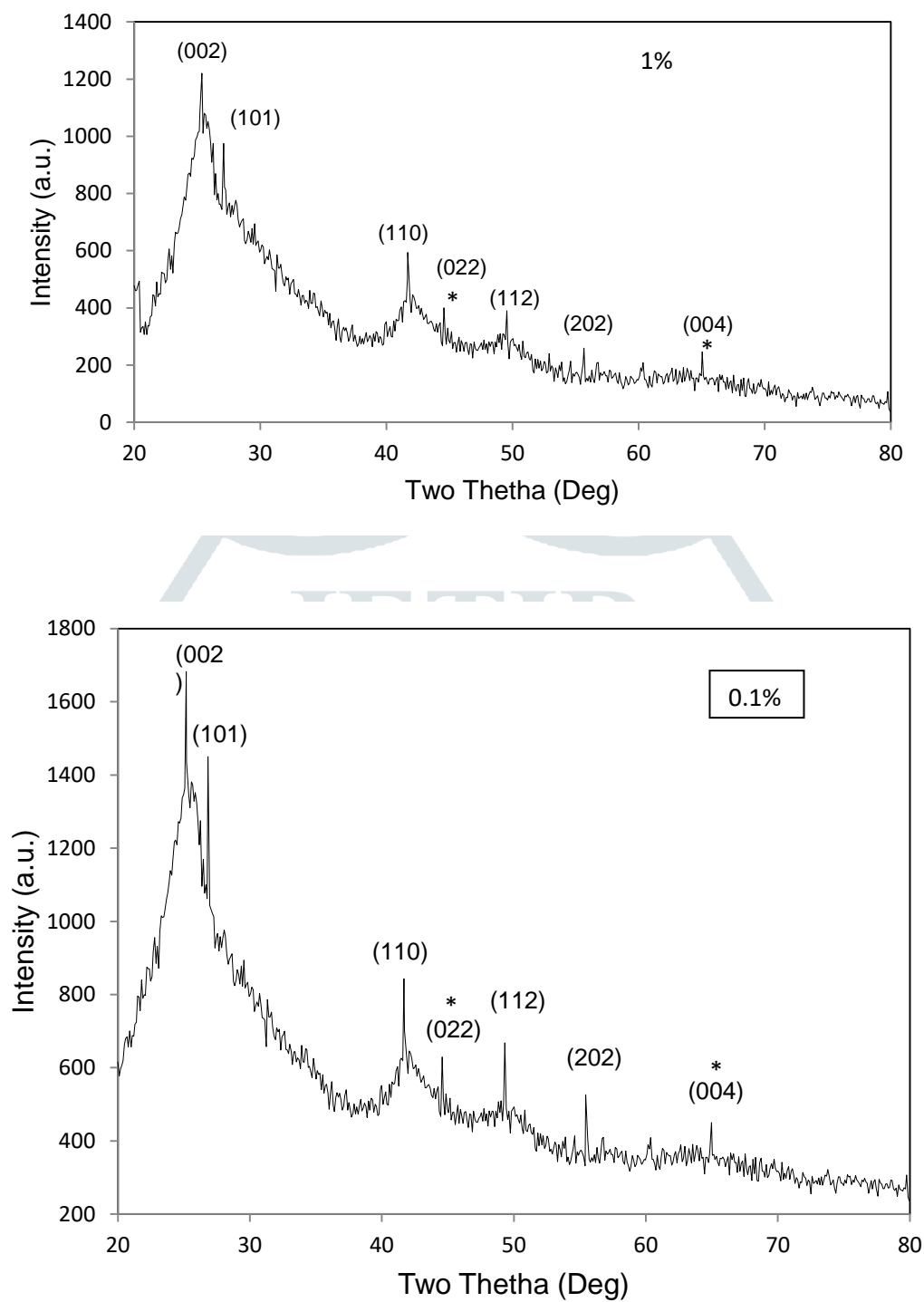
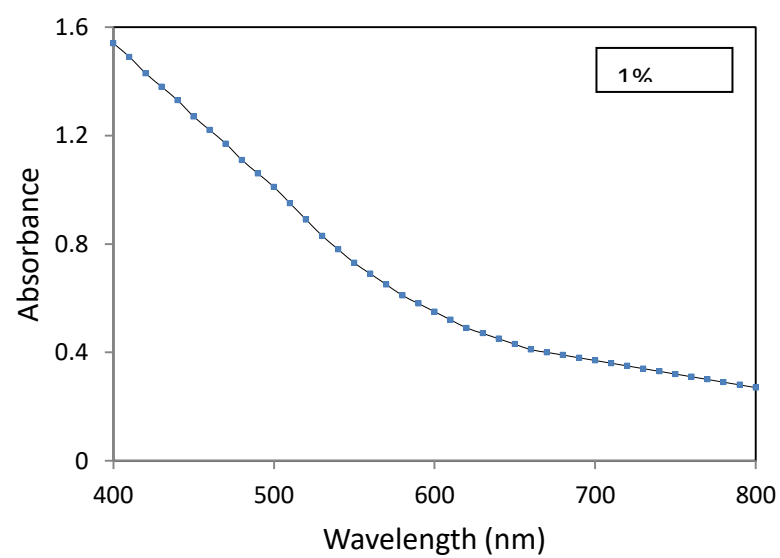
