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CHARACTERISTICS OF SLURRY COATED CdSeTe FILMS

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$CdSe_xTe_{1-x}$ films were deposited by the slurry coating technique using the $CdSe_xTe_{1-x}$ powders synthesized in the laboratory. X-ray diffraction studies indicated the formation of hexagonal phase. From EDAX compositional analysis, the individual concentrations of Se and Te in the films were estimated. Analysis of the optical data indicate the band gap to vary from 1.44 – 1.68 eV as the value of 'x' changes from 0 to 1. XPS analysis was also carried out on the films. The films were used as photoanodes in polysulphide electrolyte and it was observed that the films with composition $CdSe_{0.6}Te_{0.4}$ indicated maximum photoactivity. Mott Schottky plot indicated n-type behaviour. Spectral response measurements were made and the electrodes exhibited a quantum efficiency of 0.6.

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1. Introduction

Ternary chalcogenides of CdSe and CdTe present very interesting semiconducting properties suitable for solar energy conversion. The band gap can be tailored to suit the requirement, moreover, the ternary compound is highly stable in polysulphide electrolyte when studied in photoelectrochemical (PEC) cells. Several techniques have been employed for the deposition of CdSeTe films, vacuum evaporation[1,2], electroplating[3], pulse plating[4], brush plating[5], hot wall epitaxy[6,7],electron beam evaporation[8], molecular beam epitaxy[9],though there have been reports on slurry coated CdSeTe films[10,11], the films were deposited by sintering mixtures of CdSe and CdTe powders. In the present work, the films were deposited by slurry coating technique using the CdSeTe powder synthesized by chemical precipitation method. The results obtained on the films are presented and discussed.

2. Experimental techniques

CdSeTe powder has been stnthesized by the reaction of AR grade cadmium oxide with AR grade elemental selenium and tellurium at 80 - 90°C in the presence of oxalic acid. This technique consists of the reduction of cadmium oxide and reaction of Cd with Se and Te. This essential chemical reaction for this preparation is given below:

$$CdO + Se + Te \rightarrow CdSeTe + 1/2\ O_2 \uparrow$$

3.0 to 4.0 g of CdO powder was taken in aqueous oxalic acid solution of 1.5 to 2.0 g of Se and 0.5 to 2.5 g of Te was added to the solution. After 8 to 10 hours of refluxing at 80 - 90°C, CdSeTe powder was formed. The

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*Corresponding author: muraliramkrish@gmail.com powder was washed several times with triple distilled water. The unreacted CdO was removed by washing with hot KOH solution. Finally powder was washed thoroughly with triple distilled water, dried in vacuum at about 60°C and stored in vacuum desiccator.

By changing the selenium to tellurium ratio in the above process, CdSeTe powder with different composition of CdSe and CdTe were arrived as per the schematic chemical reaction

$$CdO + xSe + (1-x)Te \rightarrow CdSe_xTe_{1-x} + 1/2\ O_2$$

Using the above procedure, CdSexTe1-x ($0 < x < 1$) powders were synthesized. The powders were silk screen printed on steatite and titanium substrates and sintered under usual conditions. For photoconductivity measurements the films were sintered in air and for photoelectrochemical measurements the films on titanium substrates were sintered in argon atmosphere. Films of the mixed system were prepared by adding 10% of cadmium chloride and after thoroughly grinding in an agate mortar in the presence of iso propanol. The mixture was made into a paste by adding propylene carbonate. The paste was then screen printed onto steatite and titanium substrates. The printed films were dried in air at 120°C for a few hours. The films were sintered in argon atmosphere at 450 - 550°C for 30 min. Structural characterization was done on the films using x-ray diffraction studies, diffuse reflectance measurements were made to estimate the band gap. Photoelectrochemical cells were made using the photoelectrodes and polysulphide electrolyte. Capacitance voltage measurements were mace on the films and spectral response measurements were made in the wavelength range 400 – 850 nm using white light illumination.

