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CHARACTERISTICS OF PULSE PLATED CdS$_x$Se$_{1-x}$ FILMS

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CdS$_x$Se$_{1-x}$ films were deposited by the pulse plating technique at room temperature and at different duty cycles in the range 6 – 50 %. Thickness of the films are in the range of 1.5 – 2.0 micrometres. X-ray diffraction studies indicate that the films exhibited hexagonal structure with the lattice parameters changing from CdSe to CdS side as the concentration of CdS increases. The bandgap of the films varies from 1.68 – 2.39 eV as the concentration of CdS increases. EDAX measurements indicates that the composition of the films are nearly the same as that of the precursors considered for the deposition. XPS studies also supported the formation of the ternary compound. The resistivity, carrier density and mobility were estimated from Hall Van der Pauw measurements by transferring the films from the conducting substrate to an epoxy substrate.

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1. Introduction

The II-VI binary semiconducting compounds, belonging to the cadmium chalcogenide family (CdS,CdTe, CdSe), are considered to be very important materials for a wide spectrum of optoelectronic applications as having specific physical properties such as direct band-gap widths, high absorption coefficients in the visible and infrared part of the solar spectrum, good electrical properties (e.g. carrier mobility and lifetime) and increased capability in obtaining adjustable n- or p-type conductivity by doping. Several techniques were employed for the growth of thin films of the ternary CdSSe. In this work, CdS$_x$Se$_{1-x}$ films were deposited by the pulse plating technique at different duty cycles and the results obtained on these films are presented and discussed. To our knowledge this is the first report on pulse plated CdSSe films.

2. Experimental

CdS$_x$Se$_{1-x}$ films were deposited by the pulse plating technique at room temperature and at different duty cycles in the range 6 – 50 % using AR CdSO$_4$, SeO$_2$ and sodium thiosulphate. The concentration of CdSO$_4$ was kept constant at 0.25 M and the concentrations of and sodium thiosulphate and SeO$_2$ were varied from 5 mM to 50 mM. At a deposition potential of –0.75V(SCE). 20 ml of cadmium sulphate and 5 ml each of sodium thiosulphate and selenium di oxide were used for the deposition. Conducting tin oxide substrates(10 ohms/sq) were employed as substrates. The total deposition time was kept constant at 1 hour. The thicknesses of the films were measured by Mitutoyo surface profilometer and it was in the range of 1.5 - 2.0 µm. Structural studies were made by PANalytical X-ray diffractometer with CuKαradiation. Optical absorption studies were made on the films deposited on conducting glass substrates using an Hitachi U3400 UV-VIS-NIR spectrophotometer. Hall measurements were made on the films adopting the procedure reported earlier [1]. In this method, the CdSSe

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layer is mechanically transferred from the conducting substrate onto a non-conductive epoxy resin without the formation of cracks [2,3]. The electrical properties of the CdSSe layers were examined at room temperature by resistivity and Hall measurements using Van der Pauw method.

3.Results and discussion

The XRD patterns of the films of the composition $CdS_{0.5}Se_{0.5}$ deposited at room temperature and at different duty cycles are shown in the Fig.1. The peaks corresponding to (100), (002), (101), (102), (110), (103),(112), (201),((202),(203),(210) and (211) reflections were observed in all cases. The diffraction peaks shift towards higher angles with increasing x, indicating that the lattice constant decreases with S concentration. This is demonstrated in Fig.2 as a shift in the (002) orientation of the films. All the samples exhibited hexagonal structure and the lattice parameters 'a' and 'c' were calculated using the standard relation,

$$\frac{1}{d^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{c^2}$$

The calculated values of 'a' and 'c' for CdSe and CdS are in good agreement with the ASTM data. The variation of lattice constants of cadmium sulpho-selenide solid solutions with composition is shown in Fig.3. A linear variation of the lattice constants with composition indicates that Vegard's law is obeyed [4]. Similar variation has been observed for sintered pellets [5], flash evaporated layers [6], single crystals [7] and sprayed layers [8]. The films after heat treatment in argon atmosphere at different temperatures in the range 450 - 550°C, exhibited the same peaks as in the case of the as deposited films for all the compositions, but the crystallinity of the XRD patterns improved, as shown by the decrease of the FWHM of the peaks.

