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# Effects of in-situ Heat-Treatment on Residual Stress Dependent Optical Properties of ZnI2 Thin Films

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## Abstract

ZnI2, a hygroscopic chemical compound in thin film form has been investigated for residual stress dependent optical properties in in-situ heat-treated conditions up to 80oC. The tetragonal structured ZnI2 thin films were grown by thermal evaporation on glass substrates with deposition rate optimized at 1–2 nm/s and vacuum maintained at 10–6 Torr. Quartz crystal thickness monitor was used to monitor the film thickness and deposition rate during the film growth. Measurements like UV spectroscopy, X-ray diffraction and scanning electron microscopy were performed under low relativity humidity conditions (~40%). For in situ heat-treatment, films were heated inside the film growth glass chamber with inbuilt thermocouple to do temperature measurements. The in-situ heat-treatment of above-mentioned ZnI2 thin films shows a linear decrease in film thickness with increase of in-situ treatment temperature. The x-ray diffraction studies revealed a decrease in residual stress parameter with decreasing film thickness. Morphological studies support the internal stress behavior based on density effect or packing density of the films. The direct type-band gap for ZnI2 films found to increase almost linearly with increasing heat treatment temperature (and corresponding decreasing film thickness) from 3.25 eV to 4.06 eV. In-situ experiments estimate a much larger value of 8.39 eV of the band gap for a stress free perfect crystal of ZnI2 and give an indication of a large value of its deformation potential.

**Keywords:** In-Situ Heat-Treatment, Optical Properties, Physical Vapour Deposition (PVD), Residual Stress, Thin Films

## 1. Introduction

$ZnI_2$ is a hygroscopic chemical compound that readily absorbs water from the atmosphere. It exists in anhydrous form in white color. In this white form while zinc atoms are tetrahedrally coordinated, as in $ZnCl_2$, groups of four of these tetrahedra share three vertices to form "super-tetrahedra" of composition $\{Zn_4I_{10}\}$, which are linked by their vertices to form a three dimensional structure[1]. The hygroscopic nature of $ZnI_2$ makes it more difficult to study this material in thin film form. Most of the studies reported in the literature are associated with its structure[2-5], thermochemistry[6] and its glass forming ability etc[7-8]. In some of our earlier studies, we reported optical properties of $ZnI_2$ films[9-12]. We report here the effects on residual stress dependent optical properties of $ZnI_2$ films when in-situ heat-treated up to 80°C.

## 2. Experimental Details

For the present study, the $ZnI_2$ thin films were grown on a glass substrate (cover slips of 2X2 $cm^2$) at room temperature (27°C) by thermal evaporation using a molybdenum boat. For evaporation, high purity (99.999%) stoichiometric powder of $ZnI_2$ supplied by Aldrich (USA) was used in palletized form. For all thin film growths the deposition rate was optimized at 1–2 nm/s and vacuum of $10^{-6}$ Torr was maintained. All the films were of good uniform quality. Since $ZnI_2$ is highly hygroscopic, the film growth and heat-treatment of films after growth were carried out in vacuum.

All other measurements like UV spectroscopy, X-ray diffraction and scanning electron microscopy were performed under low relativity humidity conditions (~40%). The films were observed to deteriorate only

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at relative humidity more than 65%. Quartz crystal thickness monitor (HINDHIVAC-model 101) was used to monitor the film thickness and deposition rate during the film growth. The film thickness was subsequently measured using Dektek IIA surface profiler, which uses the method of a 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 the film area with an error of 3% at the edges.

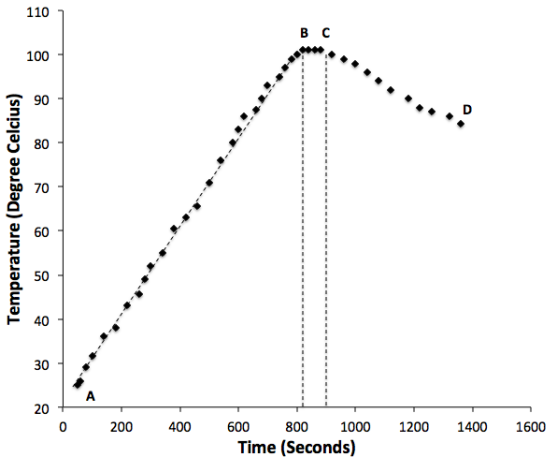


**Figure 1.** Time taken by ZnI2 films to acquire a particular temperature during in situ heat treatment.

For in situ heat-treatment, films were heated inside the film growth glass chamber itself by placing them in contact with a copper block, which is heated by a heating coil embedded in it. The voltage applied to the heating coil varied the temperature of the copper block. The temperature of the film was measured by a thermocouple placed very near to the sample on the substrate. The time in which the copper block used to acquire a predefined particular temperature is shown in the Figure1.

