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U. G. C. MINOR RESEARCH PROJECT

"Studies on Structural, Transport and Optical Properties of Indium Oxide Thin Films on Bulk Indium"

U. G. C. Project File No. **F. 47-402/12 (WRO)**

EXECUTIVE SUMMARY

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We have studied the properties of thin films of transparent conducting In_2O_3 grown over bulk Indium palettes. Indium Oxide thin films are very suitable for transparent oxide coatings for many devices where a protective layer of Indium Oxide is necessary for both complete transmission of light to the device and also simultaneously preventing any atmospheric attacks from moisture or any other physical damage. So it is essential to study the properties of Indium Oxide for full protection of the device components.

A well powdered Indium was subjected to palletization using a dye punch and palette making machine using a hydraulic press at a pressure of 5 tons. The well ground powder of Indium yielded fine palettes of nearly 1 cm diameter. Oxidation of thin films was carried out on the palettes using a muffle furnace and ambient atmosphere was air. As Indium surface shows proclivity for oxidation on the <111> surface being the most prominent for oxidation of Indium for its conversion to Indium Oxide.

Optical Properties: Thin films grown for the range of 200 ^{o}C - 300 ^{o}C were subjected to optical transmission studies using a optical spectrometer. The results showed an optical band gap of 3.10 eV to 3.5 eV indicating that it is a direct band gap. Since the optical band gap is large enough so the thin films have a very transparent nature. This property can be used for the optical coatings of Indium Oxide on devices which need an optical window for facilitating the light to reach the junction of dissimilar semiconductors.

Structural Properties: Thin films grown for the range of 200 ^{o}C - 300 ^{o}C were subjected to X-ray diffraction studies using Cu-Kα radiation. It is seen that the polycrystalline thin films of Indium Oxide show the orientation of surface as <111> as the most prominent one. This can be seen from the matching of the JCPDS data for which the interplanar distance, "d"tallies with the JCPDS values. Since the thin film is polycrystalline, so other orientations like <211> and <222> , <321> and <622> were also seen. Some peaks corresponding to the bulk Indium were also found like <110> and <002> that can be justified from the fact that X-rays penetrate deep inside the bulk palette and thus Indium peaks may be present along with the Indium Oxide.

Morphological Properties: The morphological properties of Indium Oxide were studied from Scanning Electron Microscope. The thin films were found be polycrystalline. The grain size of the as grown thin films at various temperatures and at different oxidation times were studied for ascertaining the size of grains. It is found that the grain size is in micron range – ranging from 6.41μm to 11.18 μm. The dislocation density due to grain boundary area was calculated from SEM micrograph. It was found that the dislocation density was varying from 1.5×10^6 cm^{-2} to 0.35×10^6 cm^{-2} for our thin films grown as per the conditions mentioned above.

Electrical Properties: The electrical properties of the thin films were studied by linear four probe method. The thin films of Indium Oxide were highly conducting. It was found that the thin films of Indium Oxide shows an n-type nature. The resistivity for the thin films oxidized at 200 °C for 2 hrs, 3 hrs and 4 hrs was found to vary from 30.45×10^{-3} Ωcm to 19.35×10^{-3} Ωcm respectively. For thin films oxidized at 250 °C for 2 hrs, 3 hrs and 4 hrs, the resistivity was found to vary from 25.21×10^{-3} Ωcm to 15.26×10^{-3} Ωcm respectively. For thin films oxidized at 300 C for 2 hrs, 3 hrs and 4 hrs the resistivity was found to vary from 12.21×10^{-3} Ωcm to 04.23×10^{-3} Ωcm respectively. This decrease in resistivity is due to the fact that as the oxidation temperature increases, the grain boundaries decrease leading to enlargement of grains and thus less electrical resistivity of the thin films of Indium Oxide.

The Major findings of this UGC Minor Research Project were reported in the following research papers with due acknowledgement to U.G.C. for financial Assistance:

1. Structural and Electrical Properties of Indium Oxide thin films prepared by Thermal Oxidation of Indium Palettes, *Journal of Sciene*

Information (Special Issue-9), ISSN: 2229-5836, **Feb 2014**, Pages 148-151.

