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Transmission Electron Microscope Studies of Thin Films of *CdSe* Vacuum Evaporated from Knudsen-Type Source

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ABSTRACT

A Knudsen-type evaporation source was used for the vacuum deposition of thin films of *CdSe* to study their growth and microstructure on to air-cleaved *KCl* and mica substrates under different rates of evaporation and substrate temperatures. The conditions for the growth of epitaxial films of this material onto mica have also been established and their photoconducting properties evaluated. *CdSe* films prepared by this source retain their stoichiometry and compare well with those prepared by other sources of vacuum evaporation.

1. INTRODUCTION

The normal crystal structure of *CdSe* is hexagonal (wurtzite) with a = 4.299 Å and C = 7.010 Å. It is also known to exist in the cubic polymorph which has the sphalerite structure. The two modifications are very close to each other w.r.t. their crystallographic properties and energy. They are known to co-exist, especially in thin polycrystalline films of the material.

The energy gap for *CdSe* is E_g = 1.74 *eV* and the corresponding wavelength for maximum photoconductivity emission[1] is 7200 Å. Normally prepared *CdSe* films consist of polycrystalline material having poor electron mobility.

The physical properties of thin films are structure-sensitive. So, a detailed study of microstructure and orientation of *CdSe* films, vacuum evaporated from a Knudsen[2]-type source and grown onto *KCl* and mica substrates under different rates of evaporation and substate temperatures was made to correlate the microstructure with the photoconducting properties. Also, the effect of annealing and electron beam irradiation on *CdSe* films has been studied. This paper presents electron micrographs of thin films of *CdSe* vacuum deposited by effusion from a Knudsen-type source under different conditions of vacuum deposition and treatment.

2. EXPERIMENTAL PROCEDURE

CdSe powder of 99.9999 per cent purity supplied by Koch-Light Ltd, England, was

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evaporated in a conventional vacuum chamber with a vacuum of the order of 10^{-5} Torr (i.e. 1.33 x 10^{-7} Pascal). A Knudsen-type source having an effusion aperature was used as the source of evaporant material. The rate of evaporation was varied by changing the temperature of the crucible by regulating current in tungsten spiral encircling it. The temperature of the substrate was kept constant by keeping it in thermal contact with the substrate heater. Evaporation was started when the temperature of the substrate had remained constant for about 30 min and the heating current was switched off as soon as the evaporation was over.

An aluminium shutter which could be operated mechanically from outside the vacuum was interposed between the crucible and the substrate. The shutter was kept closed till the crucible attained the required temperature and was opened only till the evaporation was over. Very thin films were backed by carbon using carbon coating technique of Bradley[3].

Films from *KCl* substrates were removed by floating off in distilled water and then picked up on standard electron microscope grids. From the mica substrates, the films were detached by using Hermann & Reimer[4] technique.

Transmission electron micrographs and the selected area diffraction patterns were taken with the help of Siemen's Elmiskop 1, operated at 80/100 KV.

To study the effect of electron beam irradiation, the films were exposed to an electron beam of moderate intensity (30 μA). For this purpose, the image of the films was formed on the screen by using a fairly spread beam. The beam current was then increased in small steps, keeping the screen under visual observation for any apparent change.

Tolansky's[5] interferrometric method was employed to determine the thickness of the films. The results were cross-checked by microbalance weighing before and after the deposition.

For photoconductivity measurements, thin films of *CdSe* were evaporated onto mica substrates through a mask made of mica sheet having a slit 2 cm x 3 mm with additional thin slits perpendicular to the main length at the two ends, for electrical connections. The mask was placed on the mica substrate, which in turn was placed on the substrate heater. After the preparation of the thin films, small pieces of copper wire were indium - soldered to the film strip for photoconductivity measurements.