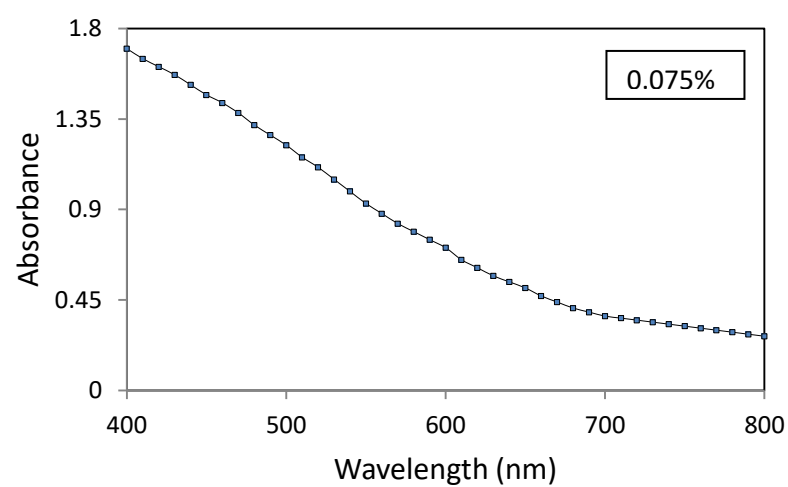
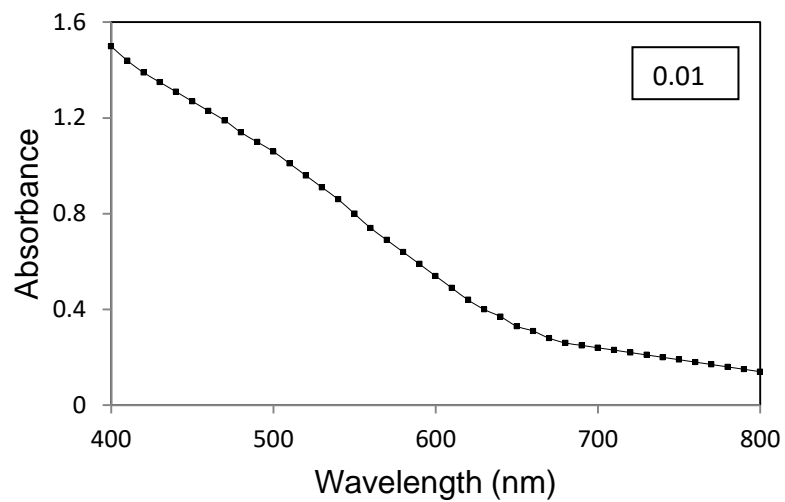