2. Effect of Oxidation Temperature on Optical Properties of Indium Oxide thin films prepared by Thermal Oxidation of Indium Palettes, *UGC Sponsored National Conference on Advanced Materials, (NCAM-2014)* ISBN No. 9789381432709, Page 202-204, held at Nabira Mahavidyalaya, Katol, District Nagpur on 1st March 2014.

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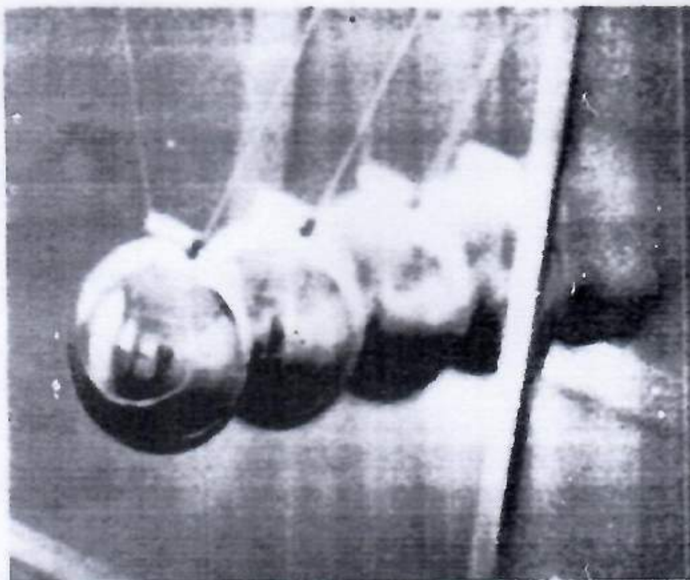

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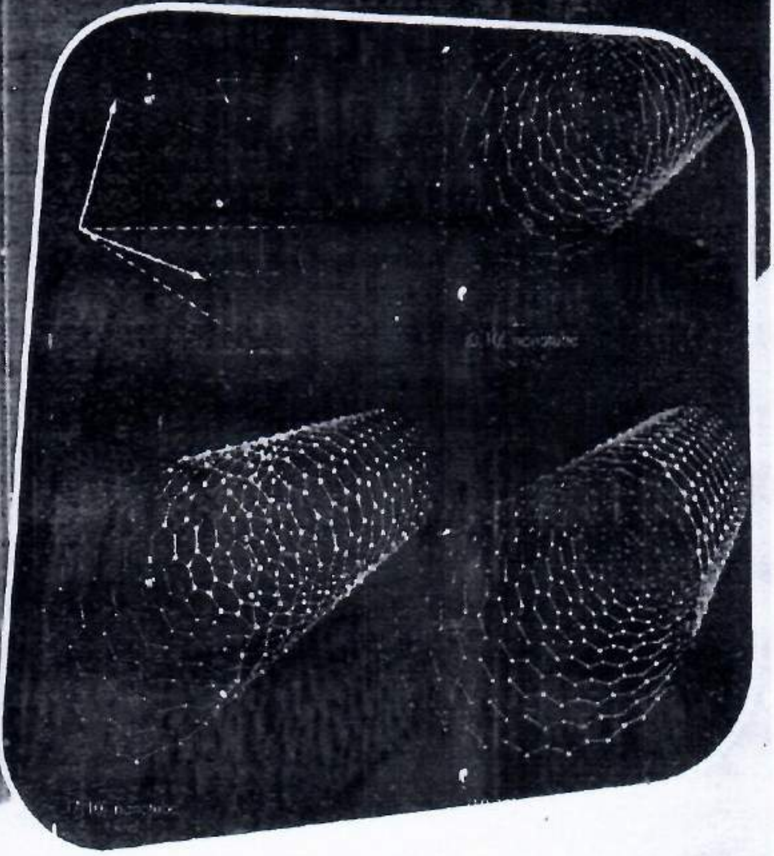

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Structural and Electrical Properties of Indium Oxide thin films prepared by Thermal Oxidation of Indium Palettes.