Carl Zeiss monochromator SPM-2 and Keithley d.c. microvolt-ammeter 150 Å were used for the measurement of photocurrent. The area of the thin film exposed to the monochromator was kept constant in all the cases. The specimens were exposed to various wave lengths from 6000 to 7800 Å in steps of 100, in complete darkness and the resultant photocurrent was measured.

3. RESULTS & DISCUSSION

3.1 Evaporation onto *KCl* Substrates

3.1.1 Substrate at Room Temperature

Figure 1. shows an electron micrograph of *CdSe* film (400 Å grown onto air-cleaved *KCl* substrate held at room temperature and at a rate of deposition of 20 Å/s. The SAD pattern in the inset shows that the film is polycrystalline. The grain size is small (~50 Å average size). The SAD pattern conforms to the hexagonal phase, but a weak cubic phase is also present.

Figure 2 shows a *CdSe* film also deposited on to *KCl* substrate at room temperature but at a higher rate of deposition (~200 Å/s). The film thickness is 200 Å. The SAD pattern shows that the film is polycrystalline and has a predominant cubic phase.

3.1.2 Substrate at High Temperatures

Figure 3 shows a *CdSe* film (300 Å), obtained by deposition onto *KCl* substrate at 300 °C and at a rate of deposition of 10 Å/s. The grain size is 300 Å. The SAD pattern shows that the film has acquired a preferred orientation with both the phases. The crystallites of the hexagonal phase are oriented with $(0001)_{CdSe}$ II $(001)_{KCl}$, while the particles of the cubic phase have $(001)_{CdSe}$ II $(001)_{KCl}$. Stacking faults are present in the individual grains.

Figure 4 shows a *CdSe* film (350 Å) obtained at substrate temperature of 300 °C, but with a higher rate of deposition (~50 Å/s). The film has

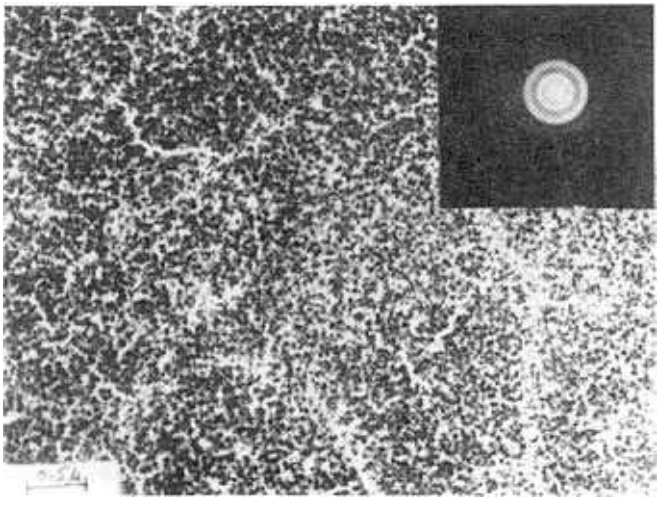

Figure 1. *CdSe* film (400 Å) deposited onto *KCl* substrate at 25 °C. Rate of deposition: 20 Å/s.

predominantly cubic phase with an orientation of (001). The grain size is large (~800 Å).

3.2 Evaporation onto Mica Substrates

3.2.1 Substrate at Room Temperature

Figure 5 shows an electron micrograph of a *CdSe* film (~400 Å) evaporated onto freshly air-cleaved mica substrate at room temperature. The rate of deposition is 15 Å/s and the grain size is ~150 Å. The film was polycrystalline and has predominantly the hexagonal phase.

Figure 6 shows a *CdSe* film (~400 Å) grown at a higher rate of evaporation (~50 Å/s). The average grain size is ~250 Å. The SAD pattern shows the presence of weak cubic phase along with the hexagonal phase.

3.2.2 Substrate at Elevated Temperature

Figure 7 shows electron micrograph of a *CdSe* film (300 Å) grown on air-cleaved mica at 300 °C. The rate of deposition is ~10 Å/s and the grain size is ~500 Å. The SAD pattern shows that the film has preferred orientation, and both the phases are present. The hexagonal phase has $(0001)_{CdSe}$ II $(0001)_{mica}$, while the cubic phase has $(111)_{CdSe}$ II $(0001)_{mica}$. The presence of stacking faults is evident.