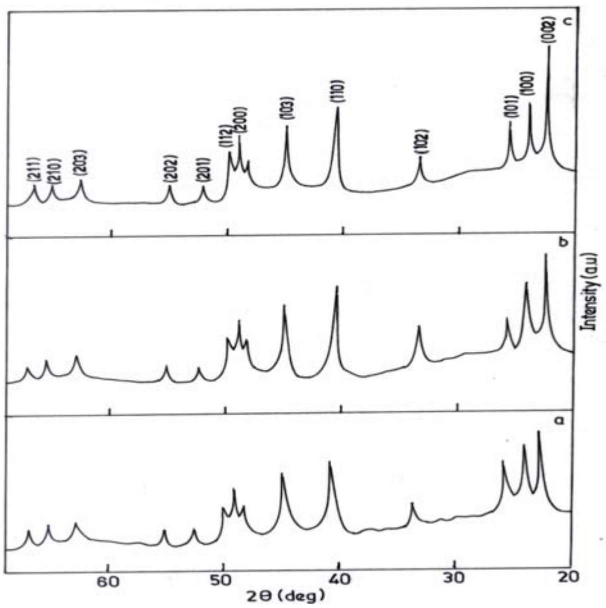

Fig.1. X-ray diffraction pattern of $CdS_{0.5}Se_{0.5}$ films deposited at different duty cycles(a) 10 % (b) 33% (c) 50 %.

Optical absorption measurements were carried out at room temperature by placing an uncoated identical conducting glass substrate in the reference beam. A plot of $(\alpha h\nu)^2$ vs hν for the films of different compositions indicates the direct band nature of the films.

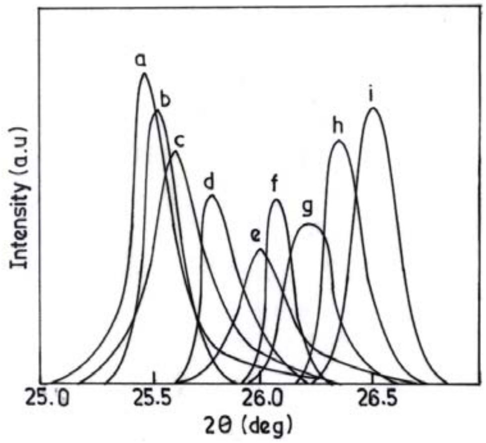

Fig.2 – Shift of the (002) peak with increase of S concentration (a) X = 0.1 (b) x = 0.2 (c) x = 0.3 (d) x = 0.4 (e) x = 0.4 (f) x = 0.6 (g) x = 0.7 (h) x = 0.8 (i) x = 0.9.

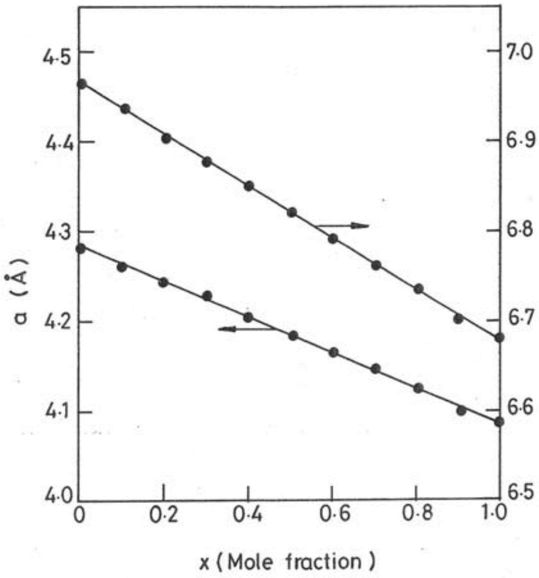

Fig.3 -Variation of lattice constant with increase of CdS concentration.