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Abstract

Thin Films of Indium Oxide were prepared by thermal oxidation of Indium pallettes in air in an open furnace for different temperatures 200°C for 2, 3 and 4 hours and 250°C for 2, 3 and 4 hours. The oxidized pellets were examined for structural studies by means of X-ray diffraction(XRD). The XRD pattern confirms formation of In_2O_3 surface. The electrical resistivity studies indicate the range of resistivity match well with the resistivity range of standard In_2O_3 thin films. Different oxidation times yield a better form of thin films by annealing of defects that might have crept during the thin film formation.

Introduction

Transparent conducting oxide In_2O_3 thin films coatings play a very important role in electronic devices like optical detectors, solar cells and photoconductors. The In_2O_3 thin films play a dual role, being high conducting and second due to its large band gap is transparent to visible light. They are also used as contact materials for deposition of other semiconducting layers like GaAs, InGaAs and InGaP solar cells. Various techniques like reactive thermal evaporation, sputtering using RF techniques, spray pyrolysis are used to grow thin In_2O_3 thin films. Here we use a technique-thermal oxidation of Indium palettes.

Experimental Techniques

Indium films are deposited on 8 mm diameter Indium pallets prepared by putting a fine Indium powder (obtained from Sigma Aldrich 99.999% purity) in a hydraulic press at a pressure of 5 tons. A suitable binder was used to realize a perfect Indium palette. The freshly prepared palettes were put in ethanol followed by methanol to remove grease impurities. The thoroughly cleaned Indium palettes were put in a muffle type furnace in an air ambient immediately after preparation to subject them for thermal oxidation. It is seen that the <111> Indium surface has largest concentration of chemical bonds which react with ambient air at temperatures of 200°C and 250°C to form a transparent conducting In_2O_3 with right stochiometric thin film over Indium palette surface. Different heating times of 2 hrs, 3 hrs and 4 hrs were followed to study if any improvement in formation of In_2O_3 thin films and the consequent effect on the electrical and optical properties if any. Philips X-ray diffraction instrument was used in the range (2θ: 0° to 90 °) with steps of 0.1 °.

Results And Discussion

Structural Characterization

X-ray diffraction Studies:

Figures 1 shows the x-ray diffractograms of (a) Indium palette (b) In_2O_3 thin films by thermal oxidation at 200°C for 2 hours, 3 hours and 4 hours. It is seen that the Indium palette shows a few characteristic x-ray diffraction peaks of Indium corresponding to the orientation of Indium polished surface. The oxidized surface when exposed to x-ray diffraction shows peaks of In_2O_3 which show a rise in intensity as the oxidation is done for a higher time duration. The d values, obtained are compared with the JCPDS data card nos 5-642 and 21-406 for peak confirmation and orientation of diffraction planes. It is seen that the oxidized surface has only few peaks of Indium indicates that the surface is almost oxidized.

Table I: XRD data obtained for pure Indium Surface of Palette.

Sr. No.	Observed d (A°)	Standard d (A°)	h	k	l
1.	2.6832	2.715	1	1	1
2.	2.4134	2.471	0	0	2
3.	2.3268	2.298	1	1	0

Table II: XRD data obtained for pure In_2O_3 thin films on Indium Palette.

Sr. No.	Observed d(A°)	Standard$d$(A°)	h	k	l
1.	2.6832	2.715	1	1	1
2.	4.1444	4.130	2	1	1
3.	2.9281	2.921	2	2	2
4.	2.7233	2.704	3	2	1
5.	2.5312	2.529	4	0	0
6.	1.7919	1.788	4	4	0
7.	1.5258	1.525	6	2	2