3. Results and discussion

The XRD patterns of the films of different composition is shown in the Fig.1a –e. The peaks corresponding to (100),(110),(103),(112), (204) and (210) reflections were observed for x values from 0.1 to 0.3, beyond x = 0.4, reflections corresponding to (100), (101), (102), (110), (112). (201), (202) and (203) reflections were observed. Moreover the intensity of the peaks were also found to increase as the selenium content began to increase. The peaks were observed to shift to higher 2θ values as the ‘x’ value increased from 0 to 1. All the samples exhibited hexagonal structure and the lattice parameters ‘a’ and ‘c’ were calculated using the standard relation,

$$1/d^2 = 4/3[(h^2 + hk + k^2)/a^2 + l/c^2]$$

‘a’ and ‘c’ values for CdSe and CdTe were taken from the ASTM data. A linear variation of the lattice constants with composition indicates that Vegard’s law is obeyed[10]. Generally the alloy structures depend on the composition and method of preparation. Conventional method of preparation resulted in CdSeTe with mixture of cubic and hexagonal phases, conversion of cubic to hexagonal phase required an additional heat treatment step[11-13]. By this synthesis method only hexagonal phase was obtained for all compositions in a single step. Composition analysis was done by EDAX study and the composition of the films materials. The data corresponding to CdLα, SeLα and SLα lines were used for estimating the composition. Diffuse reflectance measurement was made on all the films of different composition. Fig.2 indicates the diffuse reflectance spectrum for the film of composition $CdSe_{0.3}Te_{0.7}$.The results indicated that the band gap varied from 1.5 to 1.65 eV as the composition was varied from CdTe to CdSe. The variation of band gap with composition is illustrated in Table-1.

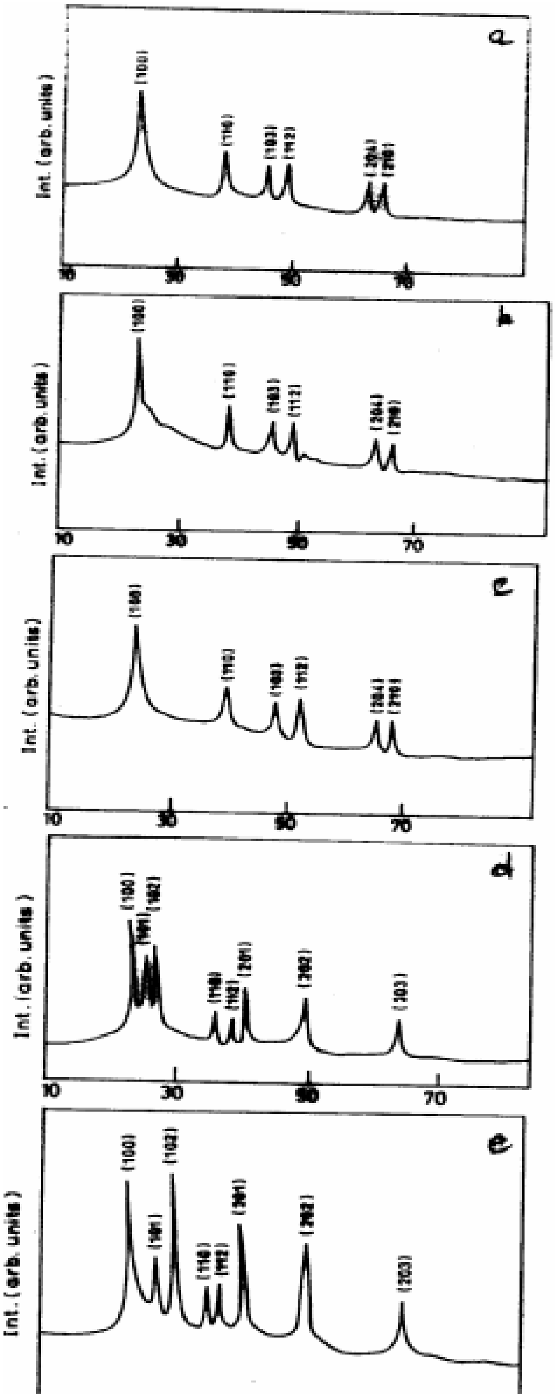


Fig.1. X-ray diffraction pattern of $CdSe_xTe_{1-x}$ *films of different compositions (a)x = 0.1 (b) x= 0.2 (c) x=0.3 (d) x= 0.4 (e) x = 0.5*

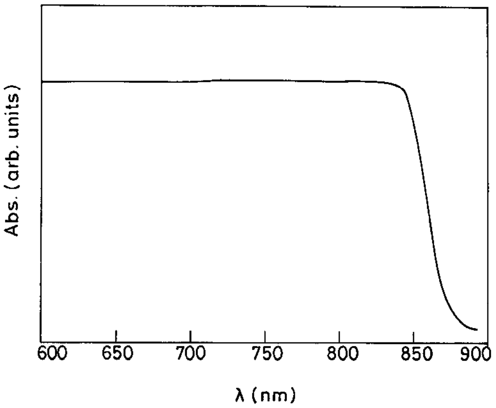


Fig.2. Diffuse Reflectance spectra of $CdSe_{0.3}Te_{0.7}$ film.