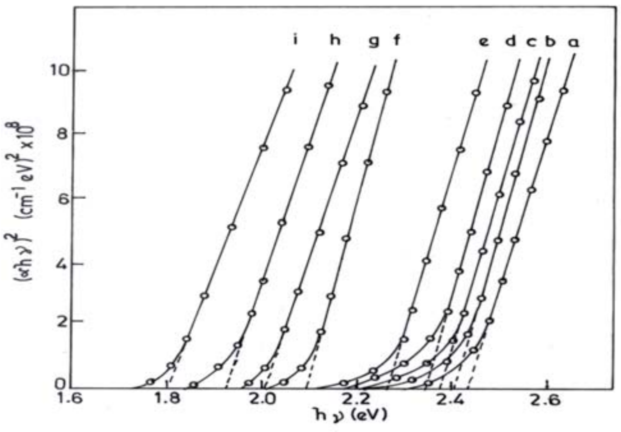

Fig.4 . (αhv)^2 vs hv plot pf the CdS$_x$Se$_{1-x}$ films (a) x = 0.9 (b) x = 0.8 (c) x = 0.7 (d) x = 0.6 (e) x = 0.5 (f) x = 0.4 (g) x = 0.3 (h) x = 0.2 (i) x = 0.1

The extrapolation the linear region to the hv axis indicates that the band gap is in the range 1.68 to 2.39 eV as the value of x increases. The band gap is found to shift towards the red region as the selenium content in the films increased (Fig.4). The variation of band gap with composition is shown in Fig.5.

EDAX measurements were made on the films of different composition deposited at 50 % duty cycle. Table.I indicates the composition of the films.

Fig.6 show the XPS spectra of Cd ($3d_{5/2}$ and $3d_{3/2}$), Se ($3d_{5/2}$ and $3d_{3/2}$) and S ($3d_{5/2}$ and $3d_{3/2}$) levels for the $CdS_{0.5}Se_{0.5}$ films. The $Cd3d_{5/2}$ and $Cd3d_{3/2}$ appeared in the range 405.7 -406 eV and 411.7 – 412.4 eV respectively, the $Se3d_{5/2}$ and $Se3d_{3/2}$ appeared in the range 56 – 60.1 eV and 60.5 – 67 eV respectively and the $S3d_{5/2}$ and $S3d_{3/2}$ appeared in the range 146.5 – 153 eV and 153 – 159.3 eV respectively as the x value changes from 0 to 1. Further, as the 'x' value increased, the area under the peak for S ($3d_{5/2}$) also increased and the area under the Se ($3d_{5/2}$) decreased. The values of binding energies obtained for the Cd, S and Se levels are in very good agreement with that reported in the literature [9]. The values of the binding energy are observed to shift from CdSe side to CdS side as the concentration of CdS in the films increases.

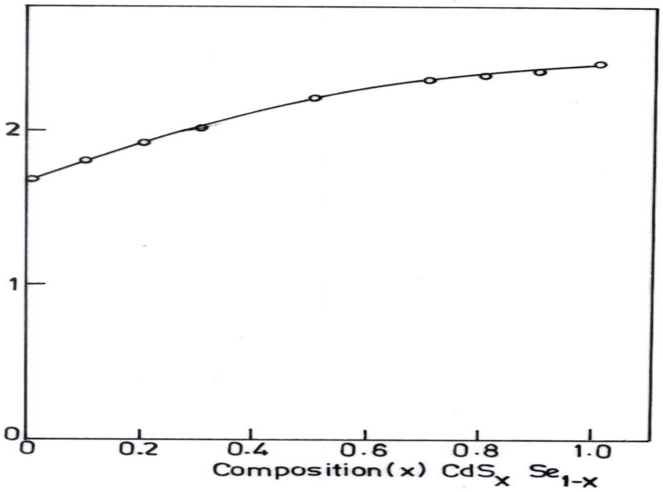

Fig.5 . Variation of band gap with increase of CdS concentration.

