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Effect of growth period on optical properties of CBD grown nano-scale ZnO thin films for application in CIGS solar cell

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Abstract

In the present study, ZnO thin films were deposited for different deposition time periods using chemical bath deposition technique on a seeded substrate at a selected pH value and concentration based on the earlier findings. In order to optimize the deposited thin film to be used as buffer layer in thin film CIGS solar cell, optical characterization was done by using UV/VIS spectro-photometry and various parameters like transmittance, reflectance, refractive index, absorption coefficients, dielectric constant, optical conductivity etc. were calculated. The highest transmittance of 92.9% was recorded for the sample with deposition time 1 hour, which further decreased to 90.8% for deposition time of 1.5 hour and then fell down to 87% for a growth period of 2 hours. A blue shift as compared to the bulk was observed in the band gaps of all the three samples. Absorbance, reflectance, absorption coefficients, refractive indices and optical conductivities were found to increase with deposition time. The study laid a foundation stone for understanding the use of as deposited ZnO nano-crystalline thin films in thin film CIGS solar cell by correlating the growth period at a optimized pH and concentration with its various optical parameters.

Keywords: ZnO; Nano-crystalline; Blue shift; Optical parameters; CIGS solar cell

1. Introduction

The solar cell industry has gained momentum in the recent past due to the increasing demand for renewable energy and the elevated problem of global climate change. Cost is an unavoidable affair in the success of any technology. Present technology based on silicon is not only less efficient but also quite expensive for large scale electricity generation. The advancement of next-generation electronic, spintronic, and optoelectronic materials depends on their inherent properties, along with the fundamental science behind these properties and materials engineering principles. The properties of a material ultimately determine its effectiveness in specific applications. The relationship between structure and property has always been fundamentally important to materials science and engineering. In the class of semiconductor metal oxides, II-VI group semiconductors at the nanoscale are recognized for their unique and extensive applications in solar cells, field-effect transistors, optoelectronic devices, diluted magnetic semiconductors (DMS), photoluminescent devices, and more. Among these, ZnO materials are multi-functional and they have received broad attention due to their well-known performance in electronics, optics and photonics [1,2,3,4]. ZnO one of the group II–VI binary compound semiconductors, with a direct wide band gap of 3.37 eV at room temperature, having optical transparency in the visible range have been considered in solar cell applications due to its stability, high electron affinity and excellent electron mobility [5,6,7]. As the band gaps of semiconductors have significant impact on their optical and electrical properties, thus importance of ZnO is further enhanced as its band gap can be tuned to desired value by reducing its particle size to nano scale [8,9,10]. Due to its n-type semiconducting nature and excellent thermal stability (melting point-1975^{o}C), ZnO-based buffer layers are becoming an attractive alternative to traditional CdS layers in CIGS thin film solar cell, contributing to the development of more sustainable and efficient thin-film solar cell technologies. Copper Indium Gallium Selenide (CIGS) solar cells are known for their high efficiency and flexibility, making them

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promising candidates for thin-film photo-voltaics. In these cells, the buffer layer plays a critical role in facilitating efficient charge separation and transport between the CIGS absorber layer and the transparent conductive oxide (TCO) layer. It protects the CIGS layer during the deposition process of the TCO layer, preventing damage from high-energy sputtering processes. The use of ZnO as a buffer layer in CIGS solar cells offers a promising pathway to achieve high efficiency, environmental safety, and low-cost manufacturing. Thin polycrystalline films of ZnO can be prepared by different methods such as spray pyrolysis [11], sputtering[12], pulsed laser deposition[13], sol-gel[14], physical vapor deposition[15], chemical bath deposition (CBD)[16] etc. Among these various techniques, CBD is the simplest and most economical method. ZnO provides a smoother interface with the CIGS layer, which can minimize defects and reduce recombination losses, potentially enhancing cell efficiency. Moreover ZnO is non-toxic and more environment friendly as compared to traditional material Cadmium Sulfide (CdS), making it a more suitable "green" alternative. The aim of present study is to deposit nano scale thin films using CBD and study their optical properties with an objective to use the deposited thin films as an efficient buffer layer in thin film hetero-junction solar cell.

