

Effect of concentration on the optical and solid state properties of ZnO thin films deposited by aqueous chemical growth (ACG)

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Abstract: Thin films of Zinc Oxide (ZnO) having different concentrations were deposited using the Aqueous Chemical Growth (ACG) method. The films were characterized using Rutherford Back Scattering (RBS) spectroscopy for chemical composition and thickness, X-Ray Diffraction (XRD) for crystallographic structure, a UV-VIS spectrophotometer for the analysis of the optical and solid state properties which include spectral absorbance, transmittance, reflectance, refractive index, direct band gap, real and imaginary dielectric constants, absorption and extinction coefficients and a photomicroscope for photomicrographs. The average deposited film thickness was 100nm. The results indicate that the values of all the optical and solid state properties investigated vary directly with concentration except transmittance which is the reverse. Thus, the optical and solid state properties of ZnO thin film deposited by the Aqueous Chemical Growth method can be tuned by deliberately controlling the concentration of the precursors for various optoelectronic applications including its application as absorber layer in solar cells.

1. Introduction

Zinc Oxide is an amphoteric oxide which exists in the form of white powder (zinc white) at room temperature^[1]. Though zinc oxide exists naturally in the earth crust (zincite), it is the synthetic ZnO produced in laboratories that are usually used in industries^[2]. Crystalline zinc oxide is thermochromic^[3]. Apart from the ability of ZnO to react with acids, it also react with bases to produce soluble zincates^[4-6]. Zinc oxide has high stability at room temperature and decomposes into zinc vapour and oxygen at about 1975⁰c^[7]. Though zinc oxide can exist in either of

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hexagonal wurtzite, cubic zinc blende and cubic (rock salt) structure, the hexagonal wurtzite structure is the most common at room temperature. The different polymorphs of ZnO do not possess the property of symmetry inversion. This and other properties such as ionic bonding account for the strong piezoelectricity of both hexagonal and zinc blende ZnO^{[8],[9]}.

The hexagonal wurtzite structure has the point group 6mm (Hermann – Mauguin notation) or C_{6v} (schoenflies notation) and a space group of P6₃mc or C_{6v}⁴. Its lattice constants are a = 3.25 Å⁰ and c = 5.2 Å⁰ [10].

The many applications to which ZnO can be put have made it to be a material for constant scientific study. The diverse applications of ZnO are derived from its unique properties which include non-toxicity, good electrical conductivity, high luminous transmittance, good substrate adherence, good optical behaviour and stability in plasma atmosphere^{[11],[12]}

ZnO has been tested and found to behave as a semiconductor having a wide bulk direct band gap of about 3.37eV at room temperature^[13] ZnO has been used for the fabrication of light emitting diodes, varistors, photo detectors, piezoelectric cantilever, gas sensors, buffer layer in solar cells and in photonic crystals^[14-21].

As a result of the strategic importance of ZnO to humanity, various deposition methods have been used for its production in the form of thin films. Among these methods are the chemical bath deposition (CBD)^[22-26], Successive Ionic Layer Adsorption and Reaction (SILAR) method^[27, 28], Spray pyrolysis method^[29], Electro deposition method^[30, 31]. The ACG method is a novel method for the deposition of ZnO thin films; hence the literature on it is sparse.

Indeed Ezema^[26] reported that “Thin films of ZnO have been used but its preparation techniques have been restricted to sputtering, vacuum evaporation, chemical vapour deposition, spray pyrolysis, molecular beam epitaxy, sol gel and pulse laser”.

Among the advantages which the ACG method have over the other methods are simplicity, low cost, reproducibility, availability of materials, environmental friendliness (non toxicity of residue), non requirement of surfactant, templates and complexing agents, low temperature requirements, ability to produce nanostructures, high purity (absence of surfactants), suitability for large scale production etc.^[32, 33].

This paper reports the effect of concentration of precursors on the optical properties of ZnO thin films deposited using the ACG method with Zn(NO₃)₂ · 6H₂O as precursor material. The spectral analysis of the optical and solid state properties was carried out using a Unico UV-2102 PC spectrophotometer.