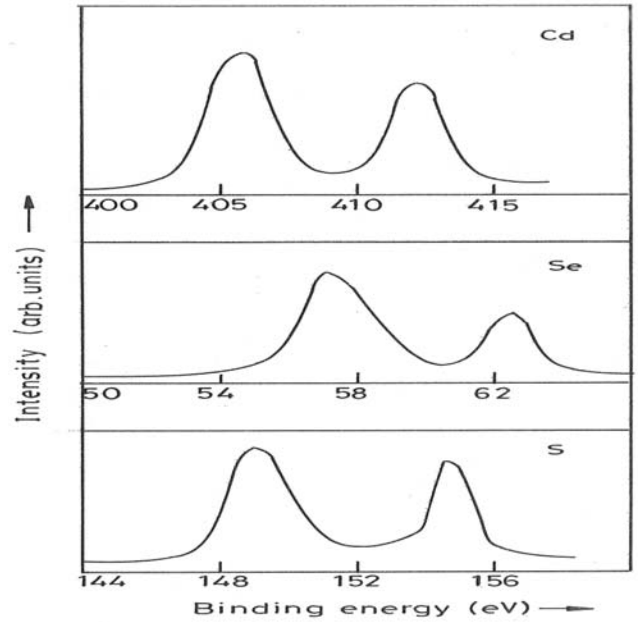

Fig.6 . XPS spectrum of $CdS_{0.5}Se_{0.5}$ films.

The resistivity (ρ) of CdS_xSe_{1-x} films was measured by transferring the films to an epoxy. The influence of composition on the resistivity of the films is depicted in Fig.7. The results on the films annealed at 550°C are only presented, since they have exhibited maximum photo-activity. The magnitude of the resistivity decreases from 12 ohm cm to 1.80 ohm cm as the ‘x’ value increases from 0 to 1.

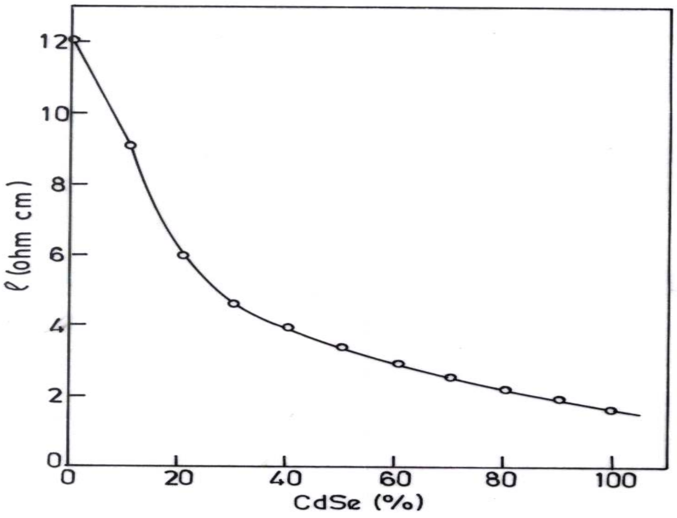

Fig.7. Variation of room temperature resistivity with increase of CdSe concentration.

The decrease in resistivity is due to decrease of selenium vacancies or increase of depth of donor level associated with the selenium vacancy [10].

Fig.8 shows the variation of Hall mobility with composition. It was observed from the figure that the Hall mobility increases as the ‘x’ value increases from 0 to 1.

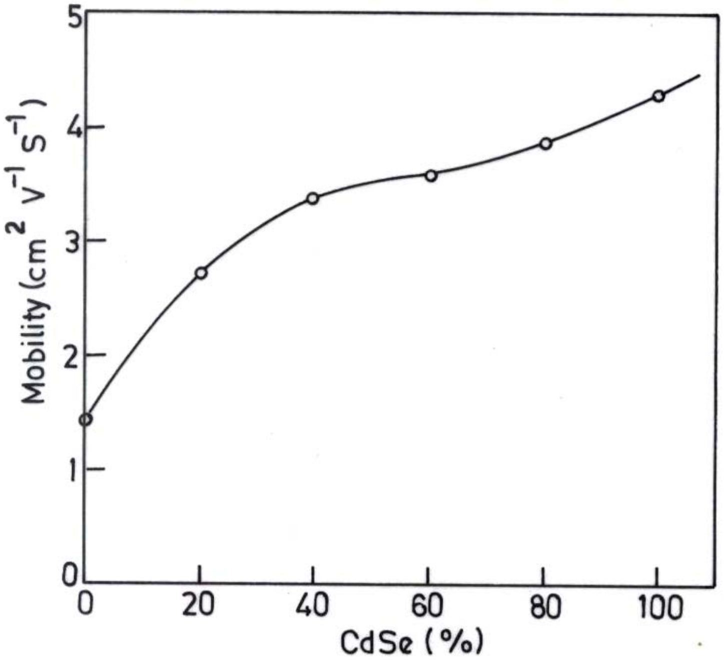

Fig. 8. Variation of room temperature mobility with increase of CdSe concentration.