The heater was switched on at point A. In the segment AB, temperature increases almost linearly. When the heater was switched off at point B, temperature remains constant for some period BC as shown and then decreases slowly. In the experiment, it is considered that a film heated in vacuum at 60°C implies heater is switched off as soon as temperature attained the value of 60°C.

The structural studies of the films were carried out by x-ray diffraction using PHILLIPS X-Pert model–1830. For morphology and chemical composition studies of the films Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Analysis (EDAX) JEOL–840 models was used. The optical-absorption measurements were carried out using an ultraviolet/visible spectrophotometer (Shimadzu UV-260). The small pieces (2 cmX2 cm) of the $ZnI_2$ film grown at room temperature and had thickness around 395 nm were used for various analyses.

## 3. Results and Discussions

The $ZnI_2$ thin films used for experimentation were grown at room temperature and found to be translucent, stoichiometric, and polycrystalline. The four samples of an as grown film of thickness around 395 nm were respectively heat treated at 40°C, 50°C, 60°C and 80°C in-situ (in vacuum) in the manner as described in experimental details.

The in-situ heat-treatment of the as grown $ZnI_2$ thin films resulted in a decrease in the thickness of the films. The variation in film thickness during in-situ heat-treatment with temperature is shown in Figure 2. Here it shall be noted that during in-situ treatment, partial vapour pressure is non measureable, thus the reason for decrease in film thickness cannot be ascertain like in our earlier study[10], where heat-treatment of $ZnI_2$ films in open air had also resulted in decrease in film thickness linearly at the rate of 0.5 nm/°C. However, here, during the in-situ heat-treatment the film thickness of $ZnI_2$ films reduced at sharper rate of 0.66 nm/°C. Important point to note is that during heat-treatment in air the films were heat treated for very short duration of 30-40 seconds only, while during in-situ heat-treatment heating time varied from 200 to 600 seconds.

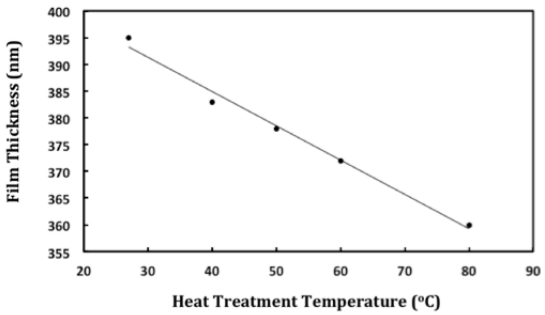


**Figure 2.** Variation in ZnI2 film thickness during in-situ heat-treatment.

The x-ray-diffraction analysis of as grown and in-situ heat-treated $ZnI_2$ thin films for structural studies reveal their tetragonal structure in agreement to earlier

reports[4,9]. The x-ray diffractograms of $ZnI_2$ films in-situ heat-treated at 40°C, 50°C, 60°C and 80°C along with that of as grown film of thickness 395 nm at room temperature (27°C) are shown in the Figure 3. There were three major peaks (101), (102) and (104) in the diffratctograms. The structural parameters of all the samples matched well with powder data ASTM card no. 10-72 and earlier report[13] as well. A few other minor peaks (201), (202) and (107) were also observed. The relative intensity of major peaks found to vary with film thickness (or in-situ heat-treatment temperature). However, no correlation was found in the variation of these intensities with other optical parameters. The different magnitude of the relative intensities of different peaks indicates a random orientation of crystallites. It is more so because major peaks represent the crystal planes parallel to substrate plane and (101), (102) and (104) are non-parallel planes. The morphological studies through Scanning electron microscope (SEM) of $ZnI_2$ films in-situ heat-treated at 40°C, 50°C, 60°C and 80°C also evidently show random orientation of crystallites as shown in the Figure 4.

