

Experimental Study on Effects of Film Thickness on Structural Characteristics of ITO Thin Film Prepared by RF Sputtering

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ABSTRACT

This paper presents the effects of low-temperature annealing and film thickness on the structural characteristics of ITO thin film for photovoltaic applications. The thin film of thickness 40nm, 60nm, and 85nm were grown on glass substrate using radio frequency magnetron sputtering technique followed by thermal annealing at 4500C. These as-grown and annealed films were subjected to X-ray diffraction [XRD] for structural analysis. The XRD patterns reveal that all as-grown samples are amorphous in nature in minor peaks. While the annealed samples are crystalline in nature with pronounced peaks at a preferred orientation [222] and monocrystalline in nature. This study shows that ITO thin films may be used as alternative materials for eco-friendly buffer layer thin-film solar cell applications.

Keywords: ITO, Corning Glass, RF Sputtering, Annealing.

1.0 INTRODUCTION

Energy is fundamental for the economic development and the improvement of the quality of life of a society or nation. According to [1], the availability and utilization of energy often reflects the standard of living of people and the Gross Domestic Product [GDP] of a nation. In Nigeria, just like in most least developed countries, [LDCs] or the so called third world economies, most households rely on the use of fossil fuels such as coal, liquefied petroleum gas, [LPG or natural gas], kerosene, premium motor spirit, [PMS or petroleum] as well as electricity and biomass [firewood, agricultural wastes, crop residues, animal dungs] as conventional energy sources. Notwithstanding the fact that Nigeria is about the eight largest exporter of crude oil and that it is also blessed with a great deal of river systems, yet Nigerian economy has continued to witness epileptic electrical power supply system as well as scarcity and geometrically escalating costs of petroleum products [1].

Generating sufficient energy to meet this growing demand has been a major global concern. For most developing countries, the draw back in both economic and technological development can largely be attributed to the very limited and unsustainable energy supply. Various energy sources are in use for energy generation. On a global scale, fossil fuel is the main energy source today that accounts for over 70% of the global energy consumption. Figure 1.1 shows the dominance of fossil fuel in the world energy scenario [2].

