Title	Effect of energetic ion irradiation on CdI_2 films
Author(s)	R. S. Rawat, P. Arun, A. G. Vedeshwar, P. Lee and S. Lee
Source	*Journal of Applied Physics, 95*(12), 7725-7730. doi: 10.1063/1.1738538
Published by	American Institute of Physics

Effect of energetic ion irradiation on CdI_2 films

R. S. Rawat[a)]
National Sciences, National Institute of Education, Nanyang Technological University, Singapore

P. Arun and A. G. Vedeshwar
Department of Physics & Astrophysics, University of Delhi, Delhi-110 007, India

P. Lee
National Sciences, National Institute of Education, Nanyang Technological University, Singapore

S. Lee
International Centre for Dense Magnetised Plasma, Warsaw, Poland

(Received 14 July 2003; accepted 18 March 2004)

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 μeV/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.*
[DOI: 10.1063/1.1738538]

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.[1] Recent studies have revived interest in cadmium iodide films.[2–5] These reports illustrate the variation of optical properties of CdI_2 film as a function of film parameters such as its thickness, deposition rate, substrate temperature, effect of heat treatment, etc. These parameters were shown to affect 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 such as film thickness, deposition rate, etc. However, residual stress in these films can also alter film properties and performance significantly. In view of the potential applications in surface science[6] and integrated electronics,[7] 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.[8] Material modification such as grain size, morphology, etc., can be achieved by bombarding material with radiation or highly kinetic ions.

The dense plasma focus (DPF) device is a pulsed plasma 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 axis beyond 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,[9] a spectroscopic source for production of highly ionized species,[10] a pump source for lasers,[11] a high flux x-ray source for lithography,[12] an electron source for microlithography,[13] and a highly energetic ion source for processing of materials[14–18] and thin-film deposition.[19–21] 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 molybdenum boat for evaporation. The film thickness was monitored during its growth by a quartz crystal thickness monitor and was subsequently confirmed by a Dektek IIA surface profiler (which uses the method of mechanical stylus movement on the surface). The movement of the stylus across the

a)Electronic mail: rsrawat@nie.edu.sg

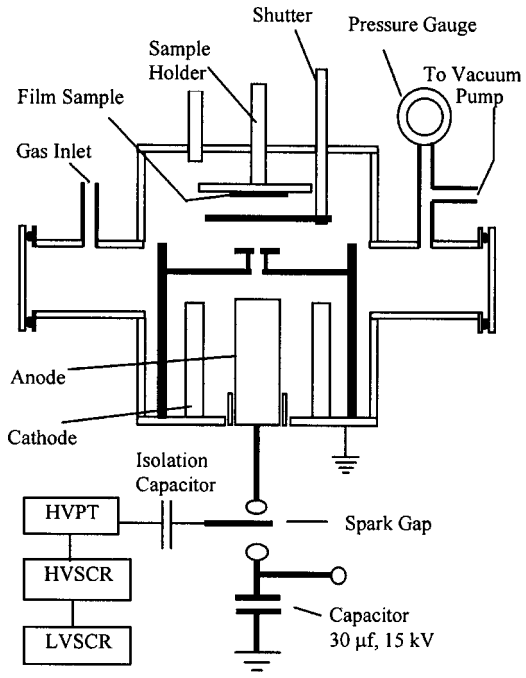

FIG. 1. Schematic of experimental setup for OPF device.

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[5] the films in this study 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,[22] is used for irradiation of cadmium iodide thin films. It is a Mather-type focus device, energized by a 30 μF, 15 kV fast discharging capacitor, with maximum storage energy of 3.3 kJ. The experimental setup along with the focus subsystems is sketched in Fig. 1. The film samples (1 cm×1 cm size) were mounted inside the DPF chamber, axial above the anode, with the help of axially movable sample holder. Thin-film samples were exposed to DPF shots at distances from 5 to 12 cm from the top of the anode.

