CHAPTER-3

GROWTH AND STRUCTURE OF CADMIUM SELENIDE THIN FILMS

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3.1 INTRODUCTION

The properties of semiconductor films are known to be highly sensitive both to small changes in their chemical composition and to crystallographic imperfections which in turn are controlled by the detailed mode of preparation and conditions for growth. An assessment of the quality of films grown with respect to various growth condition is desirable and sometimes essential for the interpretation of the physical properties.

Most of the properties of solids, such as physical, optical and electrical properties are highly dependent on structure and composition, especially in the case of semiconductors. In semiconductor devices, structure and composition determine the performance, so the optimization of growth conditions for films of required properties is very much important in the present study.

The growth of thin films of CdSe by vacuum evaporation was studied by several researchers[1-10]. It was reported that the crystallographic modification of the grown films is decided by the stoichiometry [5-9]. KUBOVY et al. had observed marked difference in structural properties and composition between films deposited at different rates of evaporation. But, CHASE et. al. could not observe any change in structural properties and composition between films evaporated at different rate of evaporation.

The present investigation is undertaken with a view to optimize the growth conditions of CdSe films and study their structural properties, which are of paramount importance for the fabrication of electronic devices.

3.2 EXPERIMENTAL

The thin films of CdSe were grown using vacuum evaporation technique. As discussed in chapter-2, a high vacuum system having an arrangement of a liquid nitrogen trap and a cold water cooled chevron baffle, was employed between the oil diffusion pump and vacuum chamber to minimize the back streaming of oil
vapour and contamination. The vacuum of the order of 2.66x10^{-5} Pa was obtained. The source material was pure CdSe powder (Koch Light Laboratory, 99.999%). Glass substrates were cleaned off different impurities by successive immersion in chromic acid and triple distilled water, and then were ultrasonically cleaned in a detergent solution (Teepol). After washing with triple distilled water, they were rinsed with H_{2}O_{2} and dried under electric bulb (100W).

The films were grown at different substrate temperatures, ranging from room temperature to about 653K employing the specially designed flat heater used for substrate heating. The substrate temperature was monitored by Chromal-Alumel thermocouple mounted on the substrate. The substrate temperature was controlled by close-loop digital temperature controller. The distance between the source and substrate was kept constant at about 12cm. After maintaining a steady substrate temperature the electrical supply to the molybdenum boat containing CdSe was switched on and was increased slowly so that temperature rose upto 1353K. The mechanical shutter over the boat was then opened for depositing the films. The thickness and the deposition rate were measured by quartz crystal digital thickness monitor (Hi Tech-DTM 101). For transmission electron microscopy (TEM) and X-ray diffraction study films of thicknesses 70nm and 500nm respectively were deposited at constant deposition rate of about 0.5nms^{-1}.

TEM investigations were performed using a Philips EM400. The films were floated from the glass substrate in a HF (one part to ten parts by volume of deionized water) solution [11]. The films were transferred to the triple distilled water as soon as they are detached from the glass substrate, to avoid any possibility of reaction or contamination with the HF solution. These clean films were then taken onto copper grids for the electron microscopic studies. The compositions of the films were analyzed by the Energy Dispersive Analysis of X-rays (EDAX-AW 9100/60) system. The grain size of the CdSe films was estimated from the electron
micrographs. The X-ray diffraction study are done using a X-ray diffractometer using CuKα-radiation (\(\lambda = 1.542\text{Å}\)).

3.3 RESULTS AND DISCUSSION

3.3.1 EFFECT OF SUBSTRATE TEMPERATURE ON THE STRUCTURE OF CdSe FILMS.

Figure 3.1(a) to 3.1(e) show the electron micrographs and corresponding selected area diffraction patterns of CdSe films grown at temperatures 303K, 373K, 473K, 550K, and 623K, respectively. The electron diffraction patterns of CdSe films grown on the glass substrate at various substrate temperatures reveals the polycrystalline nature of CdSe films. The electron diffraction pattern of film deposited at room temperature(303K) shows[Fig.3.1(a)] the presence of additional rings of selenium in the diffraction pattern, which disappears in the electron diffraction pattern of films grown at the higher substrate temperatures[Fig.3.1(b) to (e)]. MURAJEVA et al also observed the similar selenium rings in CdSe film deposited at room temperature. It is also noted that the diffraction patterns become sharper with increasing deposition temperature of films. This may be ascribed to increasing crystallite size of films.

The electron micrographs revealed that grain size of CdSe films was found to be increased as the substrate temperature increased up to 550K. Figure 3.2 shows the variations of average crystallite size(D) of CdSe films against substrate temperatures(Ts). It is observed from Figure 3.2 that the grain size of CdSe films is increased up to the substrate temperature 550K. At low substrate temperature the grain size of CdSe film was low because the intercrystalline barriers are wide, while at high substrate temperature(i.e. at 550K) the grain size of CdSe film was high because of decrease in the intercrystalline barriers. Above 550K substrate temperature the grain size almost saturates which may be due to deviation from stoichiometric composition of films.
Figure 3.1 Electron micrographs and corresponding selected area electron diffraction pattern of CdSe films deposited at (a) 303K, (b) 373K, (c) 473K, (d) 550K (e) 623K (60,000X).
Figure 3.2 Variation of grain size ($D$) with substrate temperature ($T_s$).
Figure 3.3 show the X-ray diffractogram of CdSe films grown on glass at 550K substrate temperature. It is observed from the table 3.1 that the calculated d-values are in good agreement with the standard data[12]. Table 3.1 lists the d-spacings corresponding to the selected area electron diffraction patterns shown in Figure 3.1(d) and from the X-ray diffractogram shown in Fig. 3.3. The calculated d-spacing values are comparable with standard data[12].

