# INFLUENCE OF pH ON THE STRUCTURAL, OPTICAL AND SOLID STATE PROPERTIES OF CHEMICAL BATH DEPOSITED ZnO THIN FILMS

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Zinc Oxide thin films were deposited successfully on a glass substrate using the chemical bath deposition (CBD) technique at room temperature. $Zn(NO_3)_2$ was used as source of zinc ion, while ammonium solution served as the complexing agent. Optical properties were studied extensively in the wavelength range of 200-1100nm. From the transmission spectra determined, using Unico UV-2102 PC spectrophotometer, the direct band gap energy was discovered to be in the range of 2.8 – 4.0 eV. The results show that pH has significant effect on both the optical properties and band gap energy of the films. XRD analysis showed good crystallinity of the ZnO films deposited with increase in pH.

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*Keywords:* Band gap, pH, Optical properties, Thin films.

## 1. Introduction

ZnO film is one of the metal oxide semiconductors, which have been found to be very useful as an UV detector [1]. As an important II – VI group semiconductor with versatile properties, ZnO possesses wide applications in various fields such as transducers, gas sensors, and transparent conduction electrode [2]. ZnO has relatively large direct band gap of 3.30eV at room temperature, therefore its most common potential applications are in laser diodes and light emitting diodes [3]. Many methods can be used to prepare ZnO films such as chemical bath deposition [4], spray pyrolysis [5], cathodic arc deposition [6], sputtering [7], and pulsed laser deposition [8]. Literature survey confirmed that CBD which has been well known as prevalent low temperature aqueous method for directly depositing large area thin films of semiconductors has advantages over the above mentioned techniques because it allows films to be deposited on non-planar substrates that might not be chemically or mechanically stable at high temperature. Moreover, it requires no sophisticated instrument such as vacuum systems e.t.c and the starting chemicals are usually available and cheep. The mechanisms involved in the formation of CBD films include absorption and coagulation of colloids by homogeneous reaction and ion–by–ion condensation at the surface of the substrate by heterogeneous reaction [4].

In this work, we report on the effect of pH on the structural, optical and solid state properties of ZnO thin films synthesized by chemical bath deposition method.

## 2. Experimental details

ZnO thin films were deposited on a clean glass slides by chemical bath deposition. 0.5M of zinc nitrate was prepared by dissolving 14.85g of solid zinc nitrate in 100ml of distilled water. 10ml of 0.5M of zinc nitrate was taken into a 50ml beaker to which few milliliters of analytical grade ammonia solution was added while stirring carefully and continuously to achieve the desired pH value. Three experimental set-up were made at different pH and labeled $M_1$(pH = 8.8), $M_2$(pH = 9.5) and $M_3$ (pH = 10.0). In each case, the solution was made up to 50ml by addition of distilled water. Clean glass slides were then immersed in each of the reaction baths and the baths kept in the oven at a temperature of 75$^o$C. After five hours, the substrates were removed and rinsed with distilled water and allowed to drip dry in air. The deposited ZnO thin films were annealed in the oven at 350$^o$C for an hour.

The structural characterization of annealed ZnO films was carried out by X- ray diffraction. The band gaps of the films were determined by using the transmittance measurement from Unico–UV–2102 PC spectrophotometer at normal incident of light in the wavelength range of 200 – 1100nm.The composition of the films were determined by Rutherford backscattering (RBS).

## 3. Results and discussion

### 3.1 X-ray diffraction study

Typical x-ray diffractogram of CBD ZnO thin films are presented in figure 1. The samples were grounded to below 100 mesh in an agate mortar and loaded into a 2.5cm diameter circular cavity holder and ran on an MD 10 mini diffractometer. $CuK_\alpha$ was selected by a diffracted beam monochromator. The thin films were scanned continuously between 0 and 75 at a step size of 0.03 at a time per step of 0.15. Phase identification was then made from an analysis of peak intensity versus 2θ

The XRD pattern displayed in figure 1b and 1c show several peaks. Prominent among them are the peaks at 2θ values of around 31.77$^o$, 34.42$^o$, 62.86$^o$ and 67.96$^o$, corresponding to the diffraction lines produced by (100), (002), (103), and (112) planes respectively. A close examination of figure 1 shows that the intensity of the peaks increased with increase in pH. This means that better crystallization of ZnO film takes place at higher pH. All diffraction peaks are indexed as hexagonal wurtzite structure ZnO. Figure 1a shows that the film deposited at a lower pH is amorphous.