2 Experimental Details

ZnO thin films were deposited on clean glass slides using Aqueous Chemical Growth method.

Equimolar concentrations of hydrated zinc nitrate (Zn(NO₃)₂ · 6H₂O) and hexamine in 80ml of water were used as precursors

Hexamine was used to make the zinc nitrate alkaline. Three samples having different concentrations of the precursors were prepared as shown in table 1 below:

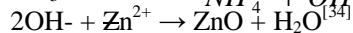
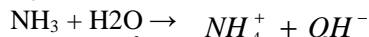
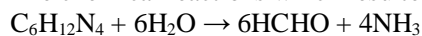
| Sample of mass | Zn (NO ₃) ₂ ·6H ₂ O | Mass of Hexane | Conc. of Zn(NO ₃) ₂ ·6H ₂ O | Conc. Of Hexane | Volume of H ₂ O |
|----------------|---|----------------|---|-----------------|----------------------------|
| C ₃ | 0.60g | 0.030g | 0.025M | 0.025M | 80.00ml |
| C ₄ | 1.20g | 0.060g | 0.050M | 0.050M | 80.00ml |
| C ₂ | 2.40g | 0.112g | 0.100M | 0.100M | 80.00ml |

Masses of samples were measured using an analytical microbalance. The masses of the components of each sample were put into a 100ml pyrex bottle together with 80ml of water. The content was properly mixed using a magnetic stirrer

The pyrex bottles were then tightly corked and carefully placed in an oven at a temperature of 90.00°C.

The average deposition time for the films was twelve hours

The chemical reactions which resulted in the crystallization of ZnO are



3 Results and discussion

The elemental composition of sample C₂ was analyzed using Rutherford Backscattering (RBS) is as shown in figure 1. Judging from the film composition shown in the table 2 below, we conclude that the elements contained in sample C₂ are Zn (0.050) and oxygen (0.950) while the glass substrate has the composition O(0.500), Si(0.120), Ca (0.100), Al (0.100) and Na (0.180). This is summarised in table 2. The thickness of the film is given as 100nm.

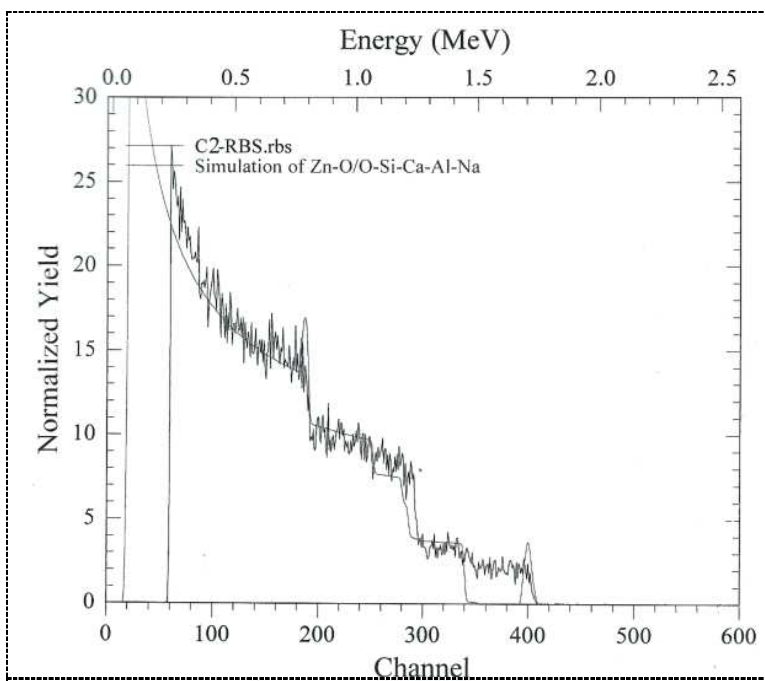


Figure 1. RBS analysis for ACG ZnO Thin Film (sample C₂).

| Table 1; Elemental composition of ZnO thin film and substrate from RBS analysis | | | | | | |
|---|--------|-------|---------|---------|-----------|--------|
| | Oxygen | Zinc | Silicon | Calcium | Aluminium | Sodium |
| ZnO thin film | 0.950 | 0.050 | - | - | - | - |
| Glass substrate | 0.500 | - | 0.120 | 0.100 | 0.100 | 0.180 |

The X-Ray diffractogram of the ACG ZnO thin films were studied to determine its crystalline nature.