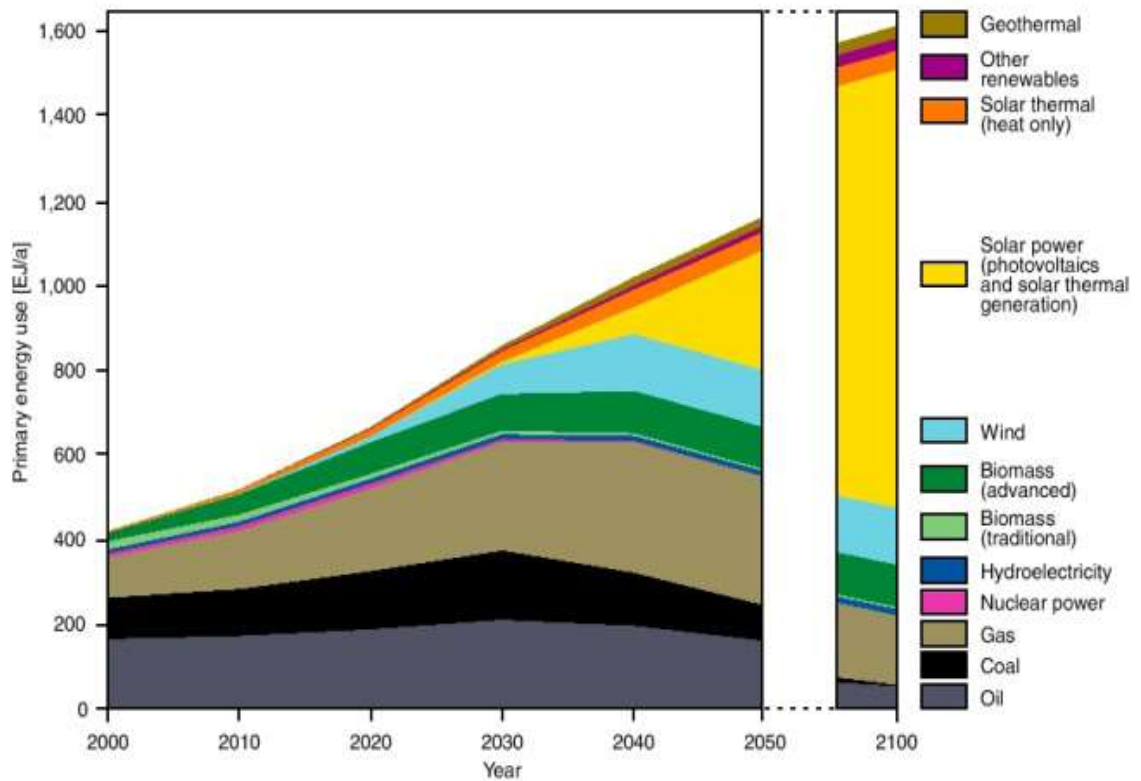


Figure 1.1: Current and projected world energy production scenario World Energy Report 2010]. [3]

Energy generation from fossil fuel has not been without effects on human lives and on the environment. The burning of fossil fuel releases greenhouse gases into the atmosphere and these gases today are believed to account for global warming. Another major challenge with the use of fossil fuel is that it is only available in very few countries and as such has led to the dependence of many countries of the world on these few oil-producing countries. A direct consequence of this is the ever-existing political and economic tension between the oil-producing nations and the rest of the world. On another hand, over-dependence on oil can be linked to the conspicuous underdevelopment of some of the oil producing nations whose economic policies are mainly oil-based. Typical examples include countries like Nigeria and Libya. The energy demand is continuously increasing by industrial development, growing population and increasing standards of modern life. The report of International Energy Agency [IEA] points out that world primary energy demand will be expanding by almost 60% within 20 years, with an average annual increase of 1.7% per year [3].

The current world energy scenario [2]. Paints a picture of an energy supply system that is not sustainable, not reliable, not sufficient, not cost-effective, and not environmentally friendly. In view of this it is only imperative that both alternative and supplementary energy sources to the depleting fossil and nuclear sources are sought. This will be a long-term roadmap to emancipating this generation from its current energy crisis and securing a better environment and future for generations to come. Energy production from renewable sources is considered sustainable. Options such as solar and wind energy are environmentally friendly and can be harnessed in most parts of the world. Energy from the sun can be harnessed directly by a thermal conversion using solar collectors or by electrical conversion using solar cells or solar power concentrators. The direct conversion of solar energy into electricity in solar cells is based on photovoltaic [PV] effect.

One of the most promising techniques is solar cells, which combine several advantages. They can be used more or less in any dimension, from the small one in a calculator up to solar power plants in the GW range. This also makes solar cells an autonomous source of energy. It is possible to cover the energy demand of small villages or street lamps at bus stops, which is especially interesting if it is not possible or too expensive to connect them to the grid. Moreover, it is a technology that is quiet, has no emissions and that has no moving parts, which makes it a technology with a quite long lifetime. Producer give guaranties of 20–25 years, but in principle much longer lifetimes are possible. For this reasons, solar cells are part of a growing industry with a decreasing development of costs. [4].

Photovoltaic power generates electricity directly from the sun with easy installation parts and without any contribution to the air pollution. Electricity generation from solar power is expected to reach 119 TWh in 2030 [3].

The photovoltaic technology has the highest investment and generating costs among all renewable energy technologies. Electricity generation from PV is economically most attractive in areas with abundant sunshine and high electricity prices. The photovoltaic involve the conversion of light into electricity by means of solar cells. The solar cells are the main building block of the electric generation from the sun light. These cells are typically made of semiconductor materials. A number of solar cells are connected to each other in series or parallel to a mounted frame called "solar module" or "solar panel". Modules are designed to supply energy at a certain voltage. Several modules can be wired together to form an array whose usage can be very practical. The solar arrays can operate continuously without maintenance, which limits their cost to the initial investment needed for their purchase and installation. The solar panels generally last 25 years or longer. [5]

The traditional material that dominates the market of these solar cells is silicon. However, silicon is limited in performance with an efficiency around 14%-19% mainly due to its single band gap [6]. Another problem regarding crystalline silicon solar cells has been the concern about the supply of high impurity silicon materials. Due to the increment in the demand for photovoltaic industry, high quality silicon materials have been tight and prices have been increasing. The high costs and shortage of pure silicon for PV applications stimulated research efforts on finding alternative PV materials and new fabrication processes. [6] Figure 1.2 below shows a photon absorption by silicon photovoltaic used in generating power.