2. Materials and methods

The deposition was carried out using a two-step process: coating of ZnO seeds on the glass substrate [17] and further growth of thin films on the seeded substrates using AR grade chemicals procured from sigma Aldrich, without any further purification on the microscopic glass slides(2 x 2cm^2)procured from Blue Cross, India. Three chemical baths were prepared with aqueous solutions of "zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$)" and "Hexamethylenetetramine (HMTA) ($C_6H_{12}N_4$)" mixed together in equal volume. The concentrations of both precursors were fixed at100 mM in each bath and were adjusted to pH-5 using concentrated nitric acid as optimized in our earlier study [18]. To optimize the growth time, one pre-seeded glass substrate was immersed into each bath and afterwards the baths were kept in an oven at 90^0C for 60 min, 90 min and 120 min respectively. After the incubation period, the glass slides were rinsed with distilled water and then air dried. The obtained ZnO thin films were characterized for their optical properties through UV-visible spectroscopy. The growth parameters for the deposition of ZnO thin films for various growth periods is given in Table (1).

Table 1 Growth parameters for thin films of ZnO deposited for various growth periods

Sample code	$Zn(NO_3)$ Conc.	HMTA Conc.	pH	Deposition Time(min)	Deposition Temp(^{0}C)
Z_{241}	100mM	100mM	5.0	60	90
Z_{242}	100mM	100mM	5.0	90	90
Z_{243}	100mM	100mM	5.0	120	90

3. Results and discussion

Chemical bath deposition is a process [19,20,21] in which thin semiconductor films are deposited on substrates immersed in dilute solutions containing metal ions and a source of sulfide, hydroxide or selenide ions. The synthesis of CBD (Chemical Bath Deposition) ZnO thin films using zinc nitrate ($Zn(NO_3)_2$) and hexamethylenetetramine (HMTA, $(CH_2)_6N_4$)involves controlled nucleation and growth of ZnO (zinc oxide) nano-particles in the solution. The solution pH plays a critical role in this reaction by facilitating the formation of ZnO through the hydrolysis and decomposition of HMTA, which serves as a slow-release source of hydroxide ions (OH^-). HMTA acts as a complexing agent and a buffer. At pH ~5, HMTA slowly hydrolyzes [22,18] to form ammonia and formaldehyde. The produced ammonia can react with water to form ammonium and hydroxide ions. The hydroxide ions released from the decomposition of HMTA react with Zn^{2+} ions to form zinc hydroxide. Zinc hydroxide is not very stable and undergoes dehydration to form zinc oxide [23]. The ZnO nuclei start to form and grow into thin films or nanoparticles depending on the deposition time and temperature.

3.1. Thickness of thin films

Optimizing ZnO thin-film's thickness enhances light transmission while maintaining electrical properties. ZnO's anti-reflective nature reduces light losses[24]. Thickness of ZnO thin films deposited for different growth time were calculated using the equation:

$$t=\frac{m}{A\rho}$$

where t is the thickness of the film, m is the weight gain, A is the area of the deposited film, ρ is the density of the film which was taken as 5.606g/cm^3 [25]. The calculated values of thicknesses of samples Z_{241}, Z_{242} and Z_{243} were found to be 535nm, 668nm and 802nm respectively.

3.2. UV-visible Absorption Spectroscopy

UV-visible spectroscopy is the most useful optical technique for studying optical and electronic properties of nano-materials. The molecules undergo electronic excitation following the absorption of light of suitable wavelength. This method is generally based on the measurement of light absorbed by a sample. Since the energy required for electronic transitions lies in the UV and visible region of the electromagnetic spectrum, it is named as UV-Visible spectroscopy [26]. When a sample is stimulated by external electromagnetic radiations, these radiations can be reflected, scattered or some of them may be absorbed by the atoms to promote them into the excited state. In absorption spectroscopy the amount of light that is absorbed is measured as a function of wavelength. Molecules of a material are able to absorb particular frequencies in electromagnetic spectrum. In this process, after transferring energy to the molecule, a decrease in the intensity of the outgoing electromagnetic radiation is observed as compared to the intensity of the incident radiation. The radiation is thus attenuated because of absorption. UV/VIS spectrophotometric scans were measured in the wavelength range 250-800nm for all the samples deposited for different growth periods using UV Visible Spectrophotometer (UV-2550) with integrated sphere assembly ISR 240A with a resolution of 1 nm.