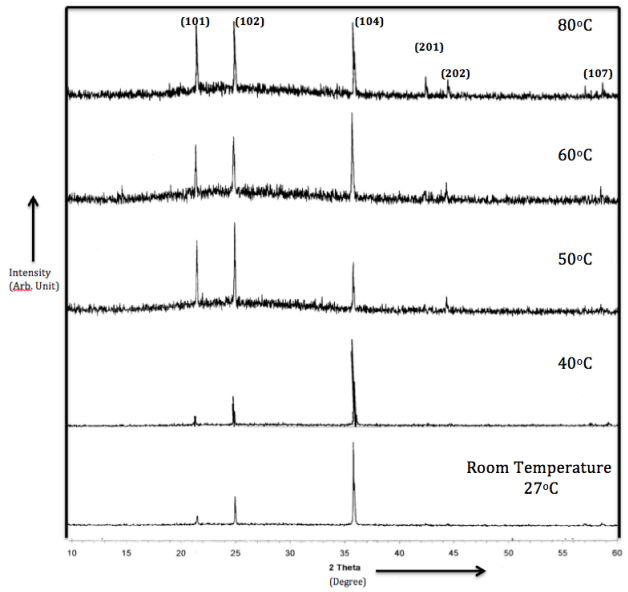


**Figure 3.** The X-ray diffraction pattern of in-situ heat-treated ZnI2 films at 27oC, 40oC, 50oC, 60oC and 80oC.

An in depth analysis of x-ray diffraction data reveals a small shift in the *d*-spacing of the diffraction peaks of different magnitude towards higher 2θ values. This behavior is an indication of presence of residual tensile or compressive strain in the films that is quite common in thin films. It is possible to estimate maximum strain present in the films by calculating the value of term $\frac{\Delta d}{d}$ for each peak (having Miller indices *h,k,l*) as described in reference[9-10] using formula.

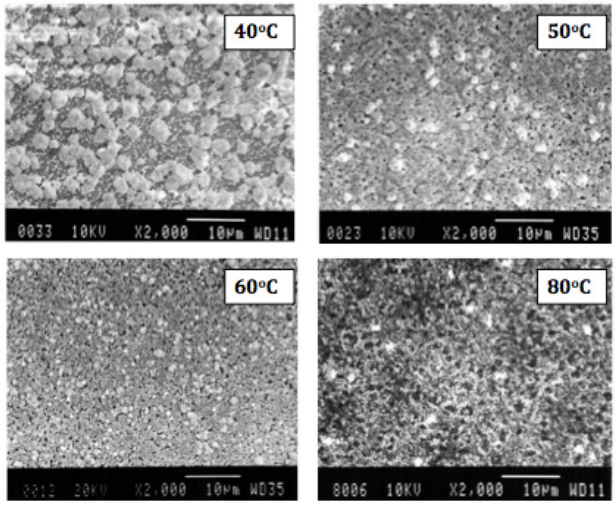


**Figure 4.** The SEM micrographs of X-ray in-situ heat-treated ZnI2 films at 40°C, 50°C, 60°C and 80°C.

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

The maximum stress present in the films then can be determined by multiplying $\frac{\Delta d}{d}$ by elastic constant of the $ZnI_2$. However, this was not found available in the literature survey. Thus, one simply can take $\frac{\Delta d}{d}$ as residual stress parameter and its average value for all possible peaks for a sample will then represent maximum stress present in it.

The value of residual stress parameter $\left(\frac{\Delta d}{d}\right)$ for different $ZnI_2$ films in-situ heat-treated at 27°C, 40°C, 50°C, 60°C and 80°C were calculated. Using film thicknesses as per corresponding in-situ heat-treatment temperature (ref.Figure 2), dependence of residual stress parameter $\left(\frac{\Delta d}{d}\right)$ on film thickness for various in-situ heat-treated $ZnI_2$ films is shown in the Figure 5. Residual stress in these films decreases almost linearly with decreasing film thickness, which in turn it decreases with increase of in-situ heat-treatment temperature.

