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Effect of energetic ion irradiation on CdI$_2$ films

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The effect of energetic argon ion irradiation, using a 3.3 kJ pulsed plasma focus device, is studied systematically on a 4H polytype (002)-oriented CdI$_2$ stoichiometric film having compressive residual stress. The CdI$_2$ films were exposed to energetic ions from the plasma focus device at different distances from the top of the central electrode. The irradiation was found to change the orientation of the film to (110) 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. © 2004 American Institute of Physics.

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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.

INTRODUCTION

Cadmium iodide (CdI$_2$) is a layered material with neighboring layers held together by van der Waals forces. Different stacking sequences of iodine layers, sandwiching cadmium layers, give rise to polytype structures. As many as 200 polytypes are recorded, however, only a few occur commonly. Recent studies have revived interest in cadmium iodide films.

The dense plasma focus (DPF) device is a pulsed plasma source that utilizes the magnetic field of a current-carrying solenoid to focus a plasma column. The device is composed of a coaxial gun in which the electrical energy of a capacitor bank, upon discharge, is initially stored as the magnetic energy behind the moving current sheath as the sheath is accelerated along the coaxial electrode assembly. A portion of this magnetic energy is then rapidly converted into plasma energy during the collapse of the current sheath towards the end of the central electrode, resulting in the formation of a short-lived, but hot (1–2 keV) and dense ($10^{25}–10^{26}$ m$^{-3}$) plasma. DPF is a source of neutrons (when operated with deuterium as a filling gas), 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 microlithography, and a highly energetic ion source for processing of materials and thin-film deposition. This article details the modification of optical properties of CdI$_2$ films by energetic argon ion irradiation in a DPF device.

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 that was pelletized before placing it in a molybdenum boat for evaporation. The film thickness was monitored during its growth by a quartz crystal thickness monitor and was subsequently confirmed by a Dektak 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 6 cm × 6 cm. The structural, chemical composition, morphology, and optical absorption measurements of the films were carried out by x-ray diffraction (XRD, Siemens D5005 X-ray Diffractometer), photoelectron spectroscopy (Shimadzu’s ESCA 750), scanning electron microscope (SEM, Jeol JSM 5310-V) and UV-Vis spectrophotometer (Varian Cary 50 UV-Vis spectrophotometer) respectively.

It was found that very slow deposition rate (1 nm/s) led to oriented film growth with tensile residual stress. However, higher deposition rates (2–5 nm/s) lead to films with varying cell parameter c with increasing film thickness. The nature of residual stress was determined from XRD data. Since the effect of tensile residual stress on film properties has been extensively studied in an earlier report, it was inferred in this study that films were grown with a deposition rate 2 nm/s to study the effect of compressive residual stress on film properties. Further, the processing of the films by argon ion irradiation is also pursued. Small pieces of the samples were cut and irradiated with highly kinetic argon ions produced by a DPF device. A simple, single-capacitor DPF device, designated as United Nation University/International Center for Theoretical Physics Plasma Focus Facility, is used for irradiation of cadmium iodide thin films. It is a Mather-type focus device, called Physics Plasma Focus Facility, is used for irradiation of highly kinetic argon ions produced by a DPF device. The working gas used was argon, which was kept at a filling gas pressure of 1.5 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. Kelly et al. have reported the total fast particle flux and its energy content (with in the energy range 50–1000 keV) as 3.2 × 10^{13} ions/stread and 0.74 J/stread, respectively, for nitrogen ions from a 4.75 kJ plasma focus device. It is a well-known fact that the plasma focus devices with similar energies have similar emission characteristics, and thus similar results may hold good for our 3.3 kJ (operated at 2.9 kJ) plasma focus device. The lateral spread, as calculated using a relation in Ref. 24, of the ion-beam energy of about 50 keV (lower bound of ion energy in the focus device) at 1.5 mbar for moving over a distance of about 2 cm to the aperture assembly, is only about 0.007 cm. Since the lateral spread is much less than the aperture dimension, we estimated the typical ion flux for our plasma focus device from a pure geometrical consideration using the results of Kelly et al. Based on the results of Ref. 23, approximate ion and energy flux at a distance of 5 cm are about 1.28 × 10^{12} ions/cm² and 18 mJ/cm², respectively, and they decrease (nonlinearly as 1/z²) to 2.22 × 10^{11} ions/cm² and 3 mJ/cm², respectively, at the distance of 12 cm from the top of the anode.