Table 3.1

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>Standard d-values</th>
<th>d-values of CdSe film deposited at 550K substrate temperature and from Fig. 3.1(d)</th>
<th>d-values obtained from diffractogram Fig. 3.3</th>
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<tbody>
<tr>
<td>100</td>
<td>3.720</td>
<td>3.72</td>
<td>3.72</td>
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<td>002</td>
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<tr>
<td>205</td>
<td>1.200</td>
<td>-</td>
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</table>

The lattice structure of CdSe can be found in two different forms: zinc blende(cubic) and wurtzite(hexagonal) types[13-17]. The zinc blende type structure with lattice parameter $a_0 = 6.05 \text{Å}$ is the stable form found in bulk crystals at
Figure 3.3 X-ray diffractogram of CdSe film deposited on the glass at substrate temperature 550K.
atmospheric pressure[18]. The wurtzite structure of CdSe has been observed in films prepared by various techniques including sublimation of the compound[19], oblique deposition of the compound in vacuum deposition[10,20,21] and sputtering[22,23].

3.3.2 EFFECT OF SUBSTRATE TEMPERATURE ON STOICHIOMETRIC OF CdSe FILMS

The composition of CdSe powder as well as films were analyzed by EDAX. The composition of CdSe powder revealed that the starting materials are stoichiometric. Figure 3.4 shows the variation of composition ratio (atomic%) of Se to Cd against substrate temperature. At composition ratio of 1.0, the film is stoichiometric. The range bar represents data taken on five separate films grown at the same substrate temperature and taking into account different seven analysis points on each film. Figure 3.4 shows the CdSe films was stoichiometric when grown in the substrate temperature range of 500K to 570K.

The possible mechanism for the growth of CdSe films deposited at different substrate temperatures may be as follows. At room temperature (303K), the deposition of the vapour flux arriving at the substrate results in the formation of selenium rich films as evident from the composition data of the film (Fig. 3.4). Irrespective of whether CdSe evaporates in a molecular fashion or in the dissociated form, on arrival at the substrate, it forms the compound and excess of selenium is maintained in the films. An increase in substrate temperature results in a decrease of volatile selenium in the films, because at higher substrate temperatures, the excess selenium re-evaporates at a faster rate than the compound in accordance with vapour pressure dependence on the temperature[24,25]. The vapour pressure of the compound remaining comparatively smaller than that of individual elements over the temperature range 500K to 570K which leads to the formation of stoichiometric films. For films deposited at substrate temperature above 570K,
Figure 3.4 Variation of the composition of thin films as a function of substrate temperature ($T_s$).
possibility of re-evaporation of films slowly increases. At substrate temperature about 653K, no film could be deposited as the re-evaporation of CdSe films from the substrate becomes considerably high.

3.4 CONCLUSIONS

The growth of CdSe thin film is found to be critically dependent on the substrate temperature. Grain size of CdSe films increases as the substrate temperature increases. The structure of CdSe powder have been found to be cubic while CdSe film deposited at substrate temperature of about 550K have polycrystalline and wurtzite structure. The film deposited at room temperature yields selenium rich, while a substrate temperature ranging from 500K to 570K produces a stoichiometric film. On increasing the substrate temperature beyond 653K, no CdSe films could be deposited.
REFERENCES

1 N. G. DHERE and A. GOSWAMI,

2 B. D. CHASE, G. C. S. COLLINS, F. R. HUNTLEY and J. W. STEEDS,

3 K. K. MURAJEVA, I. P. KALIALINKIN, V. B. ALESKOVSKY
and N. S. BOGOMOLOV

4 A. KUBOVY, J. HAMERSKY and B. SYMERSKY

5 W. GLOODE, H. LIPPWIAN and S. MUTZE

6 T. M. RATCHEVA, STAMBOLEVA, D. H. DJOLER,
YU D. TCHISTYAKOV, G. A. KRASULIN and A. V. VANIIYAKOV,

7 W. M. YIM and E. J. STOFKO,

8 L. DAWERITZ

9 D. B. HOLT, M. I. ABDALLA, F. H. KEJJI and D. M. WILCOX,

10 N. G. DHERE, N. R. PARIKH and A. FERREIRA,
Thin Solid films, 44 (1977) 83.

11 L. L. KAZMERSKI and Y. J. JUANG,

12 Powder Diffraction File, American Society for Testing Materials(ASTM),
Philadelphia, Pennsylvania, Card No. 8-496, p-156

13 M. L. GLESSER,
14 J. L. BIRMAN,

15 J. L. BIRMAN,

16 E. F. GROSS and V. V. SOBOLEV,

17 R. G. WHEELER and J. O. DIMMOCK,

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23 R. W. GLEW,

24 F. A. KROGER,

25 P. S. VINCETT, W. A. BARLOW and G. G. ROBERTS,