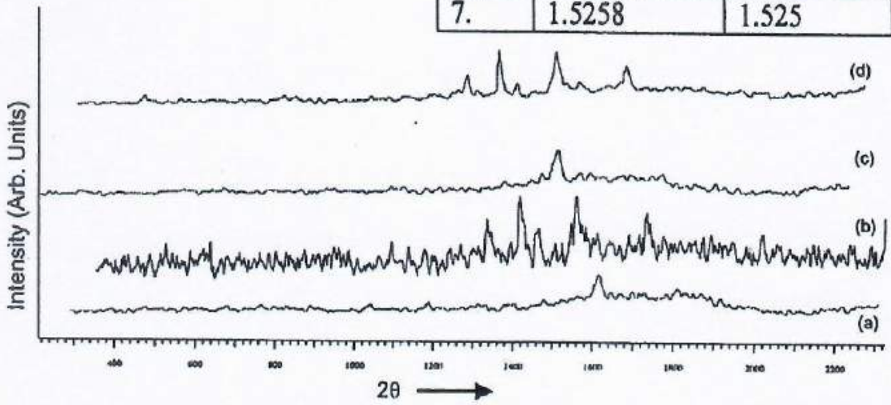


Fig. 1: Typical X-R-D Pattern of (a) Indium Pallette (b) In_2O_3 thin film at 200°C (c) 250°C (d) 300°C

Surface Morphology Studies

Surface morphology studies were performed using Scanning Electron Microscope (JEOL, Made in Japan). Typically a constant magnification of 2000X was kept for comparative studies. The grain size as calculated from SEM pictures was calculated from the formula (Wada *et al*):

$$\text{Grain Size, G.S.} = \frac{1.5\ell}{(n \times m)}$$

Where m is the micrograph magnification, ℓ is the line length on the micrograph, n is the no. of grains intercepted by the line of length ℓ cm assuming spherical grains, m is the magnification. It is seen that the grain size is due to the high temperature of growth of the thin film. The high temperatures lead to self-annealing. The process of self-annealing promotes fusion of small crystallites (agglomeration) thus reducing the grain-boundary area, which leads to increase in diffusion length of charge carriers. The higher grain size also leads to decrease in scattering from the boundaries. Self annealing process also removes excess of Indium, so that the recombination centres such as Indium acceptors are also removed.

Table for Grain Size Calculations from SEM micrographs

Sr. No.	Deposition Temperature (°C)	Grain Size (μm)	Dislocation Density (cm^{-2})
1.	200	06.41	1.50×10^6
2.	250	08.25	1.38×10^6
3.	300	11.18	0.35×10^6

(1) (2) (3)

Fig. 2.: SEM micrographs of In_2O_3 thin films at (1) 200°C (2) 250°C (3) 300°C

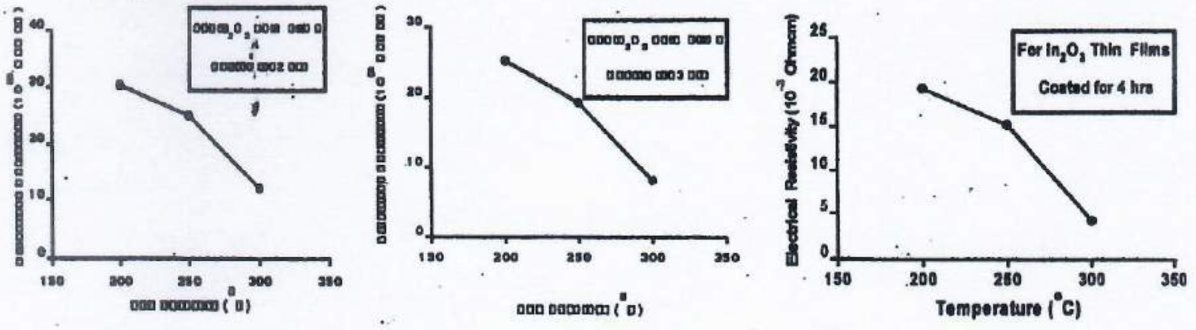
Electrical Properties

The Indium Oxide thin films exhibit n-type conductivity as determined by four probe method. The electrical resistivity for the as-grown In_2O_3 thin films were evaluated by linear four probe technique. Suitable pressure contacts were used for making ohmic contacts. The estimated values of various electrical parameters are given in the table below:

Table for typical resistivity *vs* with oxidation Temperature for various In_2O_3 thin films grown on Indium Palettes.