An aperture assembly is kept between the film sample and the anode. The details of aperture assembly are provided elsewhere.[18] It is a combination of two apertures (3.0 and 4.0 mm diameter) separated by 1.0 cm and placed at a fixed distance of 2.0 cm above the anode. This stops the plasma shock wave and also eliminates the possibility of irradiating the film samples to copper debris (contributed by the ablation of copper anode rim by the relativistic electron beam generated by sausage instabilities during the radial phase). 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 1.5 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.*[23] have reported the total fast particle flux and its energy content (with in the ion 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.*[23] 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/cm^2 and 18 mJ/cm^2, respectively, and they decrease (nonlinearly as $1/z^2$) to 2.22×10^{11} ions/cm^2 and 3 mJ/cm^2 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 CdI_2 films grown or annealed above 300 K were polycrystalline.[25] 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

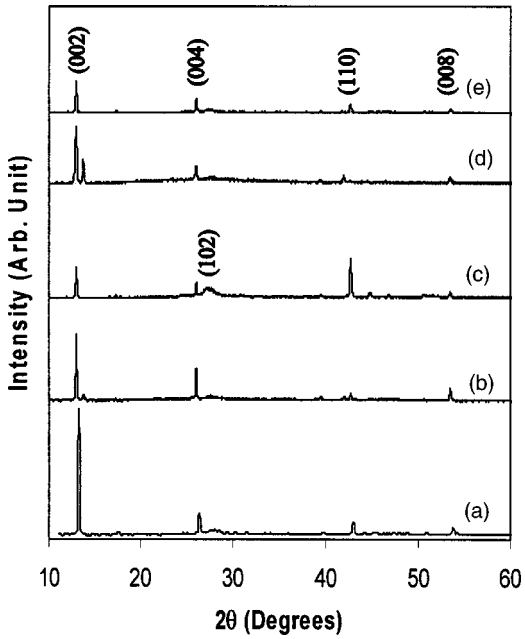

FIG. 2. X-ray diffractogram of (a) as-grown CdI_2 film, and films irradiated at (b) 5, (c) 7, (d) 10, and (e) 12 cm from the anode.

33-239) 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[2–4,26,27] 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

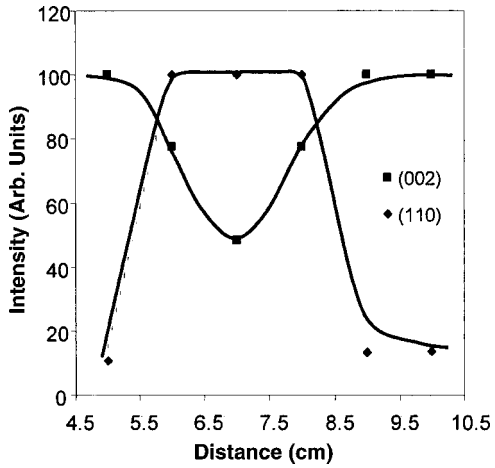

FIG. 3. Variation in intensity of two diffracting planes, (002) and (110), with changing irradiation distance of film from DPF device anode.

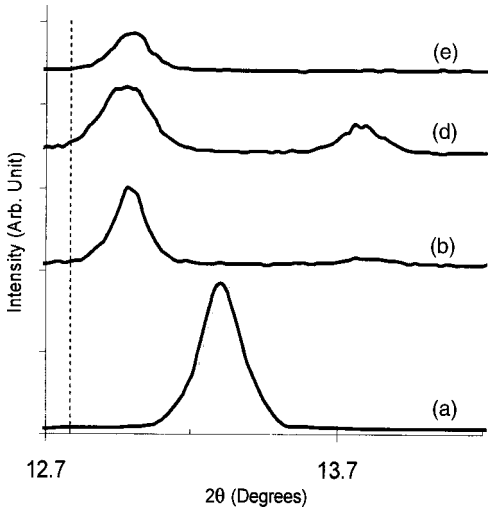

FIG. 4. Shifts in the (002) peaks of the x-ray diffractograms shown in Fig. 2. The labeling is the same as in Fig. 2.

angle (increasing d), a tensile stress can be realized. Similarly, the decrease in $\{d\}$ indicates a compressive stress.[28,29] 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 identification of samples is the same as in Fig. 2. We adopt the same method used by Tyagi, *et al.*[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