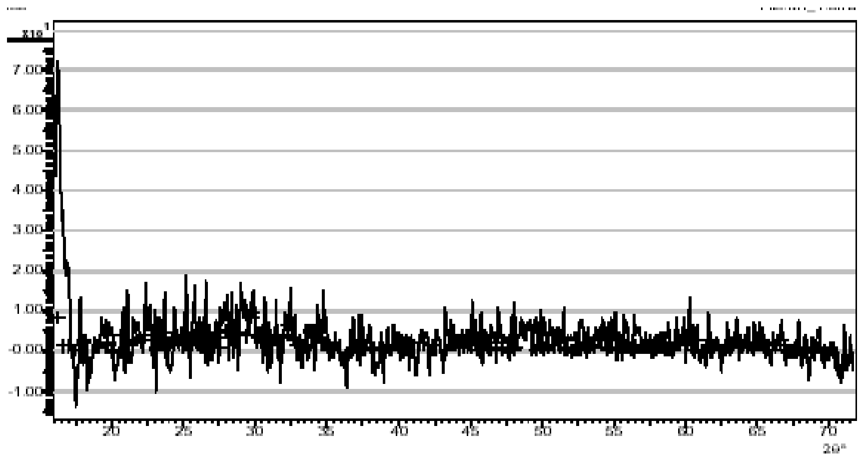


*Fig.1a: XRD of film deposited at pH 9.5*

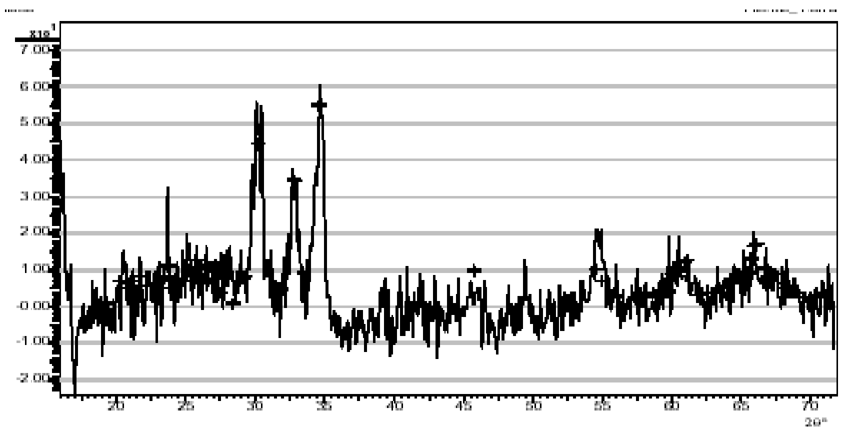


*Fig.1b: XRD of film deposited at pH 9.8*

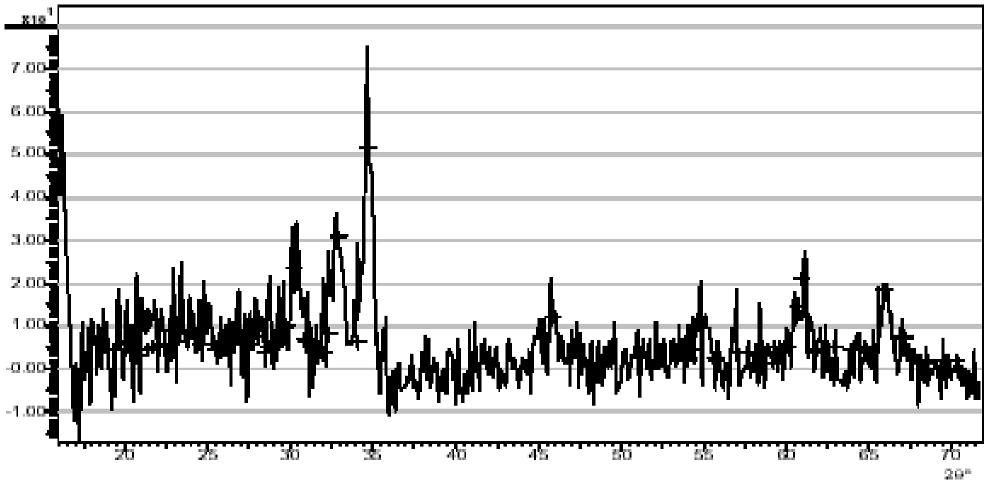


*Fig. 1c: XRD of film deposited at pH 10.0*

The grain size (D) of the films under study was determined by measuring the full width at half maximum (β) using the Scherrer formula

$$D = k\lambda / \beta\cos\theta,$$

where k is a constant taken to be 0.94, λ the wavelength of X-ray used (λ = 1.54Å) and θ is the Bragg's angle. Using Scherrer's formula, the grain size for samples $M_2$ and $M_3$ were found to be of the order of 32.20nm 30.82nm respectively.