Sr. No.	Temperature (°C)	Oxidation Time(hrs)	Resistivity (10^{-3} Ωcm)
1.	200	2	30.45
		3	25.21
		4	19.35
2.	250	2	25.21
		3	19.35
		4	15.26
3.	300	2	12.21
		3	08.12
		4	04.23

It is seen that the electrical resistivity value decreases from 30.45×10^{-3}Ωcm to 19.35×10^{-3}Ωcm for Indium samples oxidized at 200°C. It is also seen that the electrical resistivity value decreases from 25.21×10^{-3} Ωcm to 15.26×10^{-3}Ωcm due for Indium samples oxidized at 250°C. It is also seen that the electrical resistivity value decreases from 12.21×10^{-3} Ωcm to 4.23×10^{-3}Ωcm due for Indium samples oxidized at 300°C. In each case, sample was continuously heated for 2 to 3 hours. The decrease in resistivity is due to the fact that as the oxidation temperature increases, the number of grain boundaries decrease rapidly thereby increasing the grain size. Also the increase in grain size also decreases scattering of charge carriers of Indium thin films. Secondly impurities trapped at the grain boundaries get annealed out and thus diffusion length of the charge carriers increases leading to increase of mean free path.



CONCLUSION

It is concluded from the above study that the indium oxide thin films prepared by thermal oxidation of Indium Palettes in air have good conductivity. X-ray diffraction studies reveal prevalence of some traces of substrate Indium due to the substrate (palette) and maximum Indium Oxide peaks confirming that the thin films are formed.

Acknowledgements

One of the author, L.P. Damodare, thanks the University Grants Commission (WRO), Pune for financial assistance through its minor research project for pursuing this research work.

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Effect of Oxidation Temperature on Optical Properties of Indium Oxide thin films prepared by Thermal Oxidation of Indium Pallets.

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Abstract

Thin Films of Indium Oxide were prepared by thermal oxidation of Indium pallets in an ambient air open furnace for different temperatures of the range 200°C-300°C for 2, 3 and 4 hours. The oxidized pallets were examined for optical absorption studies to study the effect of oxidation on band gap of Indium Oxide thin films. Different oxidation times confirm that the fundamental transition edge is in the visible of the electromagnetic spectrum. The plots of $(\alpha h\nu)^2$ *vs* $(h\nu)$ are linear confirming that the optical transition is direct. The direct band gap variation of 3.10 eV to 3.50 eV was found for the thin films oxidized at 300°C for 4 hrs indicating the total transparency of the as-grown Indium Oxide thin films in the visible region with least defect level transitions.

Introduction

Transparent conducting oxide In_2O_3 coatings are have been playing a pivotal role in the preparation of solar cells, photodetectors and other devices which make use of optical light for photoconduction and photoconversion to electricity. Since the band gap of Indium Oxide in thin film form is large so it is totally transparent in optical region. In this paper we present our results on the optical absorption studies and effect of different oxidation temperatures on the optical band gap of thin In_2O_3 thin films.

Experimental Techniques

Indium films are deposited on 8 mm diameter Indium pallets prepared by putting a fine Indium powder (obtained from Sigma Aldrich 99.999% purity) in a hydraulic press at a pressure of 5 tons. A suitable binder was used to realize a perfect Indium palette. Clean Indium palettes were carefully put in a muffle type furnace in an air ambient immediately after preparation to subject them for thermal oxidation. It is seen that the <111> Indium surface has largest concentration of chemical bonds which react with ambient air at temperatures of 200°C to 300°C to form a transparent conducting In_2O_3 with right stochiometric thin film on the Indium palette surface. Different heating times of 2 hrs, 3 hrs and 4 hrs were followed to study how these techniques affect the optical band gap of In_2O_3 thin films in the wavelength range of 250 nm to 850 nm.

Results And Discussion

Optical Studies

The optical transmission studies of the thin films were performed at room temperature range using Shimadzu Spectrophotometer. Transmission was recorded in the wavelength range of 350 nm to 850 nm. The graph shows that the transmission corresponding to band gap was sharp in nature indicating that there are no defect state in the band gap and the transmission is direct. Also the reflectance analysis showed minimal reflectance indicating that the thin films exhibit high transmission.