The thin films were scanned continuously between 0 and 70 at step size of 0.03 and at time per step of 0.15s. The figure 2 above shows the intensity of peaks versus diffraction angle 2θ for sample C_2 ZnO thin film using CuK_{α} radiation source having a wavelength of 1.54056 \AA .

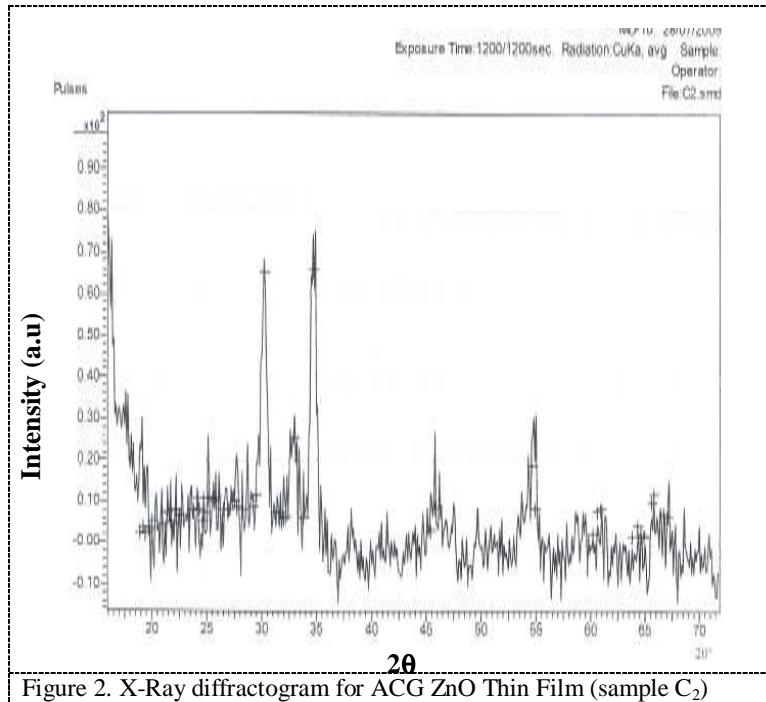


Figure 2. X-Ray diffractogram for ACG ZnO Thin Film (sample C_2)

The X-ray diffractogram reveal several peaks corresponding to directions of strong reflections. Some of the observed peaks are 31.77° , 34.84° , and 54.86° having d values of 30.14, 34.42, and 54.86 respectively.

The 34.84° agree with the preferred orientation along the (002) plane reported by Ajuba et al^[35] and Shinde et al^[36] who used the CBD and SILAR methods respectively.

The diffractogram reveal sharp diffraction peaks which is indicative of good crystallinity^[37-41].

The XRD pattern shows that film is crystallized in the wurtzite ZnO hexagonal structure (JCPDF CARD no. 36-1451)^[42].

The mean size of the crystallite was estimated to be 12nm using the Sherrer formula which is given as:-

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where $k= 0.9$

$$\lambda = 1.541 \text{ \AA}$$

θ is the diffraction peak angle (34.42°) and β is the Full Width at Half Maximum (FWHM) corresponding to the diffraction peak.

The spectral absorbance of the films is shown in fig. 3. Absorbance increases with concentration. The 0.1M concentration has a fairly constant absorbance value of about 0.34 and 0.35 at the visible and infrared regions respectively.