Table 1. Composition versus band gap values for CdSeTe films

Composition	**Band gap (eV)**
$CdSe_{0.83}Te_{0.07}$	1.65
$CdSe_{0.86}Te_{0.14}$	1.62
$CdSe_{0.65}Te_{0.35}$	1.57
$CdSe_{0.48}Te_{0.52}$	1.52
$CdSe_{0.34}Te_{0.66}$	1.50
$CdSe_{0.31}Te_{0.69}$	1.50

Fig.3 show the XPS spectra of Cd($3d_{5/2}$ and $3d_{3/2}$) and Se($3d_{5/2}$ and $3d_{3/2}$) and Te($3d_{5/2}$ and $3d_{3/2}$) levels for the $CdSe_{0.5}$ $Te_{0.5}$ films. As observed from the figures, The Cd($3d_{5/2}$ and $3d_{3/2}$) appeared at 405.0 and 411.7 eV respectively; the Se($3d_{5/2}$ and $3d_{3/2}$) appeared at 53.9 and 59.2 eV respectively, the Te($3d_{5/2}$ and $3d_{3/2}$) appeared at 576.2 eV and586.1eV respectively. Atomic concentration measurements were made on the films of different composition selecting suitable sensitivity factors for Cd,Te and Se. It was observed that these concentrations agreed well with the concentration values estimated from EDAX measurements. Further, as the 'x' value increased, the area under the peak for Se($3d_{5/2}$) also increased and the area under the Te($3d_{5/2}$) decreased.

The $CdSe_xTe_{1-x}$ electrodes of different composition were dipped in the polysulphide electrolyte and allowed to attain equilibrium under dark conditions for about 10 min. The dark current and voltage values were noted. The cells were then illuminated by the light source and the current and voltage were measured for each setting of the resistance box. The photocurrent and photovoltage were calculated as the difference between the current and voltage under illumination and the dark current and voltage respectively. The power output characteristics were obtained for the PEC cells made using the photo electrodes of different composition and

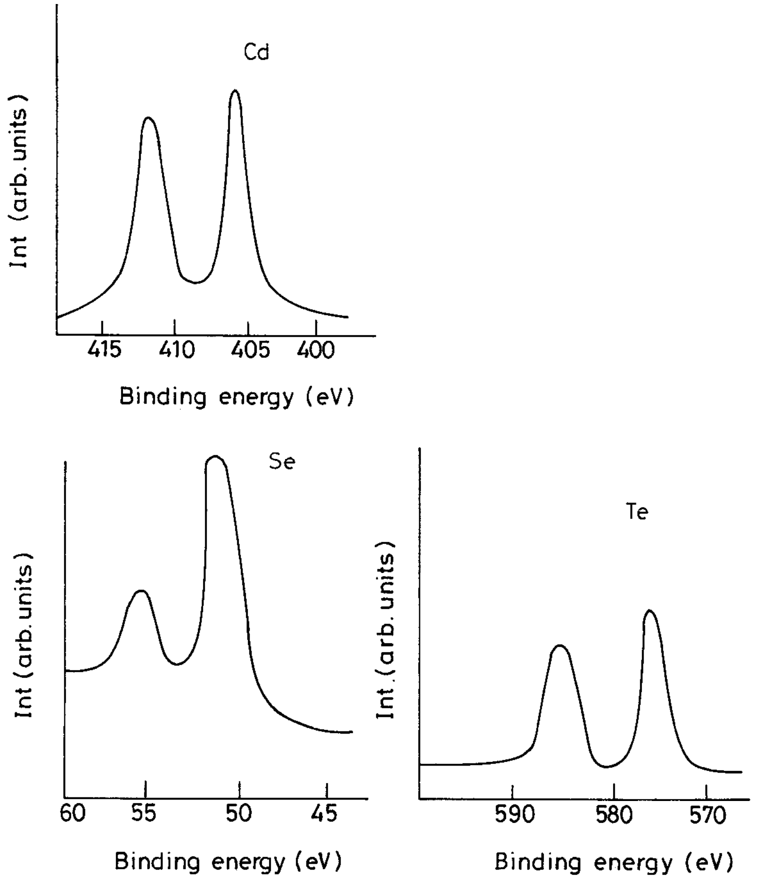
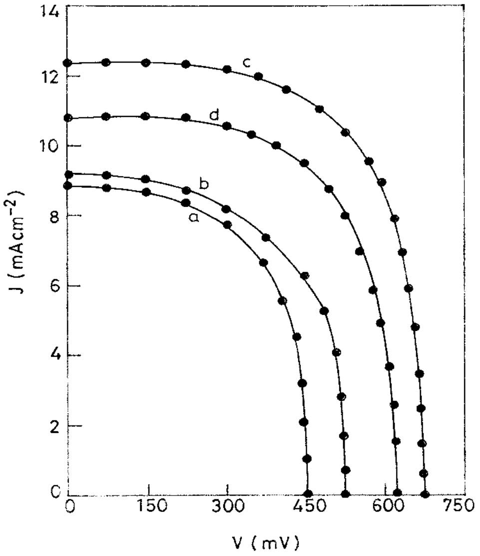