The absorption coefficient, α at various wavelengths for a sample of thickness, 't' is given by:

$$\alpha t = \log(I_0 / I)$$

Where I_0 and I are the intensity of incident and transmitted radiation respectively. For a direct transition the absorption coefficient is related to the band gap by the relation:

$$\alpha = \frac{A}{h\nu} \times \left(h\nu - E_g\right)^{1/2}$$

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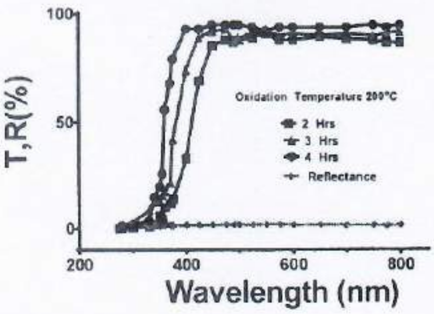
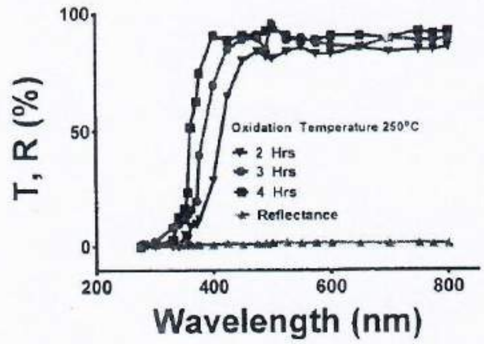
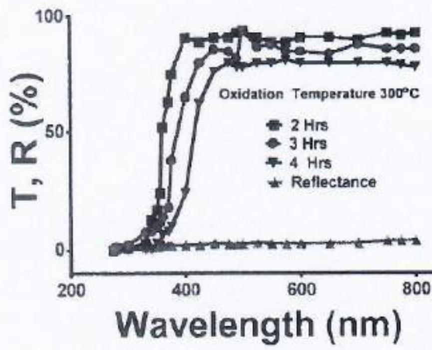
A plot of $(\alpha h\nu)^2$ vs $h\nu$ will be linear. On extrapolation of the plot to ($h\nu$) axis gives bang gap energy. E_g, usually the Optical Band Gap.

Figure 1 shows the Transmittance (%) *vs* Wavelength (λ) for the as grown In_2O_3 thin films on Indium Palette under various situations. At wavelengths greater than 350 nm the variation is smooth indicating that there might be multiple reflections in the thin film indicating the thin films might exhibit high crystalline nature with minimum grain boundary area. This indicates that there is a minimum amount of scattering of the photons within the thin films and thus the optical transmission at the band gap region is fundamental one.

Fig.1Transmisttance vs Wavelength for Indium Oxide thin films under various situations.







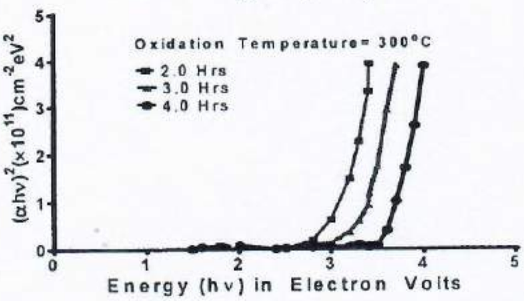


Figure.2 shows the plots of $(\alpha h\nu)^2$ vs $h\nu$ are linear. As per the intercept on the Energy (hv) axis it is found that the band gap slightly shifts from 3.1eV to 3.50eV for the thin films oxidized at 300°C for times of 2 hrs, 3 hrs and 4 hrs indicating that some amount of defect levels in the thin films contribute to decrease in the band gap at low times of oxidation and these defect levels get annealed out when the oxidation time is increased to 4 hrs.

The results obtained from band gap calculation are shown in Table 1. It is seen that the optimum temperature for obtaining good thin films of Indium Oxide are for oxidation at 300°C for 4 hours. The reason is that more oxidation times also anneal out the defects in thin films and thus the impurities trapped at the grain boundaries are removed thus reducing the defect levels in the mid of band gap and thus making the thin film more optically transparent for future device fabrication where transparent coatings are needed.