**EXPERIMENTAL RESULTS**

All the films grown at room temperature were stoichiometric and polycrystalline. The stoichiometry was confirmed by Electron Spectroscopy for Chemical Analysis. It has been reported that CdI₂ films grown or annealed above 300 K were polycrystalline. The x-ray diffractograms of as-grown and ion-irradiated films are shown in Fig. 2. Our XRD data (peak positions) agree quite well with the powder diffraction data (ASTM card 33-239). The structural polytype of the films can be identified as 4H from the cell dimensions. The various diffractograms are identified in the caption. Figure 2 displays only few representative diffractograms for the purpose of clarity, although all the samples were studied. The important observation is the (001)-oriented growth parallel to substrate plane in as-grown samples and in those plasma-irradiated at a larger distance, as revealed by the (001) major peaks. This fact is well supported by the comparison of intensities with those of the ASTM 33-239. The few (hh0) and (h01) quite intense peaks seen in the powder data (ASTM...
are negligibly small in these diffractograms, indicating the 001 preferred oriented growth. Such growth of preferred orientation of crystallite planes has been observed in earlier studies as well. However, we can see a modification in the crystallite orientation from 001 to (hh0) by the energetic ion 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 energetic argon ion irradiation. From the figure, we treat three samples irradiated at 6, 7, and 8 cm as mainly (hh0)- or 110-oriented and the rest as (001)-oriented films.

XRD data were 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 after the ion irradiation. 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. Figure 4 shows the displacement of the strongest peak, (002), from its corresponding powder data (ASTM No. 33-239), as shown by the vertical broken line. The shift to the higher side indicates a uniform compressive stress in the films. The actual residual stress can be estimated by the strain produced, given by the expression

$$\frac{\nabla d}{d} = \frac{d(\text{observed}) - d(\text{ASTM})}{d(\text{ASTM})}. \tag{1}$$

Equation (1) determines the strain produced in d spacing of (001) planes, which are the basal planes perpendicular to the c axis of the unit cell. The residual stress along this direction can then be obtained simply by multiplying the strain with the appropriate elastic constant of CdI2. The diagonal elements (e.g., C_{11}) of elastic tensor represent pure tensile or compressive components [with C_{11} = 4.91 \times 10^{10} \text{ N/m}^2, (or 4.85 \times 10^5 \text{ atm})] for CdI2 crystal. The stress on (110) for the three (110)-oriented samples was determined similarly from the corresponding peak.

We have determined the cell parameters for all the samples studied. As mentioned earlier the direct consequence of the residual stress along the c axis [i.e., on (002)], is the change in the c parameter. The c parameter determined for the ion-irradiated films at various distances from the anode was found to vary linearly with the residual stress, as shown in Fig. 5. The as-grown film had maximum compressive stress, and energetic ion irradiation relaxes this stress. Good linear behavior also indicates 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 the morphology of all the samples by SEM. The as-grown films had an average grain size of 4.8 \mu m. We have displayed a few representative SEM pictures of ion-irradiated samples in Fig. 6. Morphological
manifestations seem to be consistent with the structural studies. The morphology of samples irradiated at 7 or 8 cm is quite different from those irradiated at 9 or 10 cm because of different crystallite orientations as discussed earlier. All the samples having (002) orientation show similar morphology but with different grain sizes. However, the sample irradiated at 7 cm differs slightly in morphology from that irradiated either at 6 or 8 cm, although all three samples have same orientation (110). This could be possible because the sample irradiated at 7 cm 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 argon ion 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 energetic ion irradiation on grain size modification. This shows that plasma ions break the grains into smaller sizes depending on their energy.