Fig.3. XPS spectra of CdSe0.6Te0.4 film.

heat treated at different temperatures. Amongst the photoelectrodes, that with composition of $CdSe_{0.6}Te_{0.4}$ exhibited highest output parameters hence further studies were made only on films of this composition. Fig.4 shows the load characteristics of the $CdSe_{0.6}Te_{0.4}$ electrode heat treated at different temperatures. It was observed that the PEC output was high for electrodes heated at 525°C irrespective of composition. Photoelectrodes heat treated beyond 525°C exhibited lower V_{oc} and J_{sc} values due to change in concentration of tellurium and selenium vacancies as well as reduction in thickness. Amongst the electrodes of different compositions, it was observed that the overall output started to increase as the selenium content increased in the material. The value of V_{oc} is lower than the reported value of 0.75 V for electrodes prepared by sintering mixture in argon atmosphere at different temperatures (a) 450°C (b) 500°C (c) 525°C (d) 550°C of CdTe and CdSe[8], but the Jsc value for this composition is higher.



Fig, 4. Load characteristics of CdSe$_{0.6}$Te$_{0.4}$ films heat treated.

The value of J$_{sc}$ is higher than that reported for the brush plated electrode[4]. At intensity values beyond 80 mW cm$^{-2,}$ Voc was found to saturate as is commonly observed for photovoltaic and PEC cells, J$_{sc}$ was found to increase with increase in intensity of illumination. A plot of lnJ$_{sc}$ versus V$_{oc}$(Fig.5) yielded a straight line. Extrapolation of the line to the y-axis yields a J$_0$ value of 10^{-7} Acm^{-2}, the ideality factor was calculated from the slope of the straight line and it was found to be 1.88.

The effect of photoetching on the PEC performance was studied by shorting the CdSe$_{0.6}$Te$_{0.4}$ photoelectrode and the graphite counter electrode under an illumination of 100 mW cm^{-2} in 1: 100 HCl for different durations in the range 0 – 100s. Both the photocurrent and

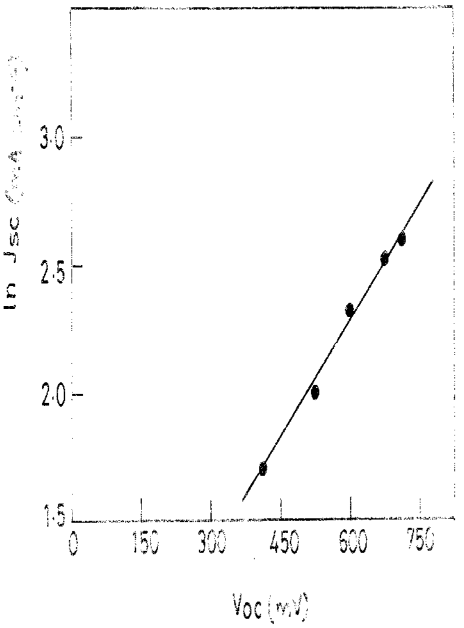


Fig. 5. Plot of ln J$_{sc}$ vs V$_{oc}$ for the CdSe$_{0.6}$Te$_{0.4}$ electrode heat treated at 525°C.

photovoltage are found to increase up to 80s photoetch, beyond which they begin to decrease(Fig.6). Photoetching leads to selective attack of surface defects not accessible to chemical etchants.