Figure 8 shows a *CdSe* film (300 Å) grown on mica substrate at 300 °C, but at a higher rate of deposition (200 Å/s). The SAD pattern reveals the predominance of cubic content.

3.3 Annealing

Figure 9 shows the film of Fig. 6 after annealing at 300 °C for 3 hr. The micrograph reveals that annealing increases the average grain size from 250 to 500 Å.

Similarly, Fig. 10 shows the film of Fig. 5 when annealed at 400 °C for 1.5 hr, after detaching from the mica substrate. The electron micrograph shows that the film has recrystallised and the average grain size has increased to 0.2 μ.

Figure 11 shows the film of Fig. 6 after exposure to electron beam of moderate intensity of about 30 μA. It is evident that the film has recrystallised but is still polycrystalline with an average grain size of 0.2 μ .

Figure 12 shows the *CdSe* film of Fig. 8 after exposure to an electron beam. The film has recrystallised and acquired single crystallinity, conforming to the hexagonal phase with (0001) orientation. The presence of fringes in the micrograph may be ascribed to the presence of stacking faults.

3.4 Photoconductivity

The photoconductive response of the *CdSe* films grown on freshly air-cleaved mica substrates under different conditions of growth was studied. It has been observed that films of maximum photosensitivity were in the range thickness 1000–1500 Å and grown onto substrates at temperatures greater than 300 °C with rates of deposition greater than 20 Å/s. These growth conditions correspond to the conditions of growth of monocrystalline films of the cubic phase.

Figure 13 shows the photocurrent *vs* wavelength response of a film (1400 Å) prepared at

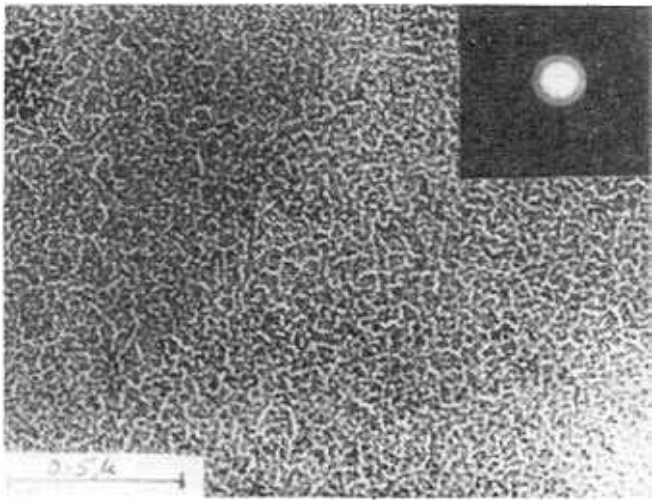

Figure 2. *CdSe* film (200 Å) deposited onto *KCl* substrate at 25 °C. Rate of deposition: 200 Å/s.

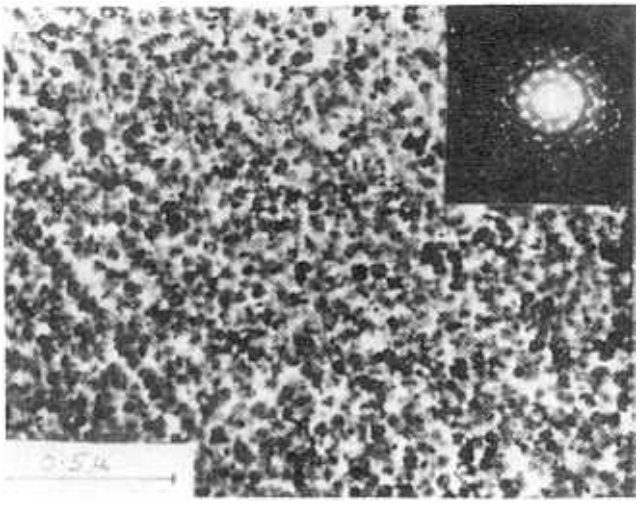

Figure 3. *CdSe* film (300 Å) deposited onto *KCl* substrate at 300 °C. Rate of deposition: 10 Å/s

a substrate temperature of 300 °C and rate of deposition of 40 Å/s.