Many models for internal stress behavior in thin films are listed in literature[13-14]. As per one model, the fractional change in *d*-spacing given by $\frac{\Delta d}{d}$ can be attributed to residual stress in the films if it is comparable

to line broadening given byΔ (2θ) where 2θ is the angle of diffraction, by the relation $\frac{\Delta d}{d}=\frac{2\Delta\theta}{2ean\theta}$. In present study, a well correlation of $\frac{\Delta d}{d}$ with Δ (2θ) indicates the presence of residual stress in the all $ZnI_2$ films in-situ heat-treated at different temperature. Usually line broadening Δ (2θ) also results because of diminishing particle size to the order of 20-80 nm. However, in the present case as per SEM analysis particle size in all cases was bigger than 200 nm. This rule out line broadening because of diminishing particle size.

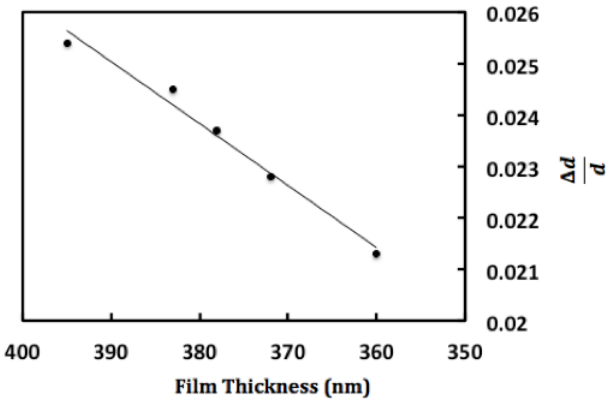


**Figure 5.** Dependence of the residual stress parameter on film thickness corresponds to respective in-situ heat-treated temperatures of 27°C, 40°C, 50°C, 60°C and 80°C.

Another model that explains internal stress behavior is based on density effect or packing density of the films[15]. The improvement in packing density and grains size distribution with in-situ heat-treatment temperature is evidently visible in SEM micrographs shown in the Figure 4. Thus in present case, presence of internal stress in $ZnI_2$ films in-situ heat-treated at different temperature is well observable both in X-ray diffraction and SEM microscopic studies. Further, these observations are also consistent with our earlier work[10]; however, the difference in grain size under two different conditions is very much noticeable.

The optical-absorption spectra recorded at room temperature in the inter band absorption region as a function of incident photon wavelength for $ZnI_2$ films in-situ heat-treated at 27°C, 40°C, 50°C, 60°C and 80°C are shown in the Figure 6. For sake of clarity, all spectrums are plotted on a same graph by displacing them vertically on y-axis taking care not to alter the relative values of absorption

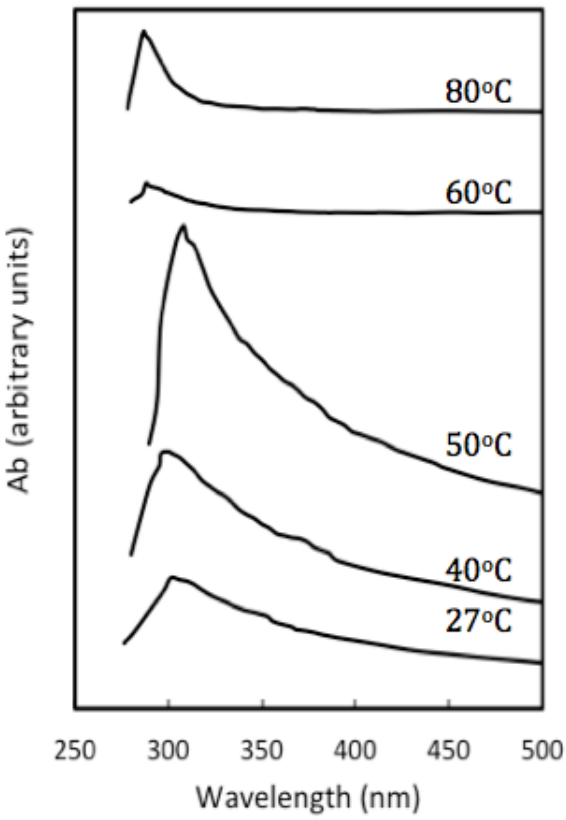


**Figure 6.** The optical-absorption spectra for ZnI2 films in-situ heat-treated at temperature identified in the figure

To determine the magnitude and nature of optical band gap from optical spectra as shown in Figure 6 was carried out by the method as described in[5,10,16] . The analysis of optical spectra yet again reveals direct type optical band gap for $ZnI_2$ films.