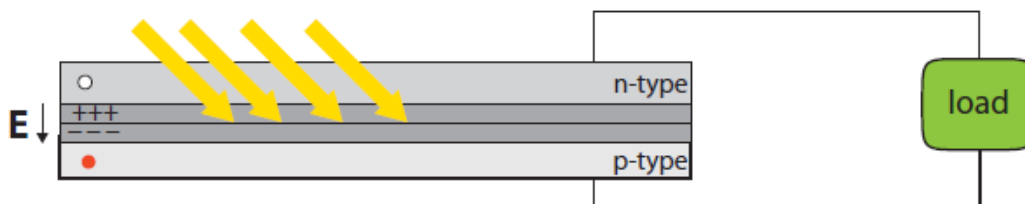


Figure 1.2: A silicon photovoltaic. Photons absorbed in the depletion region of the pro-junction can be separated and used to power a DC load

It is known that semiconductors are important in nano-devices like solar cells, light emitting diodes [LEDS], and for visible and infrared detectors. One of the most important parameters of a semiconductor that determines its use in these technologies is the band gap. To make the nano-devices more efficient, it is necessary to increase the range of the band gaps of the material to cover a wider spectral range being absorbed. By adjusting the relative portion of the materials in a ternary alloy, it is possible to tune the bandgap [1]

Indium tin oxide is one of the most widely used transparent conducting oxides because of its two main properties: its electrical conductivity and optical transparency, as well as the ease with which it can be deposited as a thin film [8]. As with all transparent conducting films, a compromise must be made between conductivity and transparency, since increasing the thickness and increasing the concentration of charge carriers increases the material's conductivity, but decreases its transparency [8]. Thin films of ITO are most commonly deposited on surfaces by physical vapour deposition. Often used is electron beam evaporation, or a range of sputter deposition techniques like rf and dc magnetron sputtering. [8]

ITO is mainly used to make transparent conductive coatings for liquid crystal displays, flat panel displays, plasma displays, touch panels, electronic ink applications, organic light-emitting diodes, solar cells, antistatic coatings and electromagnetic shieldings. In organic light-emitting diodes, ITO is used as the anode [hole injection layer]. ITO has been used as a conductive material in the plastic electroluminescent lamp of toy Star Wars type light sabers. [9]

In another study, [9] carried out a study to investigate the effect of varying film thickness on the properties of ITO film using RF sputtering. The samples with thickness values of 50nm, 200nm and 380nm were deposited and annealed at 450⁰C. The result of their investigation showed that the structural properties of the film significantly depend on the film thickness. That is the root mean square [rms] roughness and grain size increased with increasing film thickness.

[10] studied the effect of annealing on nano thick indium tin oxide transparent conductive film for touch sensors using ultra thin ITO films prepared on B270 glass substrates at room temperature by the dc pulsed magnetron sputtering method. The result of their investigation showed that, as the annealing temperature increased, the structure of the ultra thin ITO films changes from amorphous to polycrystalline. Therefore, the crystalline size in the ITO films becomes larger as the annealing temperature increases, indicating that post annealing treatment is an attractive way to improve the crystalline and other properties of ITO films because it is a simple and low-cost process.

[11] reported that Indium tin oxide [ITO] films were deposited on glass substrates by rf magnetron sputtering using a ceramic target. Then annealing was done in air and vacuum respectively. They studied the effects of annealing and structural properties of ITO films. The result of their investigation revealed that the increase in annealing temperature improves the crystallinity of the film.

Another study [8] revealed that Indium tin oxide thin films with different thickness deposited on polymer substrates, at room temperature using electron beam evaporation. The dependence of structural properties on the Indium tin oxide film thickness was studied. X-ray diffraction illustrates the amorphous structure for all the ITO prepared films.

[12] reported that ITO thin films were deposited on thick soda lime glass substrate by rf magnetron sputtering system, using a solid ITO target with purity of 4N. The result of their investigation showed that surface roughness increases from 75 to 225nm. This significant change in roughness with increasing film thickness is due to the reflecting nucleation, coalescence and continuous film growth processes.

In a related study, [9] carried out an investigation on the effect of varying film thickness on the properties of Indium tin oxide films after temperature annealing, the ITO thin films were deposited via rf sputtering onto a glass substrate. The result of their study revealed that the grain size increased from 31.17nm to 41.82nm with increasing film thickness. Thus, roughness increased with increasing film thickness.