Fig.9 shows the variation of carrier concentration with composition. It is evident from the figure that the carrier concentration increases as the composition of the films shifts towards CdS side. The carrier concentration is found to increase from 3.5×10^{16} cm^{-3} to 9×10^{17} cm^{-3} as ‘x’ value increases from 0 to 1. The

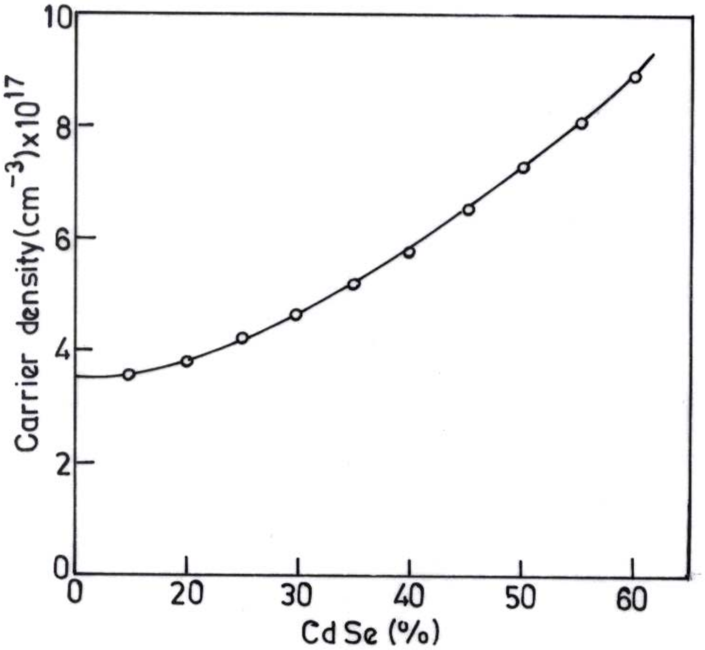

Fig.9. Variation of room temperature carrier concentration with increase of CdSe concentration.

mechanism responsible for the electrical properties is mainly due to the chalcogen vacancy concentration change as the composition of the films change from selenide to the sulphide. The resistivity of the selenide rich films is lower than the sulphide rich films.

4. Conclusions

The results of this investigation clearly points to the possibility of depositing CdSSe films throughout the entire composition range. Films with carrier density of 10^{17}cm^{-3} and mobility in the range of 4 cm^{2}V^{-1}s^{-1} and resistivity in the range of 2 – 12 ohm.cm can easily be obtained by this technique. Further work aims at the study of the optoelectronic properties these films.

References

[1] M.Miyake, K.Murase, T.Hirato and Y.Awakura, J.Electroanal.Chem, **562**,247(2004).
[2] M.Miyake, K.Murase, T.Hirato and Y.Awakura, J.Electrochem Soc, **150**, C413(2003).
[3] J.A.Von Windheim, H.Wynands and M.Cocivera,J.Electrochem Soc, **138**,3435(1991).
[4] H.Leweranz, An Introduction to luminescence of solids, Wiley,93(1950).
[5] R.H.Bube, J.Appl.Phys, **32,** 1707 (1961).
[6] F.L.Chan and D.A.Brooks, Advan X-ray Anal, **8**,420(1965).
[7] R.H.Bube, J.Phys.Chem.Solids, **1**,234(1957).
[8] L.D.Budenya, I.B.Mizetskaya and E.V.Sharkina, Tekh.Mikroelektron, **23**,539(1976).
[9] P.K.Mahapatra and A.R.Dubey, Solar Energy Mater, **32,**29(1994).
[10] E.A.Davis and F.L.Lind, J.Phys.Chem.Solids, **29**,79 (1980).