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

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 CdI_2. The diagonal elements (e.g., C_{11}) of elastic tensor represent pure tensile or compressive components [with $C_{11}=4.91\times10^{10}$ N/m^2, (or 4.85×10^5 atm)] for CdI_2 crystal.[30] 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 μm. We have displayed a few representative SEM pictures of ion-irradiated samples in Fig. 6. Morphological

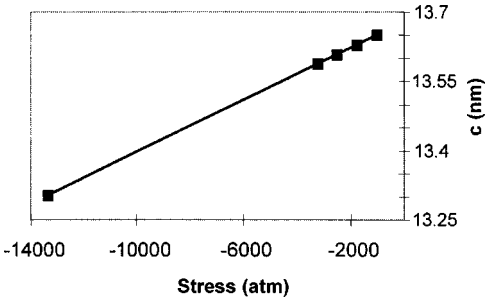

FIG. 5. Variation of residual stress with lattice parameter *c*.

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

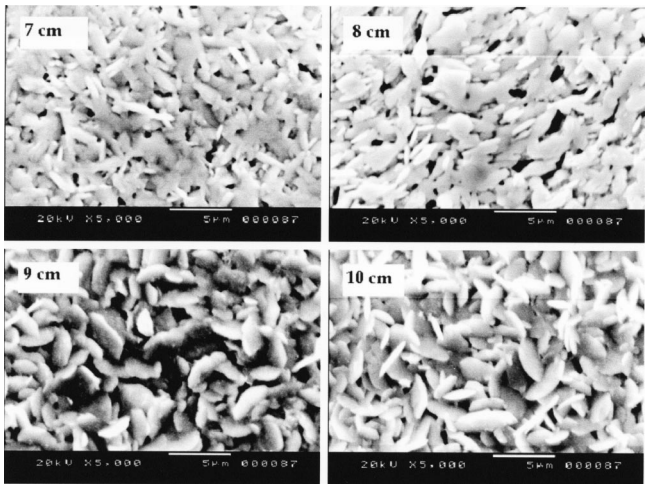

FIG. 6. SEM micrographs of CdI_2 films irradiated between 7 to 10 cm from the top of the anode.

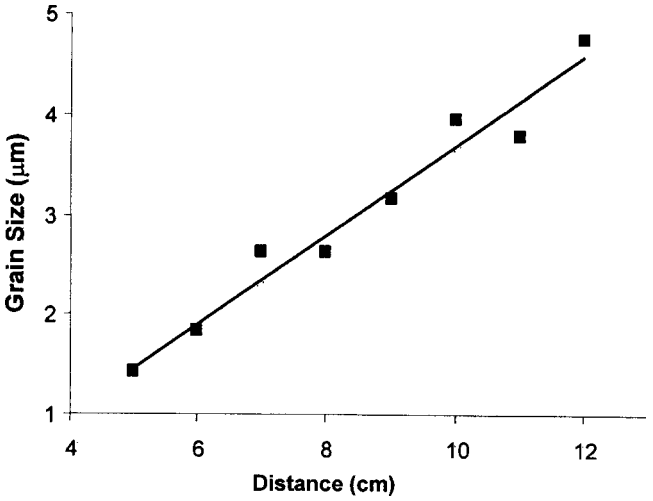

FIG. 7. Variation of grain size with irradiation distance.

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[5] 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 α was calculated as a function of incident

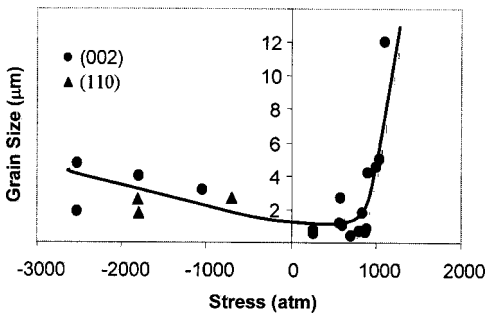

FIG. 8. Variation of grain size with residual stress in CdI_2 films. The *y* axis separates region of compressive and tensile residual stress.