Fig. 1: X-ray diffractogram of copper doped cadmium selenide.



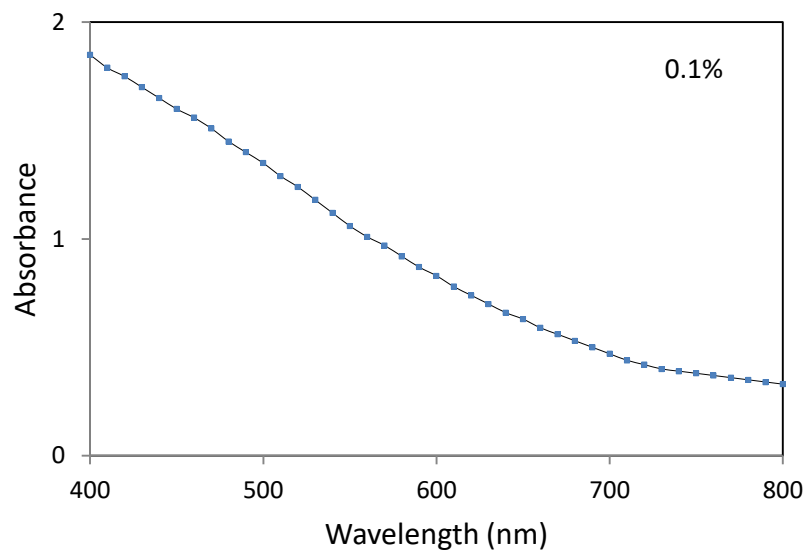
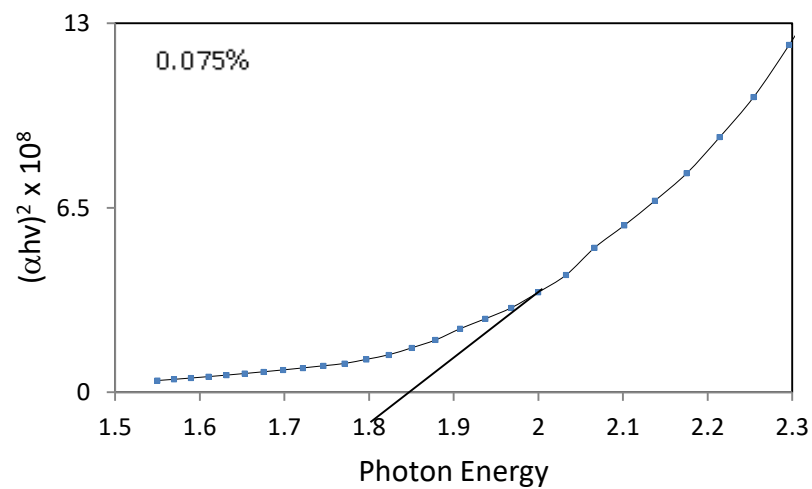
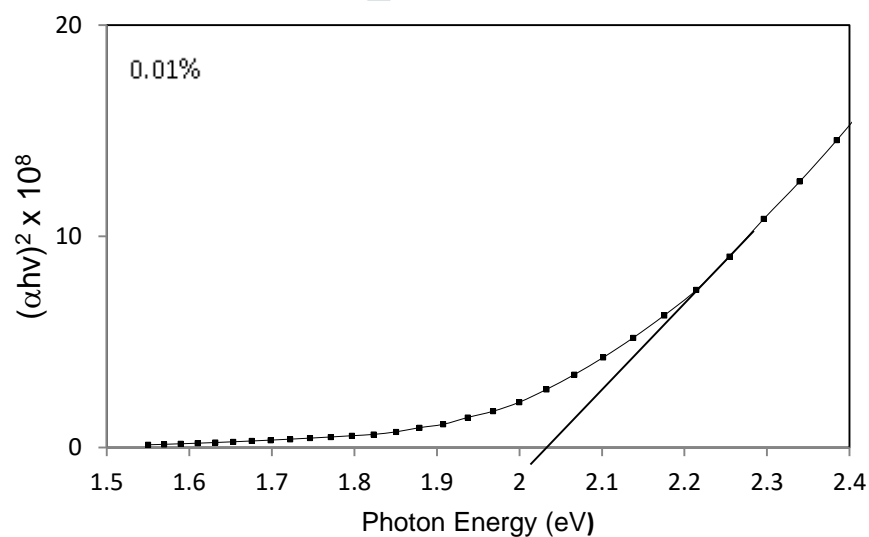


Fig. 2: Plot of absorbance in opposition to wavelength for copper doped cadmium selenide.



