Effect of Plasma Irradiation on CdI$_2$ films.

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The effect of plasma irradiation is studied systematically on a 4H polytype (002) oriented CdI$_2$ stoichiometric film having compressive residual stress. Plasma irradiation was found to change the orientation to (110) of the film at certain moderate irradiation distances. A linear decrease in grain size and residual stress was observed with decreasing irradiation distance (or increasing ion energy) consistent with both structural and morphological observations. The direct optical energy gap $E_g$ was found to increase linearly at the rate 15$\mu$eV/atm with the compressive stress. The combined data of present compressive stress and from earlier reported tensile stress show a consistent trend of $E_g$ change with stress. The iodine-iodine distance in the unit cell could be responsible for the observed change in $E_g$ with stress.

PACS numbers: 78.66.Nk, 81.15.Ef, 78.20.Ci, 68.55.Jk

I. INTRODUCTION

CdI$_2$ has a layered structure with neighboring layers held by Van der Waals forces. Different stacking sequences of iodine, sandwiching Cd layers give rise to polytype structures. As many as 200 polytypes are recorded, however only few occur commonly. Recent studies have revived interest in cadmium iodide films. These reports illustrate the variation of optical properties of CdI$_2$ film as a function of film parameters like its thickness, deposition rate, substrate temperature, effect of heat-treatment etc. These parameters were shown to effect the grain size and residual stress in the film. Thus, the optical properties were shown to have a strong correlation with the grain size and residual stress. Grain size was also shown to increase linearly with the residual tensile stress beyond the threshold. The growth of grain size and its distribution, as stated, depends on parameters like film thickness, deposition rate etc. However, residual stress in the film can also alter film properties and performance significantly. In view of the potential applications in surface science and integrated electronics, studies on ion beam effects and plasma processing have gained significance in recent years. Desired and controlled modifications of physical and surface properties have been reported on ion irradiation. Material modification such as grain size, morphology etc, can be achieved by bombarding material with radiation or highly kinetic ions (plasma). This manuscript details the modification of optical properties by plasma irradiation (highly energetic Argon ions).

II. EXPERIMENTAL DETAILS

Films of CdI$_2$ were grown on glass substrates at room temperature by thermal evaporation at vacuum better than $10^{-6}$Torr. The starting material was 99.999% pure stoichiometric powder which was pelletized before placing it in molybdenum boat for evaporation. The film thickness was monitored during its growth by quartz crystal thickness
monitor and was subsequently confirmed by Dektek IIA surface profiler (which uses the method of mechanical stylus movement on the surface). The movement of the stylus across the edge of the film determines the step height or the film thickness. The film thickness was found to be uniform over an area of 6cm × 6cm. The structural, chemical composition, morphology and optical absorption measurements of the films were carried out by X-ray diffraction (Philip PW1840 X-ray diffractometer), photo-electron spectroscopy (Shimadzu’s ESCA 750), scanning electron microscope (JOEL-840) and UV-vis spectrophotometer (Shimadzu’s UV-260) respectively.

It was found that very slow deposition rate (≤ 1nm/sec) led to oriented film growth with tensile residual stress. However higher deposition rates (2-5nm/sec) lead to films with varying cell parameter (c) with increasing film thickness. The nature of residual stress was determined from X-Ray diffraction data. Since the effect of tensile residual stress on film properties has been extensively studied in an earlier report the films in this study were grown with a deposition rate ≥ 2nm/sec to study the effect of compressive residual stress on film properties. Further, the plasma processing of the films is also pursued. Small pieces of the samples were cut and irradiated with highly kinetic Argon ions produced by a Dense Plasma Focusing (DPF) device.