4. CONCLUSIONS

CdSe films, vacuum evaporated onto *KCl* substrates at room temperature are polycrystalline. Low rates of evaporation of about (~10 Å/s) yield the films consisting mainly of hexagonal phase with weak traces of the cubic phase. As the rate of deposition is increased, the cubic phase content

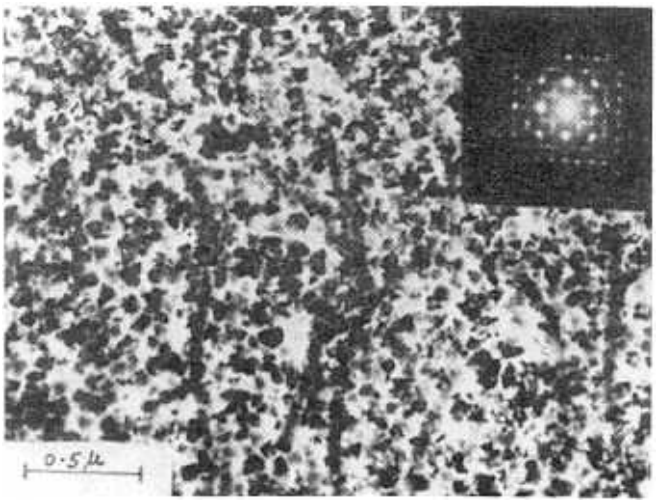

Figure 4. *CdSe* film (350 Å), deposited onto *KCl* substrate at 300 °C. Rate of deposition: 50 Å/s.

increases till at a rate of evaporation of about 200 Å/s, when the film has predominantly the cubic phase. An increase in the substrate temperature gives rise to an increase in the particle size, better orientation of the grains and a slight increase in the cubic phase. The *CdSe* films grown at substrate temperatures above 300 °C are almost single crystalline; the crystallite of the hexagonal phase take up (0001) orientation, while the cubic phase takes up (001) and (111) orientations. A rate of deposition greater than 50 Å/s and substrate temperature higher than 300 °C favours the formation of single crystalline cubic phase on *KCl* substrates with (001) orientation.

CdSe films, vacuum deposited onto freshly-cleaved mica substrates at room temperature, are polycrystalline having predominantly the hexagonal polymorph with weak traces of cubic phase. With an increase in the rate of deposition, the particle size as well as the cubic phase content increases. When the *CdSe* films are grown on heated substrates, the particle size increases and also their orientation improves. The grains of the hexagonal phase have $(0001)_{CdSe}$ II $(0001)_{mica}$, whereas the cubic phase grains have $(111)_{CdSe}$ II $(0001)_{mica}$. The cubic phase content increases with an increase in the rate of deposition. The grain size increases when the *CdSe* films are

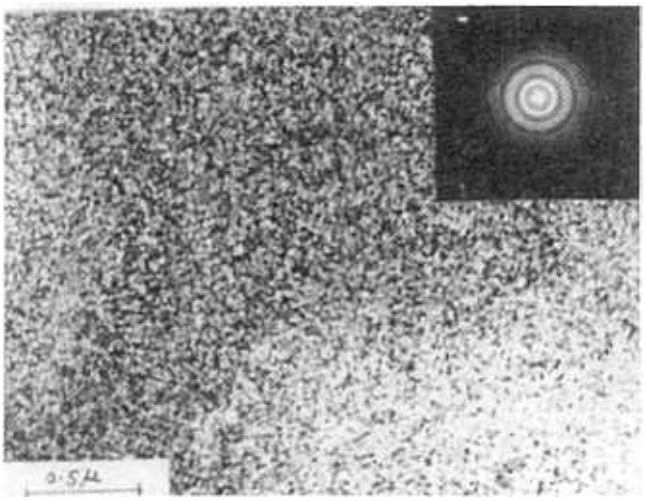

Figure 5. *CdSe* film (400 Å) deposited onto mica substrate at 25 °C. Rate of deposition: 15 Å/s.