The value of energy band gap for various in-situ heat-treated $ZnI_2$ films is calculated by plotting $(\alpha h\nu)^2$ *VS* $h\nu$ using absorption spectra of Figure 6, in which the absorption coefficient function '$\alpha$' as a function of incident photon energy '$h\nu$' was calculated using the relation.

$$\alpha=\frac{2.303A}{d}$$

Where '$d$' is film thickness and '$A$' is the Absorbance of respective optical-absorption spectrum. For the reference, two plots of $(\alpha h\nu)^2$ *VS* $h\nu$ for in-situ heat-treatment tem perature 27°C and 80°C are shown in the Figure 7.

The optical band gap ($E_g$) determined as described above for $ZnI_2$ films in-situ heat-treated at 27°C, 40°C, 50°C, 60°C and 80°C was found to have values varying between 3.25 eV to 4.06 eV. The dependence of optical

band gap ($E_g$) on treatment temperature is shown in the Figure 8. The optical band gap increases almost linearly with heat treatment temperature in the experimental range.

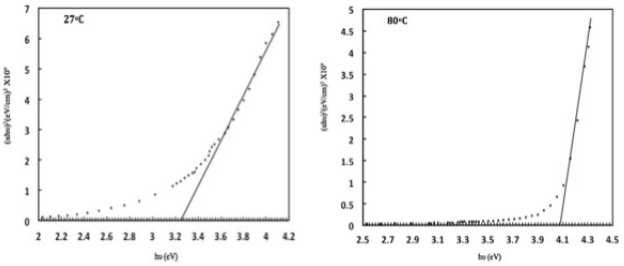


**Figure 7.** Dplot for in-situ heat-treated ZnI2 films at two different temperatures showing the direct type of transition across the band gap.

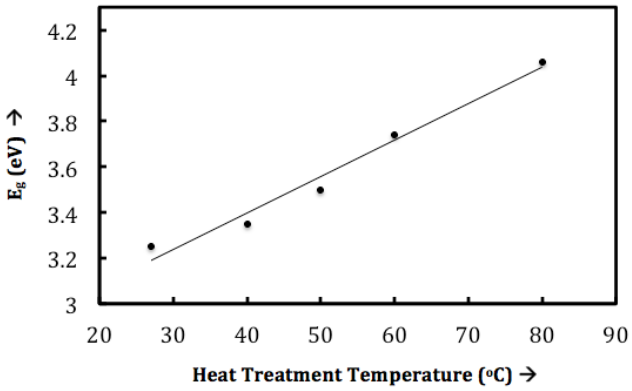


**Figure 8.** Dependence of optical band gap (Eg) on in-situ heat treatment temperature.

As thickness of in-situ heat-treated films found to decrease with increasing heat treatment temperature (shown in Figure 1) and optical band gap increases linearly with heat treatment temperature (shown in Figure 8), Figure 9 shows the dependence of optical band gap on film thickness for in-situ heat-treated $ZnI_2$ films.

The linear increase in optical band gap ($E_g$) with decreasing film thickness for in-situ heat-treated $ZnI_2$ films is in agreement to earlier observations of $ZnI_2$ films grown at room temperature but had different thicknesses[9]. However, this behavior is in contrast to the observed dependence of optical band gap of $ZnI_2$ film on film thickness from corresponding in air heat-treatment of 470 nm thick film[10]. The decrease in optical band gap ($E_g$) with film thickness in present study cannot be attributed to quantum size effect, as minimum film thickness here is too large to observe quantum size effect. Since variation in optical band gap with externally applied pressure is well known, thus in Figure 10, dependence of optical band gap of in-situ heat-treated $ZnI_2$ films on residual stress parameter (internally applied pressure in films) has been studied to ascertain the reason for variation in optical band gap ($E_g$) due to random orientation of crystallites in these films.