3.2.1. Transmittance

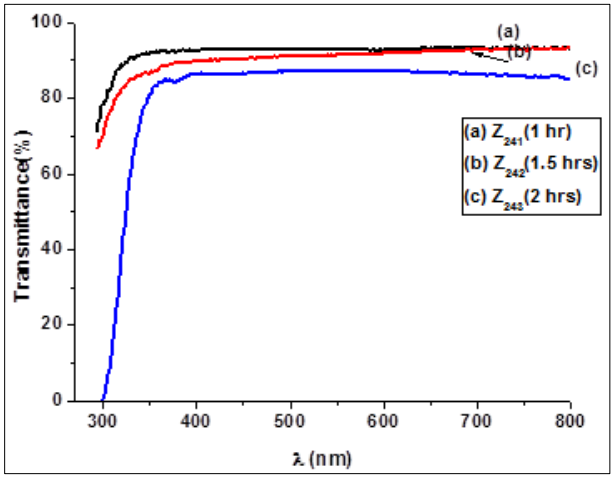

Figure 1 Transmittance of ZnO thin films for different growth period

Figure 1 shows the variation of transmittance with wave length in visible region. The highest transmittance was observed (92.9% at 500nm) for sample Z_{241}(deposition time 1 hour). Sample Z_{242} (deposition time 1.5 hour) showed a transmittance of 90.8% where as for sample Z_{243} it was observed to be 87%. This decrease in transmittance for sample Z_{243} and Z_{242} as compared to Z_{241} was attributed to the increase in thickness with deposition time. ZnO has a wide bandgap (~3.37 eV), providing excellent transparency to visible light, which ensures more light reaches the absorber layer, improving solar cell efficiency [24]

3.2.2. Absorption Coefficient

The UV-visible absorption characterization technique is based on the principle of Beer-Lambert's law which states that there is a logarithmic relation between the transmission (T) of light through a substance and the product of absorption coefficient of the substance (α) and the distance the light travels through the material i.e. path length (l). Using transmittance data in the Beer-Lambert's relation, absorption coefficient (α) at the corresponding wave-lengths were calculated. In the case of thin films the above relation is written as

$$\alpha = \frac{1}{t} \ln \left(\frac{1}{T}\right)$$

Where t = thickness and T = transmittance through the thin film. Figure 2 shows the variation of absorption coefficient with wavelength [27]. It is observed to be constant in visible region for all the three samples.

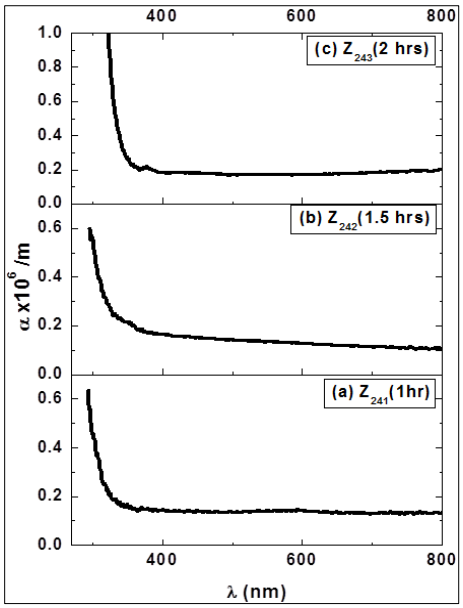

Figure 2 Absorption Coefficients for ZnO thin films with different growth periods

Absorption coefficients were found to be 0.137x10^6/m, 0.142x10^6 /m, and 0.170x10^6 /m for Z_{241}, Z_{242} and Z_{243} respectively.

3.2.3. Band Gap

The relation between the incident photon energy, band gap energy and the absorption coefficient in a direct transition is given by

$$\alpha h\nu = A(h\nu - Eg)^n$$

Where A is a constant, E_g is the optical energy gap. The value of n is $\frac{1}{2}, \frac{3}{2}$, for direct allowed and direct forbidden transitions respectively. Thus, a plot of $(\alpha h\nu)^2$ versus $h\nu$ allows one to determine the energy gap[28]