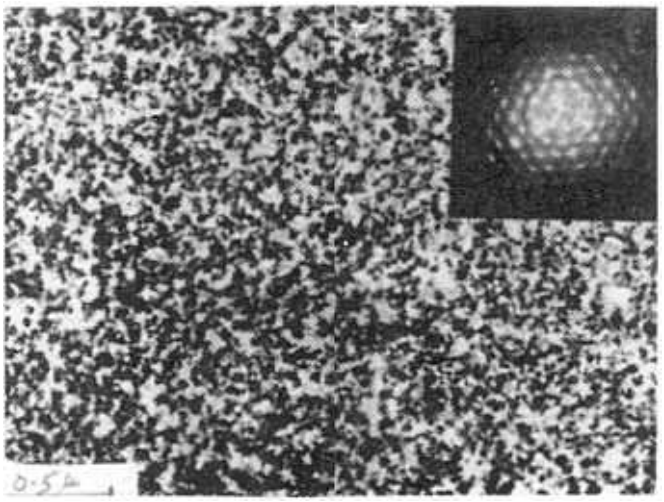

Figure 7. *CdSe* film (300 Å) deposited onto mica substrate at 300 °C. Rate of deposition: 10 Å/s.

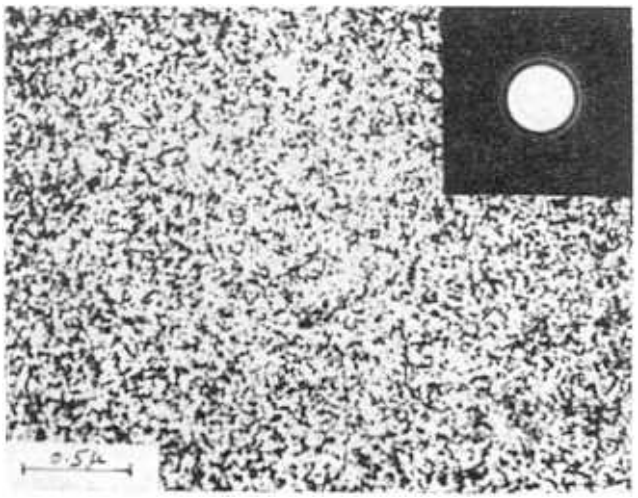

Figure 6. *CdSe* film (400 Å) deposited onto mica substrate at 25 °C Rate of deposition: 50 Å/s.

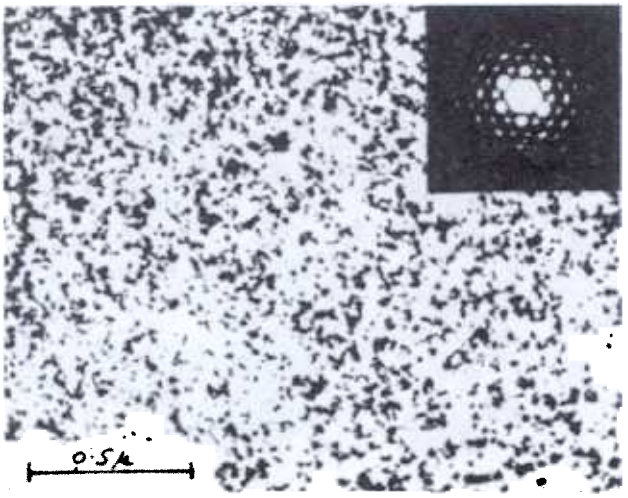

Figure 8. *CdSe* film (300 Å) deposited onto mica substrate at 300 °C. Rate of deposition: 200 Å/s.

detatched from the substrate and annealed at 300 °C. If the annealing is done at a higher temperature (400 °C), recrystallisation of the *CdSe* film occurs. However, there is no change in the orientation of the grains. This is expected because a reorientation of the grains can take place only on the substrate, and that too, in the nucleation stage, when the nuclei of condensation are mobile[6].