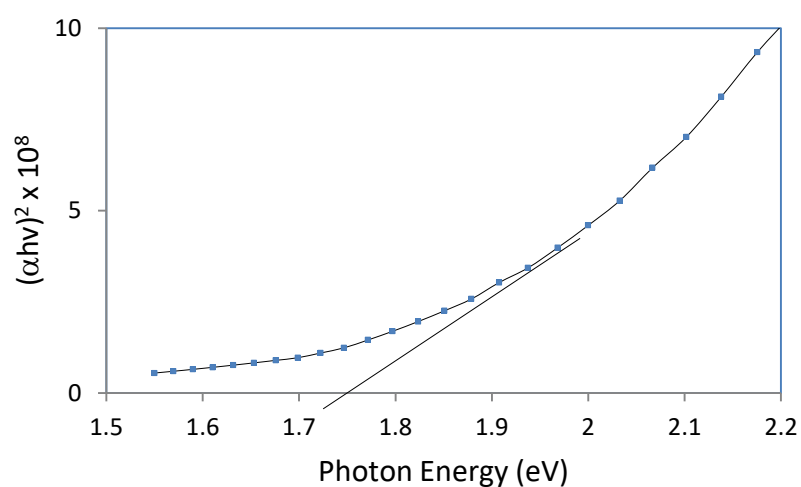
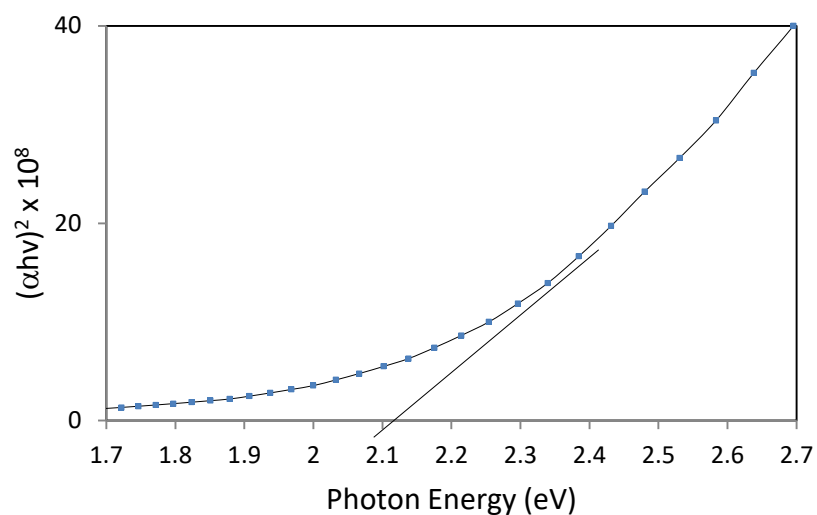
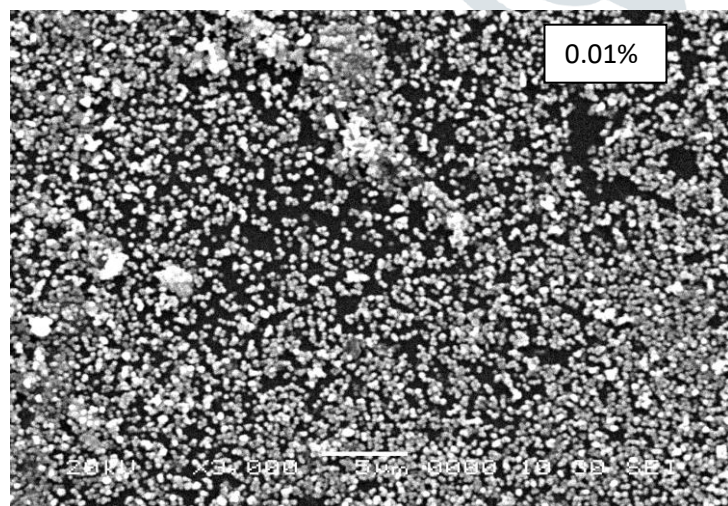


Fig 3: Computation of optical energy of copper doped cadmium selenide.