DPF is used as a source of neutrons, X-rays, energetic ions, and relativistic electrons. Being such a versatile source, it has been used in various applications such as a neutron source for pulsed activation analysis, a spectroscopic source for production of highly ionized species, a pump source for lasers, a high flux X-ray source for lithography, an electron source for micro-lithography, and a highly energetic ion source for processing of materials and thin film deposition. The Mather-type DPF device at NIE-SSC-PFF, Singapore was used. Such a device is powered by a single 30µF, 15 kV fast discharging capacitor. Self-generated magnetic fields caused by the transfer of capacitor voltage across the electrode assembly of the DPF device result in the formation of highly dense and hot plasma column during the collapse phase of plasma dynamics in the DPF device, just above the anode. Fig. 1 shows the position where the film sample is mounted inside the DPF for exposure just above the anode. An aperture assembly is kept between the film sample and the anode. This reduce the amount of copper debris (contributed by the copper anode) accumulating on the samples to be irradiated. During the entire investigation, a charging voltage of 14 kV was used for the DPF device. The working gas used was argon, which was kept at a filling gas pressure of 1 mbar. A shutter was placed between the aperture and the film sample to avoid exposing the sample to weak ion beams produced while optimizing the DPF device for strong focusing. The shutter was removed after optimum focus was achieved, thereby exposing the sample to energetic ions in the next DPF pulse. By varying the distance of the film from the anode, the average kinetic energy of Argon ions impinging the film can be varied. The argon ion energies at various distances from the top of the anode were measured by Rawat and Srivastava using a biased ion collector.

III. EXPERIMENTAL RESULTS

All the films grown at room temperature were stoichiometric and polycrystalline. The stoichiometry was confirmed by ESCA (Electron Spectroscopy for Chemical Analysis). It has been reported that CdI₂ films grown or annealed above 300K were polycrystalline. The X-ray diffractograms of as grown and plasma irradiated films are shown in fig 2. Our X-ray diffraction data agrees quite well with the powder diffraction data ASTM card 12-574. The structural polytype of the films can be identified as 4H from the cell dimensions. The various diffractograms are identified in the
caption. Figure displays only few representative diffractograms for the purpose of clarity although all the samples were studied. The important observation is the (00l) parallel to substrate plane oriented growth in as grown and plasma irradiated at larger distance samples as revealed by the (00l) major peaks. Such growth of preferred orientation of crystallite planes has been observed in earlier studies\textsuperscript{2,3,4,5,23,24} as well. However, we can see a modification in the crystallite orientation from (00l) to (hh0) by the plasma irradiation at moderate distances. This fact can be noticed explicitly in fig 3 where we have plotted the intensity of two major peaks changing with plasma irradiation. From the figure, we treat three samples (irradiated at 6, 7 and 8cm) as mainly (hh0) or (110) orientated and rest as (00l) oriented films.

X-ray diffraction data was also used to determine the residual (or internal) stress in the sample. The displacement of diffraction peaks from their corresponding powder data indicates a uniform stress developed in the film during condensation. If the diffraction peaks shift to lower angle (increasing $d$), a tensile stress can be realized. Similarly, the decrease in $d$ indicates a compressive stress\textsuperscript{25,26}. Figure 4 shows the displacement of the strongest peak, (002) from its corresponding powder data (ASTM No.12-574) as shown by the vertical broken line. The shift to the higher side indicates a uniform compressive stress in the films. The identification of samples is same as in Fig (2). We adopt the same method used by Pankaj et al\textsuperscript{4,5} to quantify the residual stress present in the film. The actual residual stress can be estimated by the strain produced, given by the expression

$$\frac{\Delta d}{d} = \frac{d(\text{Observed}) - d(\text{ASTM})}{d(\text{ASTM})}$$

Equation (1) determines the strain produced in $d$ spacing of (00l) planes which are the basal planes perpendicular to the 'c' axis of the unit cell. The residual stress along in this direction can then simply be obtained by multiplying the strain with the appropriate elastic constant of CdI$_2$. The diagonal elements (e.g. $C_{11}$) of elastic tensor represent pure tensile or compressive components. $C_{11} = 4.91 \times 10^{10}$N/m$^2$ (or $4.85 \times 10^5$atm) for CdI$_2$ crystal\textsuperscript{27}. The stress on (110) for (110) oriented three samples was determined similarly from the corresponding peak.