Exposure of *CdSe* films to the electron beam of moderate intensity inside the electron microscope shows that sufficiently high temperatures are attained for recrystallisation[7] to occur. This results in increase in the grain size. In *CdSe* films which are already highly oriented with predominantly the hexagonal phase content and also a small cubical phase content, the recrystallised films conform completely to the hexagonal phase and have only single crystal orientation. The presence of stacking faults in these

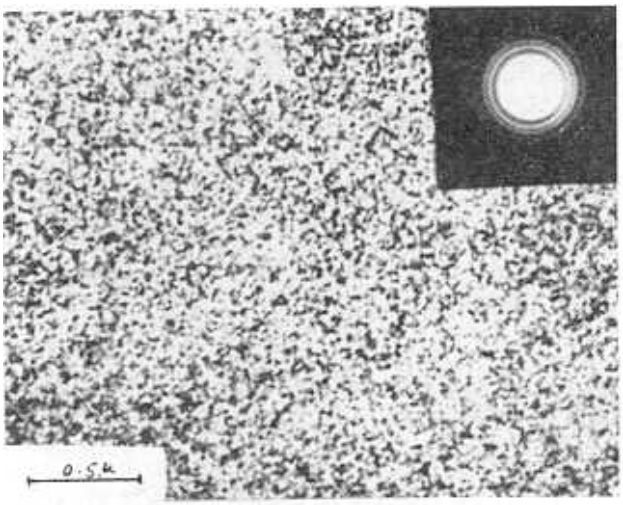

Figure 9. ***CdSe*** **film (of Fig. 6) after annealing at 300 °C for 3 hr.**

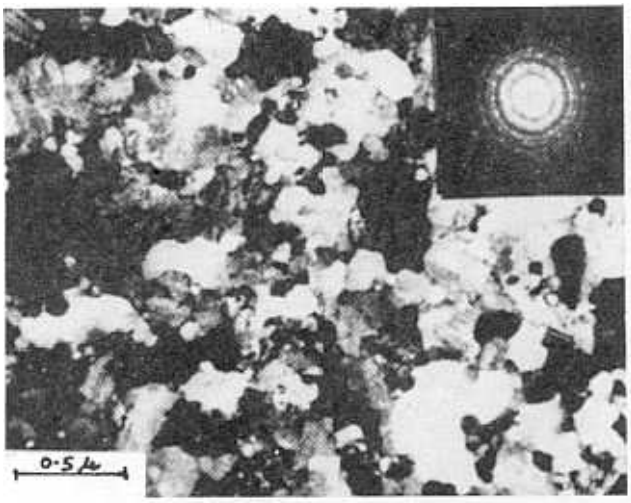

Figure 11. ***CdSe*** **film (of Fig. 6) after exposure to an electron beam of moderate intensity inside the electron microscope.**