2.0 EXPERIMENTAL DETAILS

2.1 Substrate preparation and cleaning

The corning glass substrates were kept in a dilute chemical detergent [a detergent solution used in the laboratory to solubilise biological macromolecules such as proteins] solution at 100°C in ultrasonic bath for 10 minutes to remove oils and protein molecules and rinsed with double distilled water to remove possible left detergent contaminants. To remove organic contaminants, the substrates were boiled in dilute hydrogen peroxide [H₂O₂] solution for 15 minutes. The same solutions were put into the ultrasonic bath. The substrates were extracted from the bath and rinsed with distilled water and later dried with 4N nitrogen gas before being introduced into the sputtering chamber.

2.2 Thin film deposition

The deposition begins with loading the target and securing the glass substrate[s] to the substrate holder. Sputtering was performed on a corning glass substrate under a constant flow of argon gas [99.99% purity] with a fixed target/substrate distance of 7cm. The base pressure was around 1.33×10^{-3} Pa. The thickness of the deposition films were 40nm, 60nm and 85nm. All the films were deposited at a substrate temperature of 100°C. Two batches of three sample, making a total of six samples of various thicknesses, were prepared. Before the samples were characterized to analyze their various properties, heat at a temperature of 450°C was applied to three of the samples. The ramp rate was 10°C per minute and the dwelling time was 1 hour. The samples were annealed under nitrogen gas flowing at 20 sccm per minute. The purity of the nitrogen gas was 99.99%.

2.3 Characterization

2.3.1 Structural Characterization

The X-ray tube was reported at a voltage of 45kV and a current of 40mA. XRD patterns were recorded in the range of 20° - 65° with a scan speed of 2°/min, step size of 0.2000° and scan step time of 1.10 seconds for all deposited thin films. In the Diffractometer, the X-ray source was in fixed position and the sample stage and the detector rotated simultaneously in the same plane, along the same axis [Diffractometer axis] perpendicular to the figure and located at the center of the sample stage. The sample was rotated and the detector followed the sample motion in the same direction around the Diffractometer axis by twice the speed of the sample. The angular positions and intensities of the resultant diffracted peaks of radiation from the planes parallel to the substrate surface were detected and recorded. By plotting the angular positions [i.e.2θ] and intensities of the resultant diffracted peaks of radiation, a pattern characteristics of the sample was obtained. The XRD diffractograms obtained for the samples were compared with XRD patterns of well-known material [nearly 62,000 different diffraction patterns] structures supplied by ICDD [International Centre for Diffraction Data] cards and detailed knowledge about the structure, phase composition and degree of crystallinity was obtained.

ICDD is an organization that supplies a database which consists of XRD spectra of organic and inorganic materials. It is supplied generally by manufacturer of diffraction systems. Based on the analysis of XRD patterns, valuable knowledge about the structure

of CZTS thin films was obtained. And, with the help of measured full width at half maximum [FWHM] of preferred orientation, the grain sizes D were calculated through the Scherer's formula [5]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad [1]$$

Where β is full width at half maximum [FWHM] of the preferential plane, θ is the Bragg's angle and λ is the wavelength of incidence ray.

2.4 Determination of dislocation density

The dislocation density δ is defined as the length of dislocation lines per unit volume, is the measure of the amount of defects in a crystal. Dislocations are imperfection in a crystal associated with misregistry of the lattice in one part of the crystal with respect to another part. Dislocations are not equilibrium imperfections. The dislocation density of thin films δ were calculated by using the relation [10].

$$\delta = \frac{n}{D^2} \quad [2]$$

where, n is a factor which equals unity giving maximum dislocation density and D is the grain size.

Determination of micro strain

The origin of a strain is related to lattice misfit, which in turn depends upon the growing conditions of the films. The micro strain ϵ developed in thin films was calculated by the relation [11]:

$$\epsilon = \frac{\beta \cos\theta}{4} \quad [3]$$

where β = FWHM and θ is the Bragg's angle.

Determination of lattice parameters a and c

The lattice parameter a and c values for tetragonal crystallographic system was calculated from the following equation using hkl parameters and the inter planer spacing d [7].