### 3.2 Compositional Analysis

The elemental composition and chemical states of sample $M_1$ was analysed using Rutherford Backscattering (RBS) at Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria. The RBS analysis was carried out using 2.20 MeV, $4H_e^+$ ions and 5.00μc at 16.80nA. The results are shown in Figure 2. From the film composition presented in table 1, we can deduce that the thin film of zinc oxide deposited has no impurity content. The RBS analysis also shows that the film has a thickness of 350nm, and was deposited on 15000nm thick glass substrate.

*Table 1: The composition of substrate and ZnO film from RBS analysis*

| | Oxygen | Zinc | Silicon | Calcium | Aluminium | Sodium |
|---|---|---|---|---|---|---|
| ZnO thin film | 0.280 | 0.720 | - | - | - | - |
| Glass substrate | 0.500 | - | 0.120 | 0.05 | 0.100 | 0.180 |

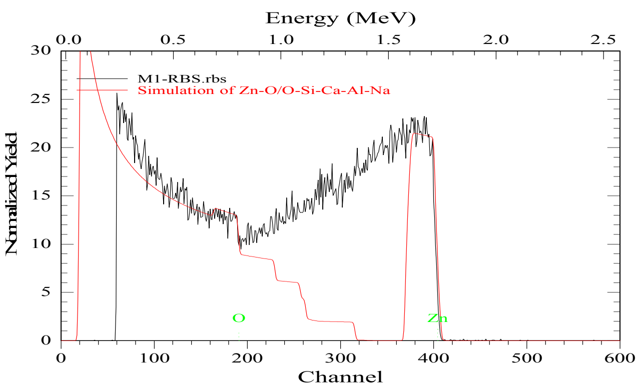


*Fig.2: RBS of ZnO thin film*

**4.3 Optical sStudies**

The transmittance for the films deposited at different values of pH was recorded in the wavelength range of 200-1100 nm and is shown in figure 3.

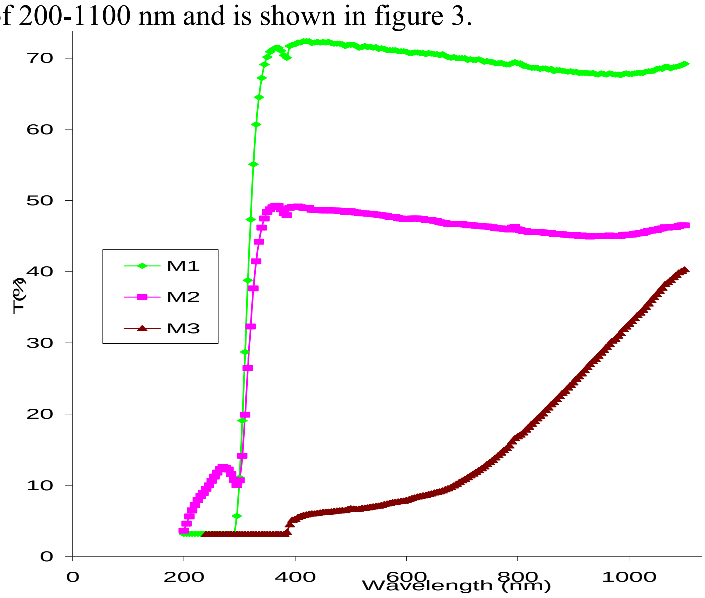


*Fig.3: Transmittance vs. wavelength for ZnO thin films deposited at different pH*

The transmittance spectra displaced in figure 3 shows that the transmittance of the film decreases with pH of the deposition bath. The film deposited at a pH of 8.8 has the highest transmittance of about 70% at a wavelength of between 400nm and 1100nm. Therefore, maximum transmittance is achieved at a low pH value. The high transmittance of the films up to the infrared region of the solar spectrum suggests that the films could be employed as a host material for optoelectronic applications [9].

Figure 4 shows the plot of the refractive index as a function of photon energy. The average value of the refractive index is in the range of 1.83 –2.28 for samples $M_1$ and $M_2$ deposited at a lower pH. The behaviour of sample $M_3$, which has the highest pH of 10.0, is quite different. Its index of refraction decreases with photon energy to a value as low as 0.09 at a photon energy of 3.44eV. This corresponds to the near-infrared region (NIR) of the solar spectrum.