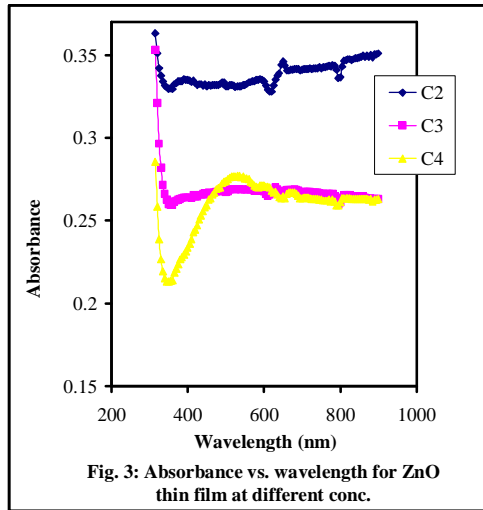


Fig. 3: Absorbance vs. wavelength for ZnO thin film at different conc.

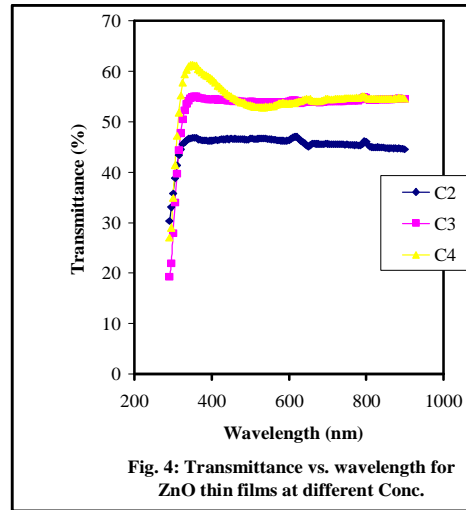


Fig. 4: Transmittance vs. wavelength for ZnO thin films at different Conc.

The 0.05M concentration has an average absorbance value of 0.28 in the visible region while the 0.025M concentration has an average absorbance value of 0.268 in the visible region.

However, the 0.05M concentration has the lowest absorbance value of 0.21 in the infrared region.

Absorption peaks clearly occurred in film C₂ at 368nm, 496nm and 656nm but were not so clearly defined in films C₃ and C₄. Ezema^[26] reported absorption peaks at 3.68nm, 449nm and 566nm using Chemical Bath Method. The difference in the absorption peaks may be due to deposition method. The spectral transmittance of the films is as shown in fig.4. Transmittance decreases with concentration in the visible region. The 0.1M, 0.05M and 0.025M concentrations has average transmittance of 45.5%, 53.2% and 54.60% respectively in the visible region.

However, the 0.05M concentration has the highest transmittance of about 61.8% in the ultraviolet region. The transmittance of the films in the visible region is generally lower than the above 85% transmittance reported using Chemical Bath Deposition method^[43].

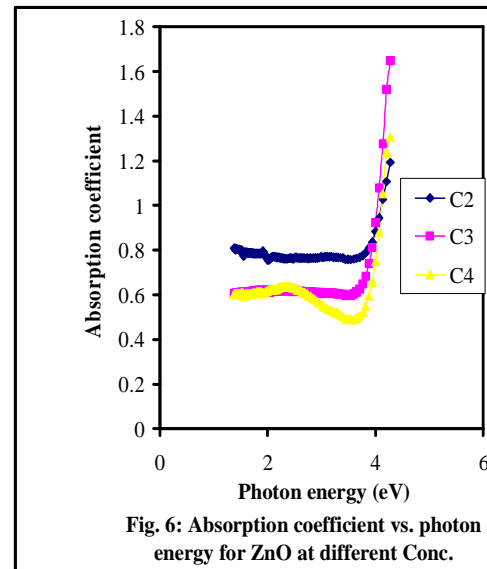
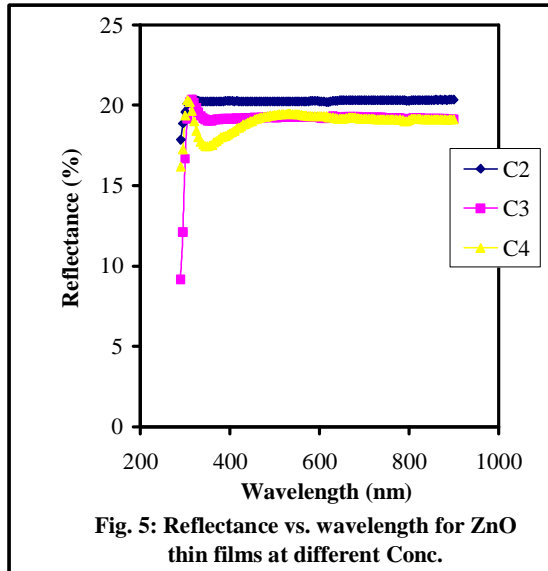
It is also much lower than the 90-95% transmittance in the UV-VIS-NIR regions for ZnO thin films deposited using spray pyrolysis method^[44, 45] and Sol. Gel method^[46].