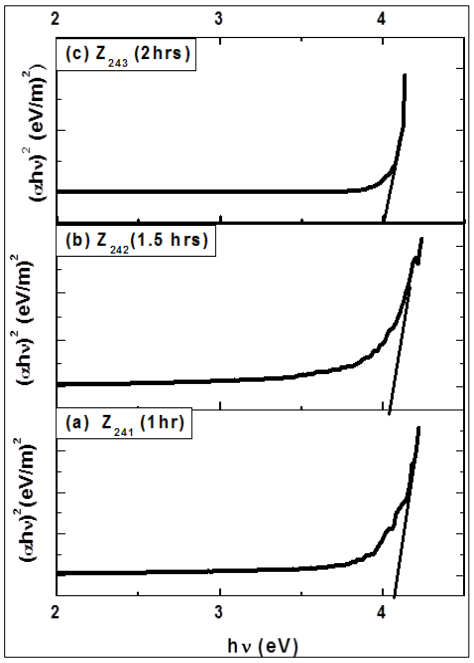

Figure 3 Band gap for ZnO thin films deposited for different growth time

The optical band gap was determined by extrapolating downward the corresponding straight line portions of the graphs between $(\alpha h\nu)^2$ and the photon energy hν, till the intersection with the energy axis [29]as shown in Figure 3. A blue shift as compared to the bulk ZnO (3.37 eV) was observed in the band gaps of all the three samples. Band gap of Z_{241} was found to be 4.10 eV, whereas Z_{242} and Z_{243} exhibited band gap values of 4.07eV and 4.0 eV.

3.2.4 Crystallite Size

As a blue shift as compared to the bulk (3.37 eV) was observed in the band gaps of all the three samples [Figure 3]. So their crystallite sizes were calculated using the effective mass approximation equation [30] for quantum confinement and were found to be 1.70 nm for Z_{241},1.73 for Z_{242} and 1.81 nm for Z_{243} respectively.

3.2.5 Reflectance

Reflectance values were observed to be 0.038, 0.049 and 0.071 for Z_{241}, Z_{242} and Z_{243} respectively as shown in Figure 4. Sample Z_{241} showed almost constant and minimum value of reflectance in the visible region. Z_{241} may also be used as antireflection coating on the window layer of thin film solar cell.

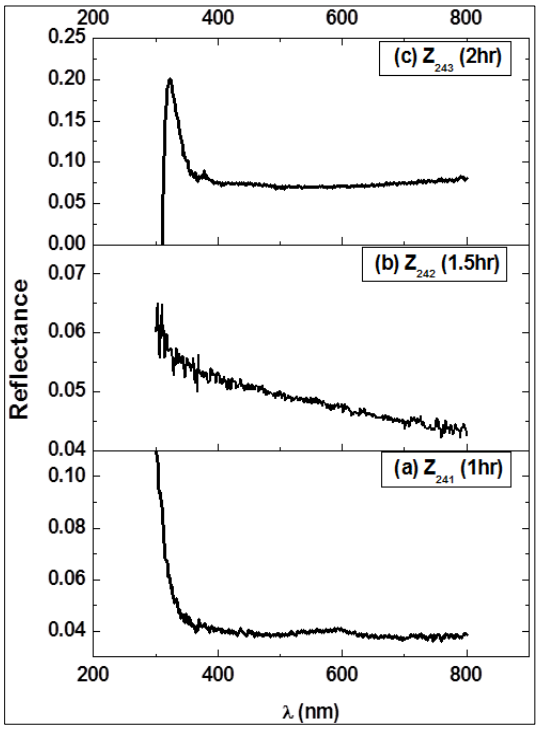

Figure 4 Reflectance of ZnO Thin Films for different growth time

3.2.6. Refractive Index

Refractive indices of all the samples were calculated using the equation [31]

$$\mathbf{n} = \frac{(1+R^{1/2})}{(1-R^{1/2})}$$

It was observed that in the visible range the values of **n** are nearly constant in the samples Z_{241} and Z_{243} (Figure 5). Refractive indices were observed to be 1.48, 1.57 and 1.71 for Z_{241}, Z_{242} and Z_{243} respectively at 500nm. The refractive index of sample $Z_{241}$was found to be significantly lower than that of bulk ZnO (2.036 at 600nm) [32,33]