A reasonably good linear variation in grain size (Fig. 7) and a nonlinear variation in ion-energy flux (Ref. 23) with the increase in thin film exposure distance from the top of the anode indicates a nonlinear relationship between grain size modification and ion energy flux. It should be noted that the grain size of the as-grown or nonirradiated sample was a maximum of 4.8 μm and almost equal to that of sample irradiated at a large distance (12 cm). One can therefore infer that a certain minimum ion energy is required to bring the morphological and structural changes in cadmium iodide films.

We further analyze the relation between residual stress and grain size as shown in Fig. 8. The positive side of the stress is tensile; those data are taken from the earlier report 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 ion irradiation. A good linear relation between the stress and grain size in the present study is the direct consequence of energetic ion 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 ion 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 are quite uniform, unlike the 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 $\alpha$ was calculated as a function of incident
photon energy near the band edge from these absorption data, as explained by Seeger.\textsuperscript{31} In general, the relation of the type\textsuperscript{31,32}

\[ a \hbar \nu = (h \nu - E_g)^n \]

was fitted to the experimental data. The best fit was obtained for $n = 1/2$, indicating the direct allowed type of transition. The value $E_g$ is determined by the extrapolation of the linear portion in the $h \nu$ vs $(a \hbar \nu)^2$ plot, as shown in the inset of Fig. 9. Obviously, a direct type of transition is evident from the present data. However, a lot of data and discussions are available in the literature on this issue. Both experiments\textsuperscript{33,34} and theoretical energy band structure calculations\textsuperscript{35–38} reveal the existence of direct and indirect bandgaps in CdI$_2$ differing by only 0.3–0.6 eV. The detailed analysis of this topic can be found in an earlier report\textsuperscript{5} 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, a similar effect should be expected from the 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 Ref. 5. However, it should be noted that we have subtracted a constant 0.5 eV from the positive side data for the purpose of matching them at zero stress. A shift of 0.5 eV 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 report.\textsuperscript{3} 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 15 $\mu$eV/atm.

There is only one report\textsuperscript{39} of an 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 4 eV 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 with triangles in the figure for comparison. The earlier report\textsuperscript{39} was on single crystal, and the direction of applied pressure was not mentioned. A consistent linear behavior with both compressive and tensile stress may well indicate a common mechanism of $E_g$ change. Referring to the electronic structure calculations of cadmium halides,\textsuperscript{39} the calculated and experimental bandgaps 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 data appear 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 an absence of an anisotropic nature.

CONCLUSIONS

The as-grown film, deposited by a thermal evaporation method, were essentially 4H polytype (002)-oriented CdI$_2$ stoichiometric films. The diffraction peaks of unexposed as-grown film showed oriented growth parallel to (001) diffraction planes. The irradiation was found to change the orientation to (110) of the film at certain moderate irradiation distances. Three samples (irradiated at 6, 7, and 8 cm) could be treated as mainly ($hh0$)- or (110)-oriented and the rest as (001)-oriented films. The displacement of diffraction peaks, towards the higher side, from their corresponding powder data indicated uniform compressive stress. The estimation of grain size from SEM and residual stress from diffractograms showed a linear decrease in grain size and residual stress with decreasing irradiation distance (or increasing ion energy), consistent with both structural and morphological observations. The morphology of the films with (002) preferred orientation was found to be similar, but with different grain sizes. The films with (110) orientation, however, were found to have a different morphology. The direct optical energy gap $E_g$ of the ion-irradiated films, found mainly in the range of 3 to 3.3 eV, was found to be dependent on compressive residual stress of the film. The $E_g$ was found to increase linearly at the rate 15 μeV/atom with the compressive stress. The change in iodine–iodine distance in the unit cell due to compressive stress could be responsible for the observed change in optical energy gap.

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