It has been reported that the transmittance of a film increases as its thickness decreases^[26]. The average thickness of the films being reported on is 100nm which is far smaller than the 0.203 μ m and 0.069 μ m thicknesses which gave average transmittances of 62% and 75% respectively that has been reported.^[26] Thus, the transmittance of films deposited by ACG method are relatively lower compared to the ones deposited by other methods even though the thicknesses are smaller.

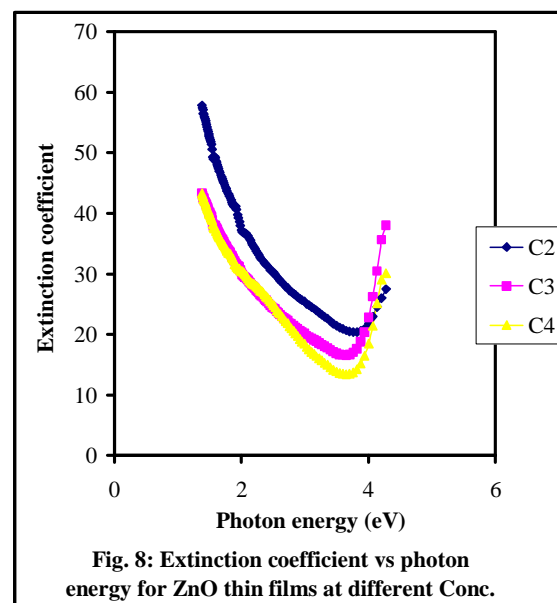
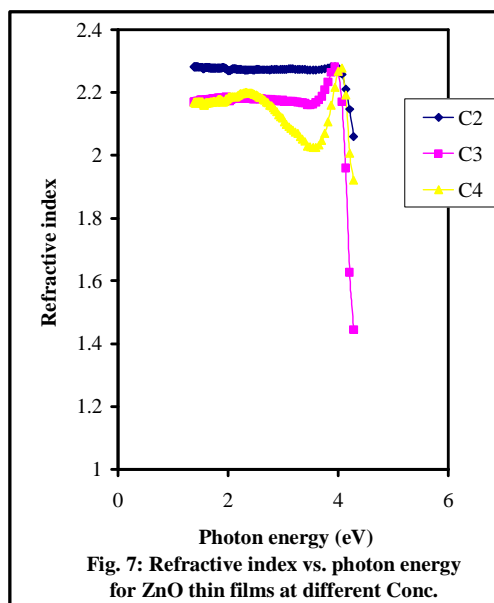
The spectral reflectance of the films being reported on is as shown in fig. 5. Reflectance increases with concentration in the visible region.

The 0.1M, 0.050M and 0.025 concentrations reflect an average of 20.25%, 19.38% and 18.88% of visible electromagnetic waves. These values are higher than the average of 12 to 17% reflectance of films deposited using Chemical Bath Method as reported by Ezema^[26].

Thus, films deposited by ACG method are better reflectors than those deposited by Chemical Bath Method. Absorption coefficient increases with concentration in the visible region as shown in figure 6. The average absorption coefficients for the 0.025M, 0.05M and 0.1M concentrations are 0.62, 0.65 and 0.77 respectively. However, in the UV region, 0.05M has the lowest absorption coefficient of about 0.49.