Table- I: Typical values obtained for the optical band gap studies for the as-grown Indium Oxide Thin films.

Sr. No.	Oxidation Temperature (°C)	Oxidation Times(Hrs)	Optical Band Gap of Thin Films in eV
1.	300	3	3.50
2.	250	3	3.25
3.	200	3	3.10

Table- II: Typical values obtained for the optical band gap studies for the as-grown Indium Oxide Thin films for 3 hours under different deposition temperatures.

Sr. No.	Deposition Temperature (°C)	Grain Size (μm)	Dislocation Density (cm^{-2})	Optical Band Gap (eV)
1.	200	06.41	1.50×10^6	3.10
2.	250	08.25	1.38×10^6	3.25
3.	300	11.18	0.35×10^6	3.50

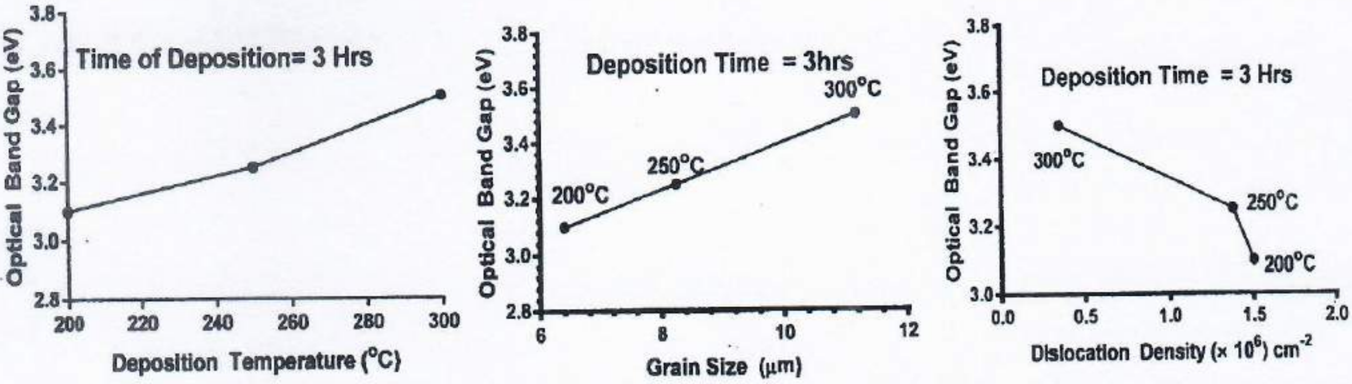


Figure 3: Optical Properties of Thin Films under various conditions of Deposition and their effect on band gap.

Figure 3 shows typical plots for the variation of Optical Band gap with Deposition temperature for 3 Hrs duration and its effect on various parameters like grain size and dislocation density. It is seen that when the thin films are deposited for a deposition time of 3 Hrs at 200°C, 250°C and 300°C respectively the grain size increases from 6.41 μm to 11.18 μm and the dislocation density falls from $1.58\times 10^6 cm^{-2}$ to $0.35\times 10^6 cm^{-2}$ respectively. Thus the thin films exhibit larger grain size and so the band gap transitions are fundamental in nature and the band gap close to the value = 3.5 eV is obtained which matches with the literature. The lower grain size and larger dislocation density leads to defect levels which play an important role in creating donor levels in the band gap and thus exhibit optical absorption at higher wavelength much smaller than the band gap.

Conclusions

It is concluded from the above study that the indium oxide thin films prepared by thermal oxidation of Indium Palettes in air have good transparency. The thin films grown at a lower temperature of 200 °C show larger dislocation density and smaller grain size which effects the optical transition process in the semiconducting Indium Oxide thin films leading to a smaller band gap. The thin films grown at 300°C for the same duration of 3 hrs yield a better sample with direct band gap of 3.5 eV which is very useful for the transparent casing for most of the devices which need to have interaction with visible light for operation.

Acknowledgement

One of the author, L.P. Damodare, thanks the University Grants Commission (WRO), Pune for financial assistance through its minor research project for pursuing this research work.

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