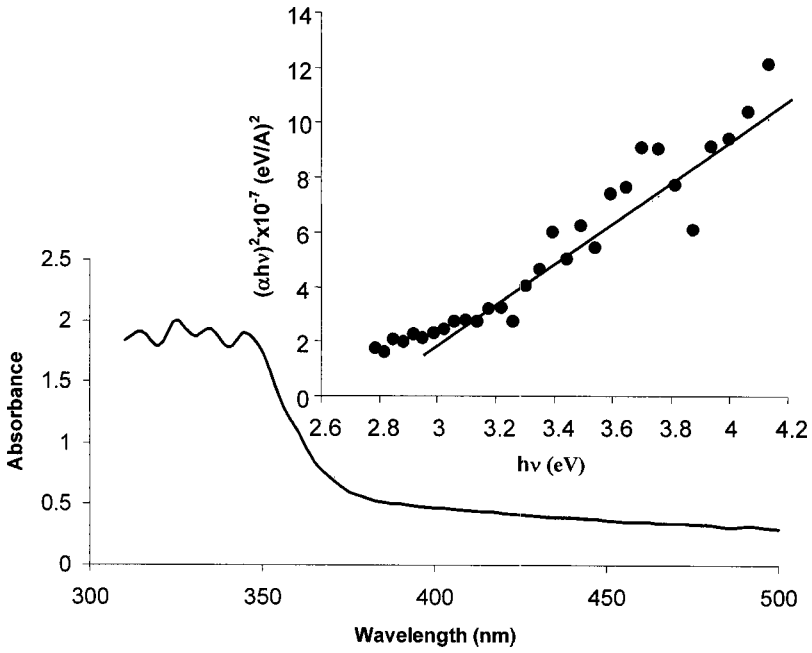

FIG. 9. The optical absorption spectra of CdI_2 film irradiated at 6 cm from the anode. The inset shows the fitting of absorption data to Eq. (2) with $n=1/2$ for determining the optical energy gap E_g.

photon energy near the band edge from these absorption data, as explained by Seeger.[31] In general, the relation of the type[31,32]

$$\alpha h\nu=(h\nu-E_g)^n \tag{2}$$

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 $(\alpha h\nu)^2$ 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[33,34] and theoretical energy band structure calculations[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[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.[5] 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 μeV/atm. There is only one report[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 μeV/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[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,[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

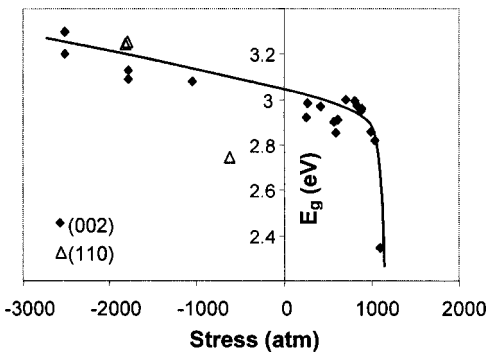

FIG. 10. Variation of bandgap E_g with residual stress for CdI_2 films.

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[5] 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[40] clearly show anisotropic optical properties of CdI_2, the calculated band structures[35–38] 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/atm 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.

ACKNOWLEDGMENTS

The 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 are also acknowledged.