Refractive index is fairly constant in the visible region as shown in figure 7. The 0.1M, 0.05M and 0.025M concentrations have average refractive indices of 2.3, 2.225 and 2.2 respectively. However, the 0.05M concentration has the lowest refractive index of about 2.05 in the UV region. It has been reported that the refractive index of ZnO films doped with Li deposited by spray pyrolysis lie between 1.60 and 2.20 at a wavelength of 500nm^[45], while Ezema^[26] gave the average refractive index of the ZnO films deposited by Chemical Bath method as being between 1.64 and 1.98 and also reported observed peak values of 2.28 at 368nm and 1.72 at 569nm. In our own case, the refractive indices for the different concentrations were generally uniform in the visible region. Extinction coefficient decreases with concentration and also decreases with increasing photon energy (wavelength) in the visible region as shown in figure 8.



The value of extinction coefficient for 0.1M concentration ranges from 37.85×10^{-3} for 2eV to 27.14×10^{-3} for 3eV in the visible region. Similarly, the values of extinction coefficient for 0.05M concentration ranges from 35×10^{-3} for 2eV to 19.64×10^{-3} for 3eV and that of the 0.025M concentration ranges from 30×10^{-3} to about 21.43×10^{-3} at 3eV in the visible region

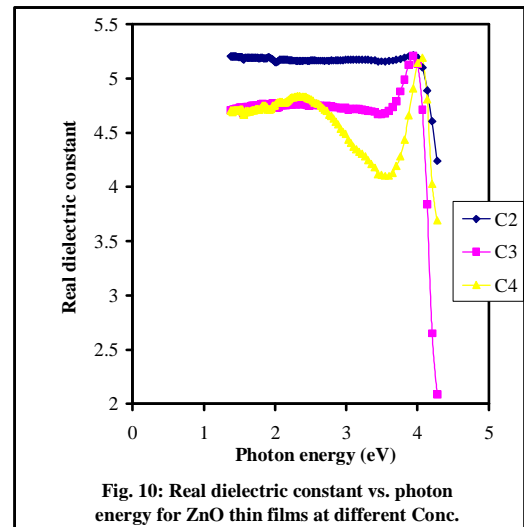
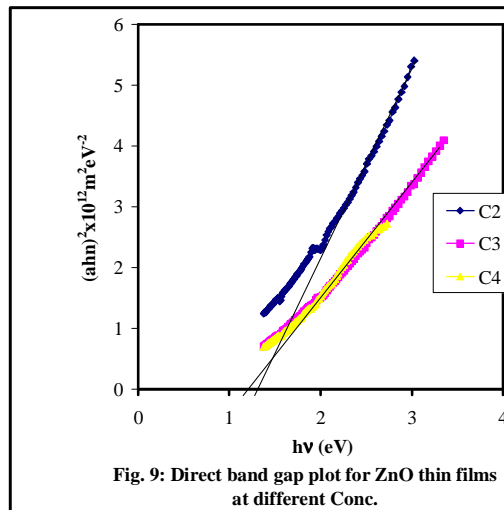
However, the 0.05M concentration has the lowest extinction coefficient of about 13.93×10^{-3} in the ultraviolet region. In general all the concentrations have the lowest value of extinction coefficient in the higher energy region (between 3eV and 4eV) and the maximum value in the low energy region (between 1eV and 2eV). Low and high values of extinction coefficient at high and low energy regions respectively have been reported^[26].

The band gap increases with concentration as shown in figure 9. The average band gap for the 0.025M, 0.05M and 0.1M concentrations are 1.16eV, 1.22eV and 1.4eV respectively.

These values are lower than the direct band gaps of ZnO films deposited by Chemical Bath method^[26] which lie between 1.60eV and 1.80eV.

Our values are also far lower than 3.29eV band gap obtained for aluminium doped ZnO deposited using radio frequency (r.f) magnetron sputtering^[18], and intrinsic band gap of 3.20eV for ZnO films deposited by spray pyrolysis^[29]. The low values of the direct band gap obtained indicate that the ZnO thin film materials prepared by ACG method are suitable for use as absorber layers in solar cells. The low values of the band gaps obtained in this work may be due to preparation conditions Ezema et al^[26].