We have determined the cell parameters for all the samples studied. As mentioned above the direct consequence of the residual stress along 'c' axis, i.e. on (002), is the change in 'c' parameter. The 'c' parameter determined for the plasma irradiated films at various distances from the anode was found to vary linearly with the residual stress as shown in figure 5. The as grown film had maximum compressive stress and plasma irradiation relaxes this stress. Good linear behavior also indicates the well oriented film growth. However, it should be noted that we have not included three data points of (110) orientation here although there is a little stress on (002) as well caused by that on (110).

We have characterized all the samples for their morphology by SEM. The as grown films were having an average grain size of 4.8µm. We have displayed few representative SEM pictures of plasma irradiated samples in fig 6. Morphological manifestations seem to be consistent with the structural studies. Morphology of samples irradiated at 7 or 8cm is quite different from those irradiated at 9 or 10cm because of different crystallite orientations as discussed earlier. All the samples having (002) orientation show similar morphology but with different grain size. However, the sample irradiated at 7cm differs slightly in morphology from that irradiated either at 6cm or 8cm although all three samples have same orientation (110). This could be possible because the sample irradiated at 7cm has minimum number of (002) planes parallel to the substrate plane as compared to other two samples, shown by peak intensities of fig 3. Nevertheless, we can analyze the effect of plasma irradiation on grain size from morphological studies. We
have shown such an analysis explicitly in fig 7. Quite good linear behavior shows a definite role of plasma irradiation on grain size modification. It should be noted that the grain size of as grown or unirradiated sample was maximum (∼4.8µm) and almost equal to that of sample irradiated at large distance (12cm). This shows that plasma ions break the grains into smaller sizes depending on its energy. It is quite well known that the ion energy decreases linearly with distance from anode. Therefore, a reasonably good linear behavior in fig 7 may not be surprising and indicates a good processing method to modify grain sizes. We further analyze the relation between residual stress and grain size as shown in figure 8. The positive side of the stress is tensile and those data are taken from the earlier report5 for the purpose of comparison. The negative side of the plot indicates the present data of compressive stress. The main difference between the two sides is the plasma irradiation. A good linear relation between the stress and grain size in the present study is the direct consequence of plasma processing. As mentioned earlier, the bigger grains with considerable stress in as grown film break into smaller grains with reduced stress and better packing due to plasma irradiation. Possibly, the modification in grain size and its packing reduces the residual stress. In contrast, the positive side indicates the development of residual stress due to the grain size growth and its distribution. Even the morphology supports this. In the present study the grain size and its distribution is quite uniform unlike earlier report. Therefore, the linear relationship in the present study further justifies and supports the other characterization results.

We have also studied the optical absorption of all the samples. A typical absorption spectrum of one of the samples is shown in fig 9 for the purpose of illustration. The absorption coefficient α was calculated as a function of incident photon energy near the band edge from these absorption data as explained by Seeger28. In general, the relation of the type28,29

$$\alpha h\nu = (h\nu - E_g)^n$$

was fitted to the experimental data. The best fit was obtained for n= 1/2 indicating the direct allowed type of transition. The value of E_g is determined by the extrapolation of the linear portion in the ($\alpha h\nu$)$^2$ vs $h\nu$ plot as shown in the inset of fig 9. Obviously a direct type of transition is evident from the present data. However, lot of data and discussions are available in the literature on this issue. Both experiments30,31 and theoretical energy band structure calculations32,33,34,35 reveal the existence of a direct and indirect band gaps in CdI_2 differing by only 0.3-0.6eV. The detailed analysis of this topic can be found in earlier reports and the references cited therein. However, we do not further elaborate on this issue here. We have found the residual stress dependent E_g in this study. There may be several reasons for the change in E_g of the material. The effect of hydrostatic pressure on E_g is well known due to the changing atomic distances in the unit cell. Therefore, similar effect should be expected from residual stress as well. We have plotted E_g as a function of residual stress in fig 10 to examine such a correlation. Again, the negative side of the stress represents the present data while positive side is taken from the reference5. However, it should be noted that we have subtracted a constant 0.5eV from the positive side data for the purpose of matching them at zero stress. A shift of 0.5eV will not alter the basic trend or the qualitative behavior of E_g with stress.