[1] G. C. Trigunayat, Solid State Ionics **48**, 3 (1991).
[2] P. Tyagi, A. G. Vedeshwar, and N. C. Mehra, Physica B **304**, 166 (2001).
[3] P. Tyagi and A. G. Vedeshwar, Bull. Mater. Sci. **24**, 297 (2001).
[4] P. Tyagi and A. G. Vedeshwar, Eur. Phys. J.: Appl. Phys. **19**, 3 (2002).
[5] P. Tyagi and A. G. Vedeshwar, Phys. Rev. B **66**, 075422 (2002).
[6] U. Gerlach and O. Meyer, Surf. Sci. **103**, 534 (1981).
[7] T. A. Skotheim, R. L. Elsenbaumer, and J. R. Reyxold *Handbook of Conducting Polymers* (Marcel Dekker, New York, 1998), pp. 589–638.
[8] M. A. Loudiana, A. Soamid, and J. T. Dickinson, Surf. Sci. **141**, 409 (1986).
[9] E. B. Aurahan and Y. Porath, Nucl. Instrum. Methods **123**, 5 (1975).
[10] E. H. Bekener, J. Appl. Phys. **37**, 4944 (1966).
[11] N. P. Kozlov, V. A. Alekseev, Yu. S. Protsov, and A. B. Rubinov, JETP Lett. **20**, 331 (1974).
[12] Y. Kato and S. H. Bee, Appl. Phys. Lett. **48**, 686 (1986).
[13] P. Lee, X. Feng, G. X. Zhang, M. H. Liu, and S. Lee, Plasma Sources Sci. Technol. **6**, 343 (1997).
[14] R. S. Rawat, M. P. Srivastava, S. Tandon, and A. Mansingh, Phys. Rev. B **47**, 4858 (1993).
[15] R. Sagar and M. P. Srivastava, Phys. Lett. A **183**, 209 (1993).
[16] M. P. Srivastava, S. R. Mohanty, S. Annapoorni, and R. S. Rawat, Phys. Lett. A **215**, 63 (1996).
[17] P. Agarwala, S. Annapoorni, M. P. Srivastava, R. S. Rawat, and P. Chauhan, Phys. Lett. A **231**, 434 (1997).
[18] R. S. Rawat, P. Arun, A. G. Videshwar, Y. L. Lam, P. Lee, M. H. Liu, S. Lee, and A. C. H. Huan, MRS Bull. **35**, 477 (2000).
[19] C. R. Kant, M. P. Srivastava, and R. S. Rawat, Phys. Lett. A **226**, 212 (1997).
[20] C. R. Kant, M. P. Srivastava, and R. S. Rawat, Phys. Lett. A **239**, 109 (1998).
[21] R. S. Rawat, P. Lee, T. White, L. Ling, and S. Lee, Surf. Coat. Technol. **138**, 159 (2001).
[22] S. Lee, T. Y. Tou, S. P. Moo, M. A. Eissa, A. V. Gholap, K. H. Kwek, S. Mulyodrono, A. J. Smith, A. Suryadi, W. Usada, and M. Zakullah, Am. J. Phys. **56**, 62 (1988).
[23] H. Kelly, A. Lepone, A. Marquez, M. J. Sadowski, J. Baranowski, and E. S. Sadowska, IEEE Trans. Plasma Sci. **26**, 113 (1998).
[24] H. Kelly and A. Marquez, Meas. Sci. Technol. **6**, 400 (1995).
[25] S. Kondo, T. Suzuki, and T. Saito, J. Phys. D **31**, 2733 (1988).
[26] R. D. Bringans and W. Y. Liang, J. Phys. C **14**, 1065 (1981).
[27] R. M. Yu, Philos. Mag. **16**, 1167 (1967).
[28] L. I. Maissel and R. Glang, *Handbook of Thin Film Technology* (McGraw-Hill, New York, 1970) p. 9-8.
[29] B. D. Cullity, *Elements of X-Ray Diffraction* (Addison-Wesley, Palo Alto, 1978) p. 102.
[30] *Semiconductors-Basic data*, 2nd ed., edited by O. Madelung (Springer-Verlag, Berlin, 1996), p. 188.
[31] K. Seeger, *Semiconductor Physics* (Springer-Verlag, Berlin, 1973), p. 339.
[32] A. H. Clark, *Polycrystalline and Amorphous Thin Films and Devices*, edited by L. Kazmerski (Academic, New York, 1980), p. 135.
[33] D. L. Greenway and R. Nitsche, J. Phys. Chem. Solids **26**, 1445 (1965).
[34] P. A. Lee, G. Said, R. Davis, and T. H. Lim, J. Phys. Chem. Solids **30**, 2719 (1969).
[35] J. V. McCanny, R. H. Williams, R. B. Murray, and P. C. Kemeny, J. Phys. C **10**, 4255 (1977).
[36] J. Bordas, J. Robertson, and A. Jakobsson, J. Phys. C **11**, 2607 (1978).
[37] R. Coehoorn, G. A. Sawatzky, C. Haas, and R. A. de Groot, Phys. Rev. B **31**, 6739 (1985).
[38] I. Pollini, J. Thomas, R. Coehoorn, and C. Haas, Phys. Rev. B **33**, 5747 (1986).
[39] A. D. Brothers and J. T. Pajor, Phys. Rev. B **14**, 4570 (1976).
[40] S. Kondo and H. Matsumoto, J. Phys. Soc. Jpn. **50**, 3047 (1981).