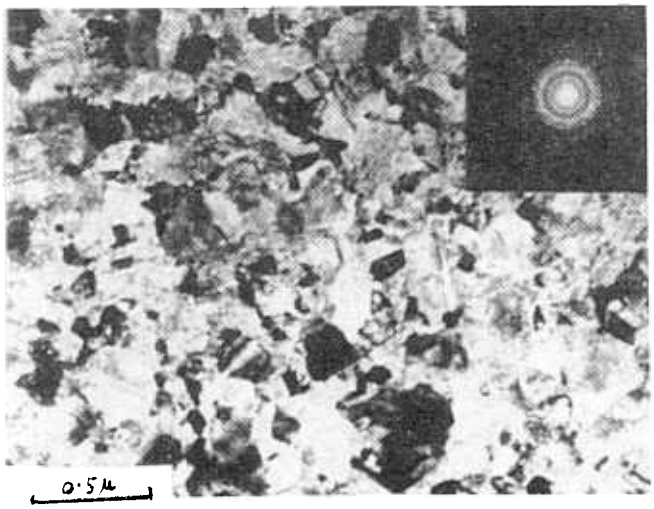

Figure 10. ***CdSe*** **film (of Fig. 5) after annealing at 400 °C for 1.5 hr.**

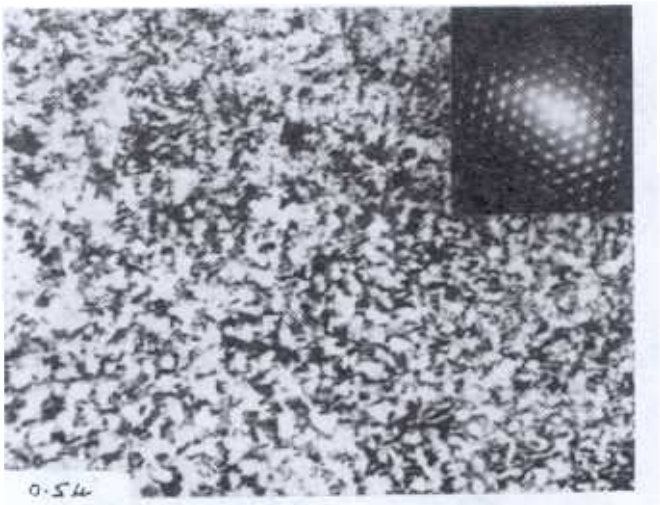

Figure 12. ***CdSe*** **film (of Fig. 8) after exposure to an electron beam of moderate intensity inside the electron microscope.**

films show that the cubic phase content gets incorporated in the hexagonal phase in the form of stacking faults.

The photoconducting current maxima at 7200 Å in Fig. 13 shows that the films have retained their stoichiometry after effusion from the Knudsen[8]-type source, thereby establishing the utility of this source for vacuum deposition of $A^{II}B^{IV}$ compounds, the family to which *CdSe* belongs.

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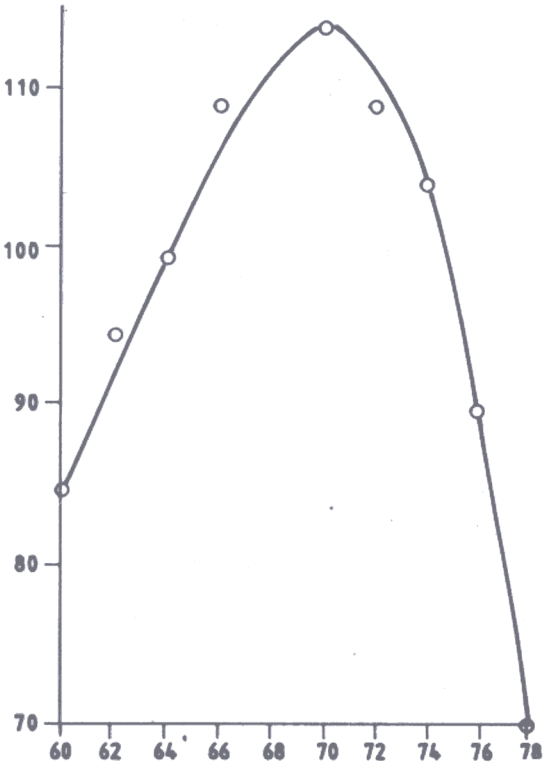

Figure 13. Photoconductive response of *CdSe* film 1400 Å thick grown onto mica substrate at 300 °C. Rate of deposition: 20 Å/s.

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