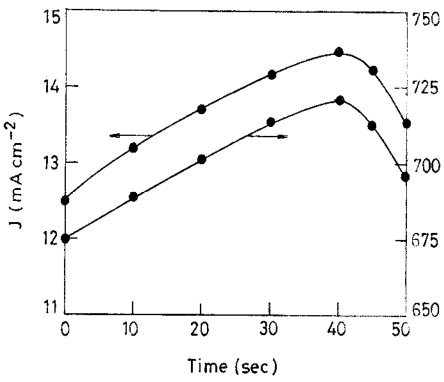


Fig.6. Effect of photoetching time on open circuit voltage and short circuit current density for $CdSe_{0.6}Te_{0.4}$ films heat treated in argon atmosphere at 525 °C.

It is observed that during photoetching the V_{oc} increased from 0.675 V to 0.72 V and J_{sc} increased from 12.5 mA cm -2 to 14.5 mA cm^{-2}. The decrease in photocurrent and photovoltage beyond 80s photoetching can be attributed to separation of grain boundaries due to prolonged photoetching [14]. The photovoltaic parameters of the electrodes of different composition is shown in Table-2. The short circuit current density and efficiency of the photoelectrodes are nearly equal to the earlier reports.

Table 2. Photovoltaic parameters of $CdSe_xTe_{1-x}$ electrodes (Intensity of illumination : 80 mW cm^{-2})

Comp	**Voc**	**Jsc**	**ff**	**η**	**Rs**	**R_{sh}**
(V)	**(mA cm^{-2})**		**(%)**		**(Ω)**	**(kΩ)**
x= 0.1	0.47	4.0	0.60	1.42	30	1.50
x= 0.2	0.48	5.0	0.48	1.43	25	1.50
x= 0.3	0.50	6.3	0.49	2.07	22	1.50
x=0.4	0.51	7.9	0.62	2.65	18	1.50
x=0.5	0.51	9.0	0.65	3.75	15	1.80
x=0.6	0.69	12.3	0.66	7.05	12	2.25
x=0.7	0.63	11.3	0.68	7.00	14	2.10
x=0.8	0.58	10.5	0.58	5.64	15	1.80
x=0.9	0.52	9.0	0.54	3.18	18	2.00
x=0.6	0.73	14.4	0.63	8.25	9	2.50

(After photoetching)

Mott Schottky plots were studied using 1M Na_2SO_4 as the blocking electrolyte and a EG&G PARC impedance analyzer model 6310. The $CdSe_xTe_{1-x}$ films of different compositions were used as the working electrode and SCE was used as the reference electrode. The frequency was fixed at 1 kHz and the bias voltage was varied in the range –0.8 to +0.4V(SCE), the value of C was estimated from the imaginary part of the impedance using the relation,

$$C = 1/2\pi fZ$$

Fig.7 exhibits the Mott Schottky plots for the films of different composition and heat treated at 525°C. The nature of the plot indicates n-type behaviour. Extrapolation of the plots to the voltage axis yields V_{fb} values in the range -1.1 to -1.2 V(SCE). The value of N_D estimated from the slope of the plots yields value in the range of $10^{17}cm^{-3}$. These values are in agreement with the carrier density values obtained from Hall measurements. Amongst the electrodes, the electrodes with composition $CdSe_{0.6}Te_{0.4}$ exhibited maximum $V_{fb,}$ hence the higher open circuit voltage for the above electrode.

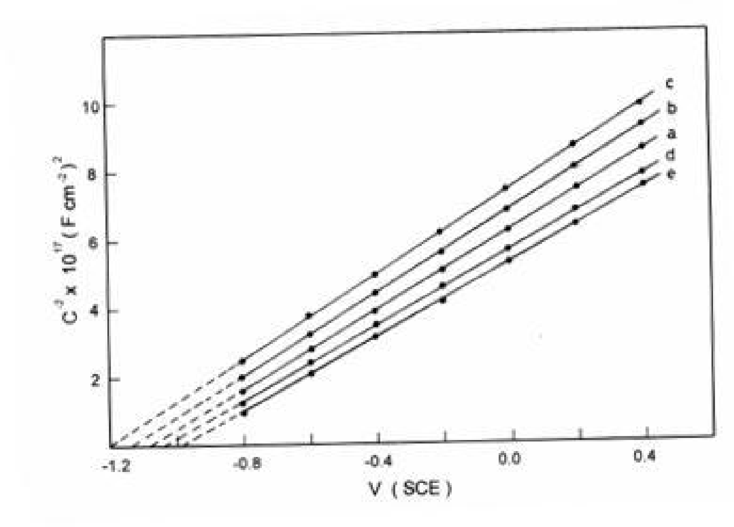


Fig. 7. Mott-Schottky plots of CdSeTe electrodes of different composition heat treated at 525°C (a) x= 0.2 (b) x = 0.4 (c) x = 0.6 (d) x = 0.7 (e) x = 0.9.