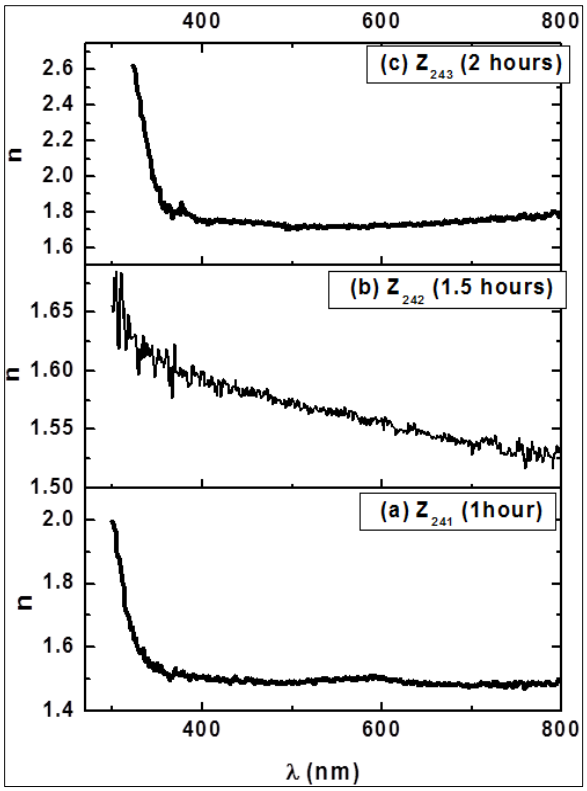

Figure 5 Refractive Indices of ZnO thin films for different growth periods

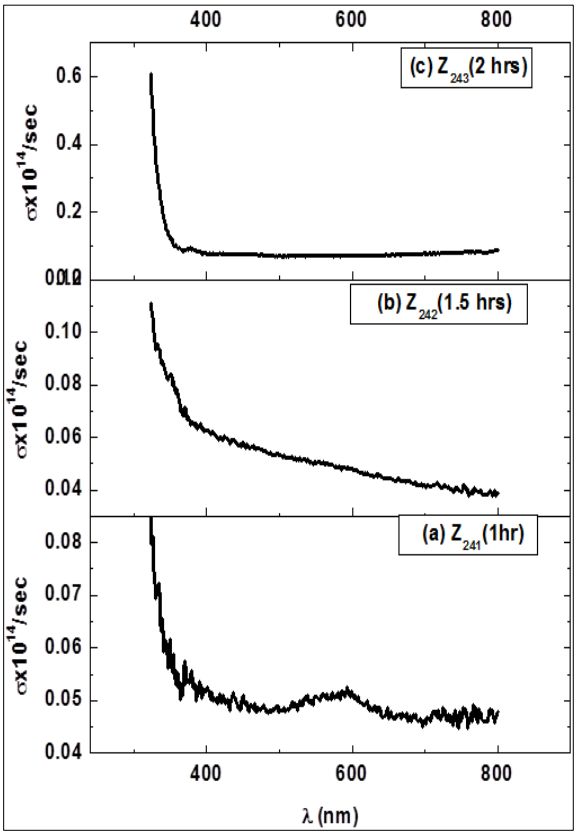

Figure 6 Optical conductivities of ZnO thin films as a function of growth periods

3.2.7. Optical Conductivity

Refractive index and absorption coefficient, which are calculated using UV-Vis data, can also be used to calculate optical conductivity of a material using the following relation [34].

$$\sigma = \frac{nc\alpha}{4\pi}$$

Optical conductivities for samples Z_{241}, Z_{242} and Z_{243} at 500nm were observed to be $0.048x10^{14}$/sec, $0.053x10^{14}$/sec and $0.68x10^{14}$/sec (Figure 6) respectively.

4. Conclusion

It was observed that in acidic bath (pH=5) the solution remained transparent during deposition indicating a slow chemical deposition process. As a result thin films deposited at this pH with a growth period of 1 hour exhibited very high transmittance and low refractive index. Due to slow and controlled precipitation, short range grain size was found to be quite small owing to a blue shift in the band-edge. So it is concluded that as such deposited nano-crystalline ZnO thin film deposited for a growth period of 1 hour from a chemical bath with 100mM of aqueous solutions of "zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$)" and "Hexamethylenetetramine (HMTA) ($C_6H_{12}N_4$)" mixed together in equal ratio (1:1) and with pH adjusted at 5 is suitable for application in CIGS thin film solar cells as a buffer layer.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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