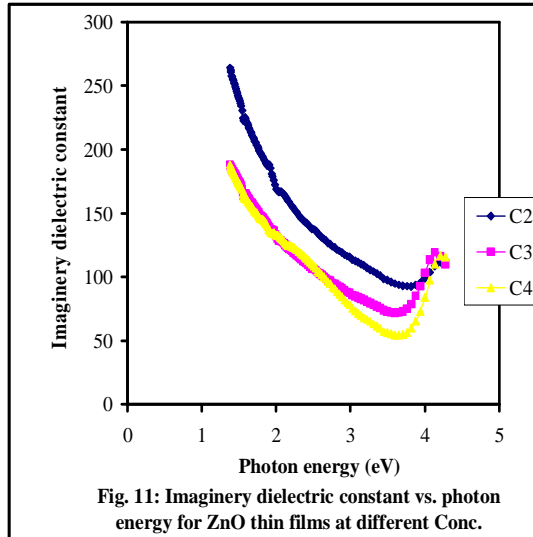
Real dielectric constant increases with concentration in the visible region as shown in figure 10. The 0.025M, 0.05M and 0.1M concentrations have average real dielectric constants of 4.76, 4.85 and 5.15 respectively in the visible region of the electromagnetic spectrum.



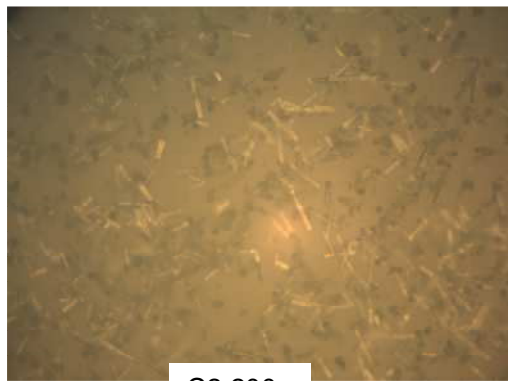
However, the 0.05M concentration has the lowest real dielectric constant of about 4.09 in the ultraviolet region. Figure 11 is the Imaginary dielectric constant that increases with concentration in the visible range.

The 0.1M, 0.05M and 0.025M concentrations have average values of imaginary dielectric constant which ranges from 180.3×10^{-3} for 2eV to 118.18×10^{-3} for 3eV, 143.93×10^{-3} for 2eV to 78.785×10^{-3} for 3eV and 143.93×10^{-3} for 2eV to 89.39×10^{-3} for 3eV respectively. This shows that the imaginary dielectric constant decreases with increasing photon energy (decreasing wavelength) for all concentrations in the visible region.

However, the 0.05M concentration has the lowest imaginary dielectric constant of about 56.06 in the ultra violet region. All concentrations have their lowest imaginary dielectric constant values in the ultra-violet region.



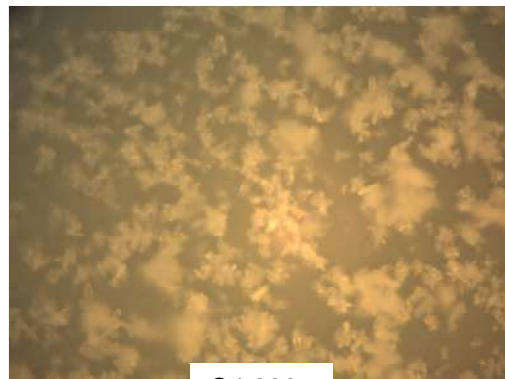
The photomicrographs as shown in figure 12 indicate uniform deposition of the ZnO thin films on the glass substrate. While C2 and C3 show stretches of rod C4 shows clusters of thin films on the substrates .



C2 200x



C3 200x



C4 200x

Fig. 12: Photomicrographs of ACG ZnO thin films

4. Conclusion

Crystals of ZnO have been successfully grown on glass slides in the form of thin films from the aqueous solution of hexahydrated zinc nitrate and hexamine after the fashion of Lionel Vassieres^[47]. The concentration of the precursors was found to vary directly with absorbance, reflectance, absorption coefficient, extinction coefficient, refractive index, direct band gap, real dielectric constant and imaginary dielectric constant. The transmittance of the thin films was found to vary inversely with the concentration of the precursors. The results indicate the suitability of ZnO thin films prepared by the Aqueous Chemical Growth method for various optoelectronic applications such as absorber layer in solar cells.

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