As in the case of CdTe or CdSe, the electronic mechanism in $CdSe_xTe_{1-x}$ films are associated with the lattice Se and Te vacancies(V_{Te} & V_{Se}), which are known to behave both as shallow donor centers and deep electron traps[16]. Tellurium and selenium vacancies are generated as a result of partial electrode evaporation during the annealing step. The higher the annealing temperature, the greater is the selenium and tellurium vacancy concentrations. The minority carrier diffusion length decreases due to the vacancies of tellurium and selenium behaving as recombination centers[16]. For an efficient control of the vacancy concentration, the annealing treatment has to be performed in an inert atmosphere (eg.,He) containing a few ppm of oxygen in order to facilitate oxygen chemisorption. Chemisorbed oxygen behaves as an efficient electron acceptor[17] able to compensate the excess concentration of free electrons, which results in an efficient control of carrier density. This effect was evidenced when, after annealing, if the electrode was heated in hydrogen atmosphere at 200°C, the oxygen is desorbed, electrons are freed and the carrier density increases.

The results on the photoelectrochemical investigation, can be explained on the above basis. Higher values of the open circuit voltage were observed as the selenium concentration increases due to the larger value of the flat band potential. Maximum value of open circuit voltage was obtained for the composition $CdSe_{0.6}Te_{0.4}$. As the selenium concentration increases, though the V_{oc} is less, the short circuit current is higher owing to the lower resistivity value compared to CdTe.

5. Conclusion

The results of this investigation clearly indicate that CdSeTe films of different composition can easily be prepared by a chemical method. The band gap of the films cane be varied in the range of 1.50 – 1.65 eV. Films with composition $CdSe_{0.6}Te_{0.4}$ have exhibited maximum photo output. The short circuit current is higher than earlier reports.

References

[1] P. J. Sebastian, V. Sivaramakrishnan, J. Appl.Phys, **65**,237(1989).
[2] S. A. Fayek, S. M. El. Sayed, J. Phys. Chem Solids, **63**,1(2002)
[3] M. Abramovich, M.J.P.Brasil, F.Decker, J.R.Moro, P.Motisuke, N.Muller-st and P.Salvador, J.Solid state chemistry **59**, 1(1985).
[4] K.R.Murali, V.Swaminathan and V.Subramanian, J.Appl.Electrochemistry, **32**, 1151(2002).
[5] K.R.Murali, J.Mater.Sci, **38**, 3845(2003).
[6] S.Velumani, Xavier Mathew, P.J.Sebastian, Solar Energy Mater.solar cells. **76**, 359(2003).
[7] N. Muthukumarasamy, S. Jayakumar, M. D. Kannan, R. Balasundaraprabhu, P. Ramanathasamy, J.Cryst.Growth., **263**, 308(2004).
[8] R. Islam, H. D. Banerjee, D. R. Rao, Thin solid films. **266**, 2252 (1995).
[9] Nobuo Matsumura, Takuya Sakamoto and Junji Saraie, J.Cryst.Growth, **251**, 602(2003).
[10] G. Hodes, Nature. **285**, 29(1980).
[11] M.Sharma, S.Kumar, L.M.Sharma, T.P.Sharma and M.Hussain, Current Applied Physics. **4**, 419(2004).
[12] H.Leweranz, An Introduction to luminescence of solids, Wiley,1950,93.
[13] J.A.Vannechiten and T.Bergstre, SSER.Phys.Rev, **B1**, 3351(1970).
[14] K.R.Murali, V.Subramanian, N.Rangarajan, A.S.Lakshmanan, S.K.Rangarajan, SPIE's International Symp on Applied Science and Energy1536, San Diego, (1991)289.
[15] M.S.Broding, N.I.Vitirikhovski, D.A.Kilon, I.B.Mize, T. Skay, Soviet Phys. Semicond, **6,** 601(1972).
[16] R. K. Pandey, R.B.Gore and A.J.N.Rooz, J.Phys.D.Appl.Phys, **20**, 1059(1987).
[17] J.Segui, S.Hot Chandani, D.Baddau and R.M.Leblanc, J.Phys., **94**, 8807(1991).
[18] R.S.Becker, T.Zheng and J.Elton, J.Electrochem Soc **132**, 1824(1985).
[19] S.Menezes, H.T.Lewerenz, G.Betz,K.J.Bachman and R.Koltz, J.Electrochem Soc, **131**, 3030(1984).