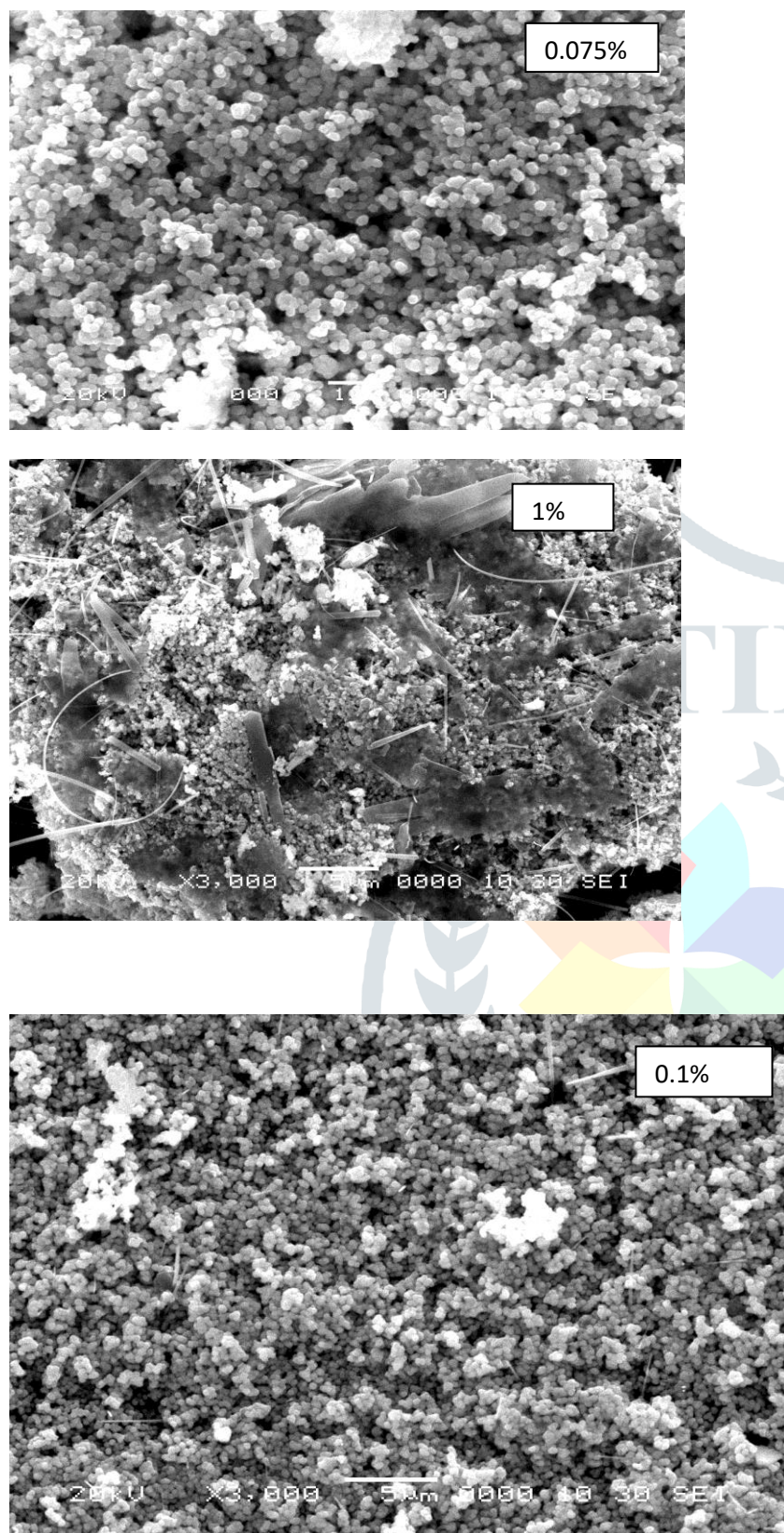


Fig 4: Microscopic image of copper doped cadmium selenide.