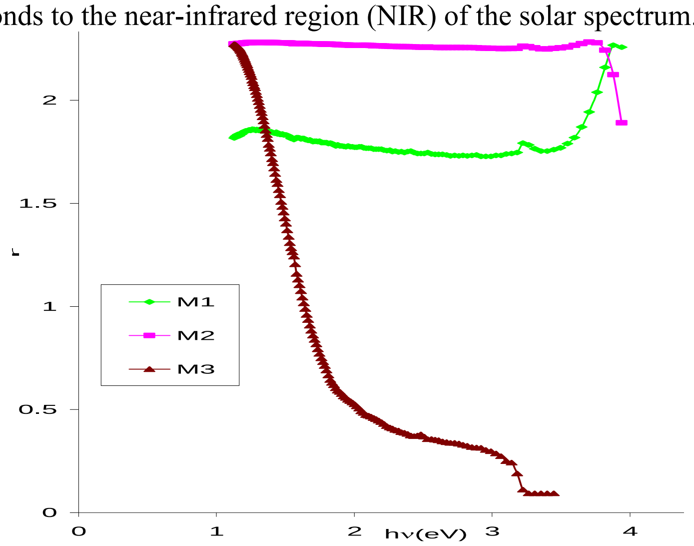


*Fig.4: Refractive index vs. photon energy for ZnO thin films*

*deposited at different pH*

Figure 5 shows the plot $(\alpha h\nu)^2$ vs. hν of ZnO thin films prepared at different pH value, which is calculated from transmittance and film thickness. The transmittance for both samples $M_1$ and $M_2$ is within 50 – 70% in the VIS region. According to transmittance spectrum, the absorption coefficient, α of the film was estimated by the expression,

$$T = e^{-\alpha d}$$

where T is the transmittance and d is the thickness of the films. The relation between the absorption coefficient and incident energy hν is expressed is by Tauc's relation as [13]:
$\alpha = A(h\nu - E_g)^n / h\nu$,
where A is a constant, hν is the photon energy and α is the absorption coefficient, while n depends on the nature of the transition. For direct transitions n = ½ or ⅔, while for indirect ones n = 2 or 3, depending on whether they are allowed or forbidden, respectively. The best fit of the experimental curve to a band gap semiconductor absorption function was obtained for n = ½.

The values obtain for ZnO thin film lie in the range of 2.8 – 4.0eV. These observed band gap are within the range of the values reported in literature [10,14]. A close observation of figure 5 shows that the energy gap decreased with increasing pH value. The properties of high band gap values exhibited by these films together with high transmittance in the visible region suggest that that these films could be employed as window layer in solar cell architecture.

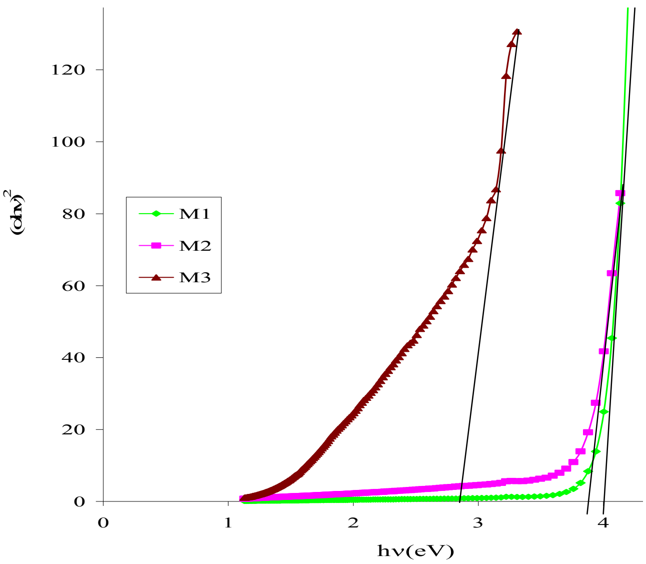


*Fig.5: The plot of $(\alpha h\nu)^2$ vs. hν for ZnO thin films deposited at different pH*

## 4. Conclusions

Zinc oxide (ZnO) thin films were deposited at various pH values using the CBD method. The films were studied using X-ray diffractometer and optical spectrophotometer. The pH value influences the structural and optical properties and the band gap energy of the films. The high transmittance of ZnO thin films in the visible spectrum can be employed to serve as coating for energy-saving or heat-protecting windows. The coatings let the visible part of the spectrum in but either reflects the IR back into the room or does not let the IR radiation into the room (heat protection) depending on which side of the window has the coating [3]. Again ZnO thin films with high transparency in visible spectrum can be used as a transparent electrode in the field of optoelectronic displays and in the field of photovoltaic solar energy conversion as well [11]. Band gap energy of the films deposited here falls within the range of 2.8 -4.0 eV. Literature review shows that the band gap energy lower than 1.9 eV is used as absorber materials in solar cell architecture while those with higher band gap energy can be used as window layer [12]. Therefore, ZnO thin films deposited in this work could be used as window material for solar cell applications.

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