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad [4]$$

3.0 RESULT AND DISCUSSION

3.1 Structural characterization

The XRD patterns of ITO grown at substrate temperature of 100°C are shown in the Figures 2.2 to 2.4 below. In the XRD pattern for 40nm sample as deposited, there is no pronounced peak, which confirm the amorphous nature of the sample. While in the case of the annealed sample there is presence of single pronounced peak. The dominant peak observed at $2\theta=34^\circ$ is due to the reflection from a plane with preferred orientation [222], which corresponds to the intensity of 95.a.u.

In the XRD pattern for the 60nm as deposited sample, there is no pronounced peak which indicated the amorphous nature of the ITO film. However, in the case of annealed sample, there is presence of single peak also observed at $2\theta=34^\circ$ with intensity of 75a.u. Similarly, in the XRD pattern for 85nm, no peak was also observed for the not annealed sample. While in the case of annealed sample, there is a pronounced peak also observed at $2\theta=34^\circ$ with intensity of 70a.u. This result shows that annealing temperature improved transparent conducting film. This result was in conformity with the report of [8] and [9].

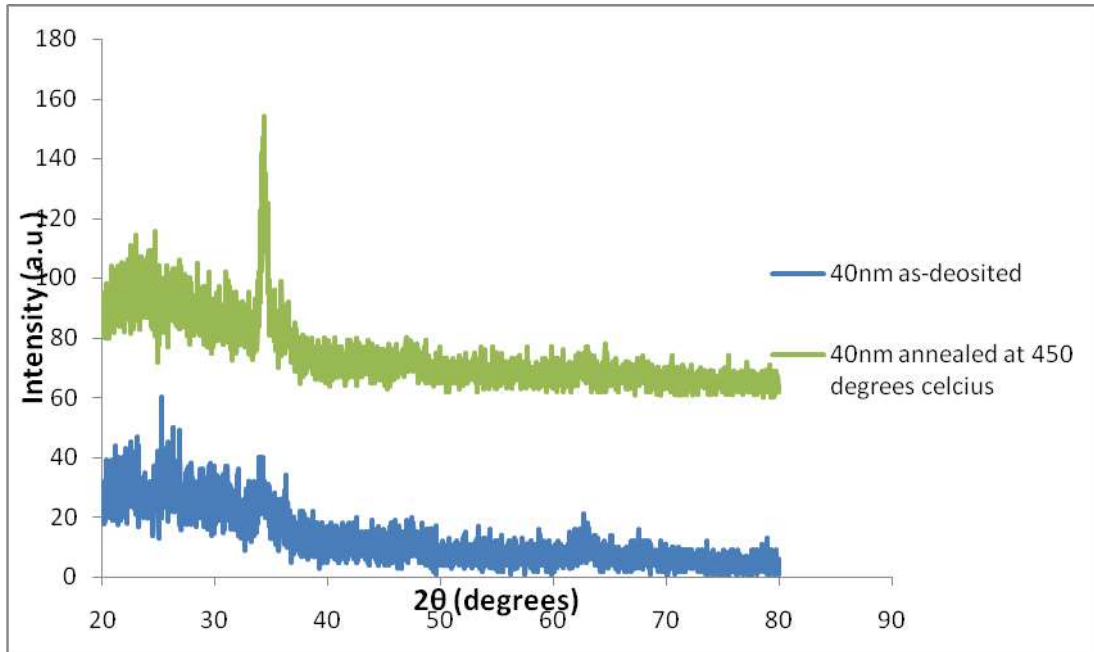


Figure 2.2: Variation of intensity with 2θ for 40nm

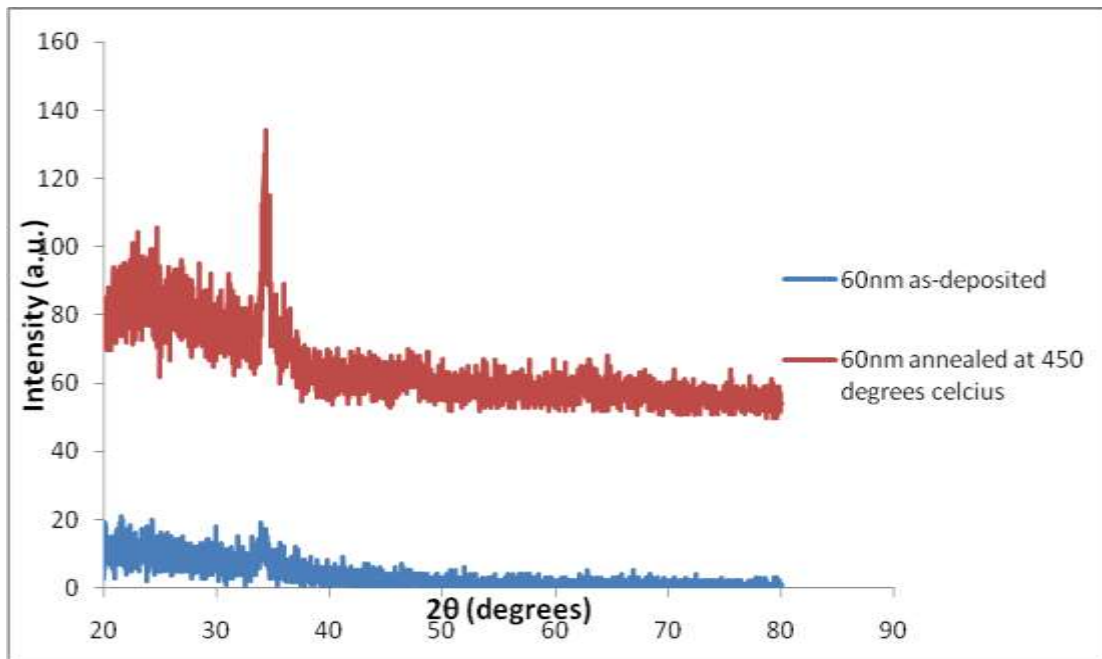


Figure 2.3: Variation of intensity with 2θ for 60nm

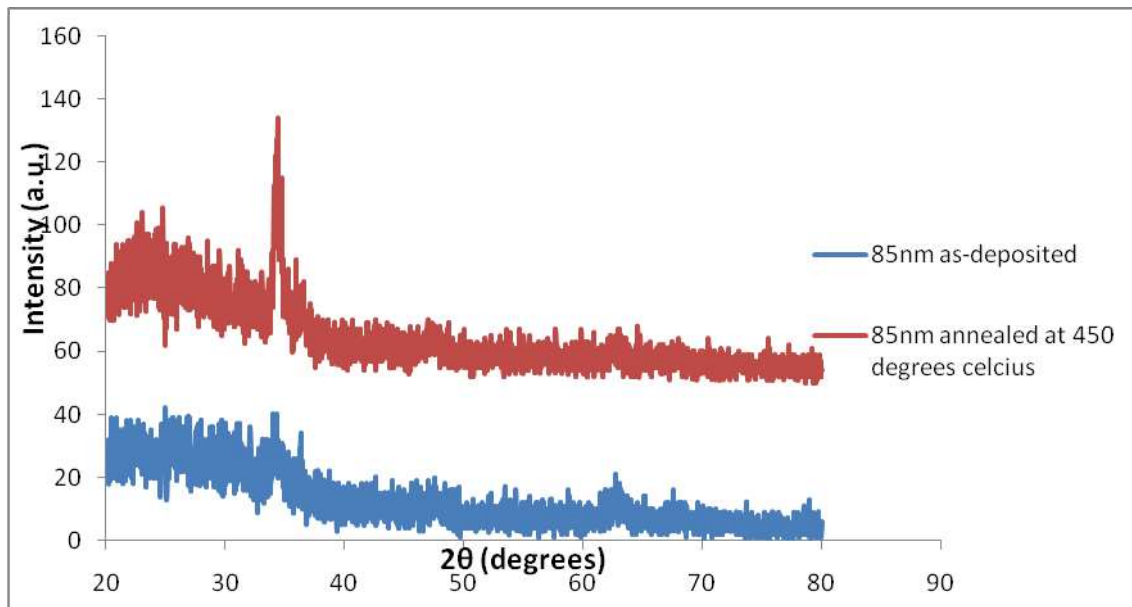


Figure 2.4: Variation of intensity with 2θ for 85nm

4. CONCLUSION

Indium tin oxide ITO have been grown on corning glass substrates by rf magnetron sputtering at substrate temperature of 100°C . X-ray diffraction [XRD], Scanning Electron Microscope [SEM], Spectrophotometer and four point probes were used to characterize the grown films. The XRD patterns of the grown ITO thin films reveal that the single preferred orientation along the [222] plane was obtained for all the annealed samples which indicate the mono crystalline nature of the films.

Therefore, the structural properties of the grown ITO films are suitable for optoelectronics and PV applications.

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