V. ACKNOWLEDGMENT

The authors are thankful to Principal Dr. S. B. Dharap for encouragement and support. Our sincere thanks to the Chemistry teaching and laboratory staff or their constant motivation. We would also like to express our gratitude to Ms. Vishakha Vinod Bhabad for helping us in the research work.

REFERENCES

1. Perna G., Capozzi V., Minafra A., Pallara M., Ambrico M., Eur. Phys.J. B 32,339(2003)
2. Kane E., Phys.Rev.131,79(1969)
3. Haufe A., Schwabe R., Fieseler H., Ilegems M., J. Phys. C 21, 2951 (1988)
4. Deshmukh L., Holikatti S., More B., Mater.Chem.Phys. 39, 743 (1995)
5. Pawar S., Deshmukh L., Ind.J.Pure Appl.Phys.22, 315 (1884)
6. Pavaskar N., Menezes C., Sinha A., J. Electrochem.Soc. 124, 743 (1977)
7. Gerischer H., Electroanal.Chem.58, 263 (1975)
8. Deshmukh L., Palwe A., Sawant V., Sol.Energy Mater.20, 341 (1990)
9. Chate P., Hankare P., Sathe D., J. Alloy Compd.505, 259 (2010)
10. Jatar S., Rastogi A., Bhide V. (1978) Photoelectric properties of pure and aluminum doped CdS films. Pramana 16: 477-486
11. Hake S., Chate P., Sathe D., Hankare P., Bhuse V. (2014) Studies on hexagonal cadmium selenide thin film deposited by chemical route using ascorbic acid. J Mater sci: Mater Electron 25: 811-816
12. Murali K., Sivaramamoorthy K., Kttaisamu M., Bahadur S. (2009) Photoconductive studies on electron beam evaporated CdSe films. Physica B 404: 2449-2454
13. Padmanbhasarma H., Subramanian V., Rangarajan V., Murali K. (1995) A comparative study on CdSe synthesized at low temperature. Bull. Mater. Sci 18: 875-881
14. Hann D., Mishra K., Rajeshwar K. (1991) Anodic electrosynthesis of cadmium selenide thin films: characterization and comparison with passive/transpassive behavior of the CdX (X=S,Te) counterparts. J. Electrochem. Soc. 138: 100-108
15. Pawar S., Moholkar A., Rajpure K., Bhosale C.H. (2007) Electrosynthesis and characterization of Fe doped CdSe thin films from ethylene glycol bath Appl. Surf. Sci. 253: 7313-7317
16. Hankare P., Chate P., Sathe D., (2009) CdS thin films: Synthesis and characterization Solid State Science 11: 1226-1228
17. Hankare P., Manikshete A., Sathe D., Chate P. (2010) Structural, optical and microscopic properties of chemically deposited Mo_{0.5}W_{0.5}Se₂ thin films. J. Mater. Sci.: Mater. Electron. 21: 698-701.
18. Chate P., Sathe D., Hankare P., Sankpal U., J. Mater. Sci. 24, 2000 (2013)
19. Hake S., Chate P., Sathe D., Hankare P., Bhuse V., J. Mater. Sci. 25, 811 (2014)
20. Fawade E. (2006) the effect of doping ratio on the optical properties of CdSe films. Um-Salma Sci J. 3: 180-185.
21. Tauc J., Grigorovici R., Vancu A. (1966) Optical properties and electronic structure of amorphous germanium, *Phys status Solidi (b)* 15: 627-637
22. Singh S., Limaye M., Lalla N., Kulkarni S. (2008) Copper ion induced photoluminescences tuning in CdSe nanoparticles. J. Lumin. 128: 1909-1912