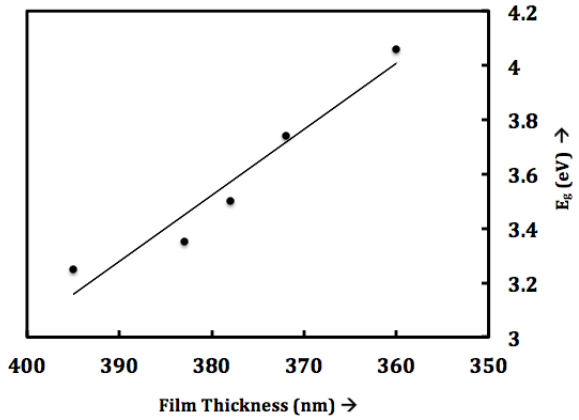


**Figure 9.** Dependence of optical band gap on film thickness for in-situ heat treated ZnI2 films.

Figure 10 shows a linear dependence of optical band gap ($E_g$) on residual stress parameter $\frac{\Delta d}{(d)}$ for in-situ heat-treated $ZnI_2$ films. Similar linear dependence of optical band gap ($E_g$) on residual stress parameter $\frac{\Delta d}{(d)}$ was observed in our earlier studies for room temperature as grown and in-air heat-treated $ZnI_2$ films[9-10]. However, in case of in-situ heat treatment the decrease in optical band gap ($E_g$) on residual stress parameter $\frac{\Delta d}{(d)}$ is much steeper than that in case of room temperature as grown and in-air heat-treated $ZnI_2$ films. This variation possibly can be due to less water content presence in in-situ heat-treated films (which is natural) in comparison to as grown and in-air heat-treated films. Even in present study, the value of residual stress parameter of the as grown film matches with earlier studies while the difference is quite noticeable in case of in-situ heat-treated samples. The intercept of linear fit of Figure 10 for in-situ experimental data on $ZnI_2$ films gives the band gap a value of 8.39 eV for a stress free perfect crystal if linearity is presumed throughout the lower region of stress and slope gives the magnitude of decrease as -204 ev/$\frac{\Delta d}{(d)}$. In comparison, the as grown and in-air heat-treated $ZnI_2$ films data was respectively

had much lesser values of 4.75eV and -65 ev/ $(\Delta d/d)$[10]. As per refrence[17], the higher values of these parameters in present study are an indicator of a larger deformation potential for $ZnI_2$ and a lot of empty space between its layers. However, we cannot calculate or estimate the values of deformation potential from present studies because of lack of information about elastic constants for $ZnI_2$ in the literature. Even then, present study is quite useful for further studies on structure of layered compounds.

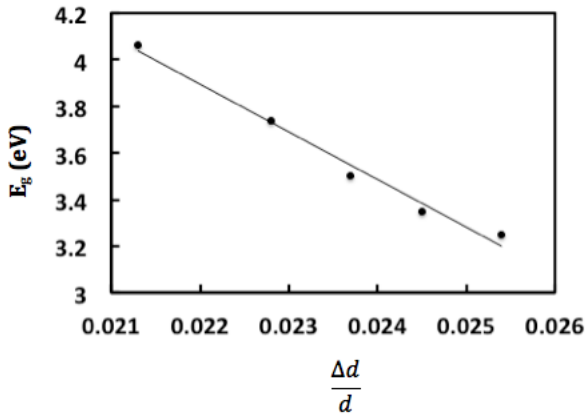


**Figure 10.** Dependence of optical band gap on residual stress parameter () for in-situ heat-treated ZnI2 films.

## 4. Conclusions

The in-situ heat-treatment of $ZnI_2$ thin films grown by thermal evaporation shows a linear decrease in film thickness with increase of in-situ treatment temperature. The x-ray diffraction studies reveal a decrease in residual stress parameter with decreasing film thickness. The internal stress behavior based on density effect or packing density of the films was evidently supported by morphological studies through SEM micrographs. The optical absorption measurement of in-situ heat-treated $ZnI_2$ thin films reconfirms a direct type-band gap for this material that increases almost linearly with heat treatment temperature from 3.25 eV to 4.06 eV in the experimental range. The earlier observed trend of linear increase in optical band gap ($E_g$) with decreasing film thickness for room temperature as grown and in-air heat-treated $ZnI_2$ films was observed for in-situ heat-treated $ZnI_2$ films as well. In comparison, in-situ experiment estimate a much larger value of 8.39 eV of the band gap for a stress free perfect crystal of $ZnI_2$ and give an indication of a large value of its deformation potential.

## 5. Acknowledgments

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