A reasonably good linear behavior of E_g with stress indicates a definite cause of stress on E_g. The sharp decrease with tensile stress has been discussed in the earlier report5. The overall linear behavior encompassing both positive and negative sides of stress may be indicating a common reason for the E_g modification. The amount of change of E_g with pressure is given by the slope and is equal to 15µeV/atm. There is only one report36 on experimental study
regarding hydrostatic pressure effects on optical excitations in cadmium halides in the range 1000-3500 atm. They have found a linear increase of 5.5 $\mu$eV/atm for an optical edge at 4eV in CdI$_2$. The present data are also in the similar range and show a bit higher rate of change. The agreement can still be treated as good. However, the little discrepancy between the two could be due to the anisotropic nature of the layered structure of CdI$_2$. For example, even in the present study $E_g$ of (002) and (110) oriented films has different slopes with pressure. We have shown $E_g$ of (110) orientation by triangles in figure for comparison. The earlier report was on single crystal and direction of applied pressure was not mentioned. A consistent linear behavior with both compressive and tensile stress may well be indicating a common mechanism of $E_g$ change. Referring to electronic structure calculations of cadmium halides, the calculated and experimental band gaps decrease with increasing anion-anion distance in CdCl$_2$ to CdI$_2$. The exact modification in band structure due to the fractional change in anion-anion distance is hard to estimate at present. Therefore, we feel that the changing I-I distance in CdI$_2$ due to the residual stress is responsible for the observed changes in $E_g$ with pressure. The amount of change in I-I distance may be different in differently oriented films and may be different as observed here. The present data along with earlier similar ones seem to be very much consistent and decisive. We hope this will be quite useful in understanding the interesting layered structured materials like CdI$_2$ which has been quite diverging. Although many experimental results clearly show anisotropic optical properties of CdI$_2$ the calculated band structures show very little or absence of anisotropic nature.

**IV. CONCLUSIONS**

The present study highlights the usefulness of plasma processing of CdI$_2$ films in modifying its structural and morphological properties. A good linear relationship between ion energy (or irradiation distance) and material parameters like cell parameter, grain size, residual stress etc. indicates the processing as a good technique. The consequent changes $E_g$ correlates well with the residual stress in the film. The combined data of $E_g$ versus compressive and tensile residual stress show a consistent trend hinting the possible cause as changing iodine-iodine distance in the unit cell. This could be a useful, decent information and feedback for revising band structure calculations of CdI$_2$ which is otherwise diverging.

**Acknowledgments**

Authors are thankful to the National Institute of Education, Singapore, for providing the ARF grant RP 17/00/RSR to fund the research project under which this investigation has been performed. The discussions with Pankaj Tyagi is also acknowledged.
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FIG. 1: Schematic of experimental set-up for dense plasma focus device.
FIG. 2: X-Ray diffractogram of (a) asgrown CdI₂ film, and films plasma irradiated at (b) 5cm, (c) 7cm, (d) 10cm, (e) 12cm from the anode.

FIG. 3: Variation in intensity of two diffracting planes (002) and (110) with changing irradiation distance of film from DPF device anode.
FIG. 4: Shifts in the (002) peaks of the X-Ray diffractograms shown in figure 2. The labelling are the same as in figure 2.

FIG. 5: Variation of residual stress with lattice parameter 'c'.
FIG. 6: SEM micrographs of CdI$_2$ films irradiated between 7 to 10cm from the anode.

FIG. 7: Variation of grain size with irradiation distance.
FIG. 8: Variation of grain size with residual stress in CdI$_2$ films. The 'y' axis separates region of compressive and tensile residual stress.

FIG. 9: The optical absorption spectra of CdI$_2$ film irradiated at 6cm from the anode. The inset shows the fitting of absorption data to eqn 2 with n=1/2 for determining the optical energy gap $E_g$. 
FIG. 10: Variation of band gap ($E_g$), with residual stress for CdI$_2$ films.