The Study of Chemically Deposited ZnO Thin Films for Possible Device Applications

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Date of publication (dd/mm/yyyy): 24/06/2017

Abstract – A study on the Deposition and Characterization of ZnO Thin Films by Solution Growth Technique using Ammonia (NH3) as a complexing agent. Zinc oxide thin films were successfully deposited on glass slides under certain deposition condition of 60°C-100°C of 1M solution of NaOH, using solution growth technique. X-ray fluorescence (XRF) and Rutherford Backscattering Spectroscopy (RBS) analyses confirmed that the films were ZnO thin films. The films of ZnO showed optical transmittance of 20.6%-65.6% in the UV, 70.2%-79.2% in the visible and 79.5%-81.6% in the near-infrared regions of electromagnetic spectrum. ZnO films were found to exhibit absorbance of 25.5%-68.6% in the UV, 10%-18.3% in the visible region and 8.8%-9.96% in the near-infrared regions of electromagnetic spectrum. ZnO thin films, exhibited low reflectance, throughout the electromagnetic spectrum (9.6%-20.3%). Direct band gap values of 3.31eV is obtained for ZnO thin films. The thickness of 0.082μm thickness was obtained for ZnO films by gravimetric method. Other properties investigated were the refractive index, optical conductivity, absorption coefficient and dielectric constants. From the spectral qualities, ZnO thin film may be found useful in heat mirror application. The sample of ZnO thin films are also found interesting as semiconductor materials for electronic applications.

Keywords – Absorbance, Transmittance, Band Gap Absorption Coefficient, Reflectance.

I. INTRODUCTION

Energy technology plays important role in our lives and in nation building to ensure table electricity. This cuts across the socio-economic and political lives of the citizenry both in rural and urban areas. In spite of the fact that energy lies around us in vast quantities within the dynamic forces of nature - the sun, winds, tides, and waves; there must be a technological means of converting them from a low grade form to a high one in order to achieve a desired purpose. The depletion and problems caused by the existing energy source: fossil fuel and nuclear energy have encouraged researchers to continue to search for most efficient and economic mode and device for tapping the huge solar energy available on earth. Oxides such as tin oxide and zinc oxide are examples of transparent conducting oxides (TCOs). Others are the oxides of cadmium, indium, etc.

These oxides play important roles in many large and small scale applications, some of them are passive (e.g. cold/heat mirrors and selective window coating) and others are active (e.g. solar cells and flat panel displays (FPDs)). The FPDs have wide variety of applications ranging from instrument panels for airplanes and automobiles, video phones, consumer electronics as well as special requirements for medical and military establishments. These diverse applications of FPDs have varying display requirements that have met with optical enhancement (Lewis and Paine, 2000).

ZnO thin films have useful properties, such as high optical transparency in the visible and near infra-red regions of electromagnetic spectrum (Zainelabdin et al., 2010).

ZnO thin films can be fabricated by different methods such as hydrothermal deposition (Amin et al., 2010), chemical bath deposition (Onwuemeka et al., 2014).

II. EXPERIMENT

The following constitute the chemical bath for optimum deposition: 20ml of 0.5M solution of zinc chloride, 5ml of 1M solution of NH3 solution and 15ml of 1M solution of NaOH varied between 60°C-100°C. Ammonia solution in this work, was used as the complexing agent.

Several bath compositions were employed, but the optimum result was achieved with the specification noted above. Equally good and uniform depositions were obtained using 0.5M, 0.25M, 0.1M, 0.2M solution of zinc chloride.

The solutions for deposition were made in 50ml beakers and 76mm x 26mm x 1mm commercial- quality glass microscopic slides were used as the substrates.

1M solution of sodium hydroxide solution (NaOH) varied between 60°C-100°C was quickly transferred to the 50ml beaker containing the zinc complex. The process was repeated for varying parameters such as concentration, volume of complexing agent, temperature, time of growth and pH.

Reaction Mechanism

0.5M solution of 20ml of zinc chloride (ZnCl2) was allowed to react with 1M solution of ammonia (NH3) in 50ml beaker. A white gelatinous precipitate was formed, which dissolved in excess NH3(aq) when stirred forming tetra-ammine complex zinc ion. The reaction is shown in eqn. (1.1)

\[ \text{ZnCl}_2 + 4\text{NH}_3(aq) \leftrightarrow \text{[Zn(NH}_3)_4]^{2+} + 2\text{Cl}^- \] (1.1)

Ammonia (NH3(aq)) in this reaction is the complexing agent. It controls the rate of ion – by – ion interaction,
thereby moderating the rate of formation of precipitate. It also creates an alkaline medium for good formation of deposits. When 1M solution of 15ml of sodium hydroxide (NaOH) varied between 60°C-100°C was added in the content, it was observed that the transparent solution formed by ZnCl₂ and NH₃(aq) changed to white precipitate when NaOH solution was added. This resulted in the formation of Zn(OH)₂ on the substrates immersed in the beaker containing the reactants. The reaction is given in (1.2)

\[ [\text{Zn(NH}_3)_2]^{2+} + 2\text{Cl}^- + 2\text{NaOH} \rightarrow \text{Zn(OH)}_2(s) + 2\text{NaCl} + 4\text{NH}_3(aq) \]  (1.2)

The zinc hydroxide Zn(OH)₂ deposited on the substrate, oxides in air to ZnO.H₂O.

The formation of zinc oxide films is due to the hydrolysis of Zn²⁺ in aqueous solution to form ZnO thin films as shown in (1.3).

\[ \text{Zn(OH)}_2 \rightarrow \text{ZnO.H}_2\text{O} \]  (1.3)

By annealing ZnO.H₂O at 300°C, for 1 hour, ZnO thin films are formed. This is given in equation (1.4).

\[ \text{ZnO.H}_2\text{O} \rightarrow 300^\circ\text{C} \rightarrow \text{ZnO + H}_2\text{O} \]  (1.4)

III. RESULTS AND DISCUSSION

The radiant energy impinging on a thin film surface may be reflected, absorbed or transmitted as well as minimally scattered. Our interest is to measure the transmittance and absorbance of the sample from the Ultraviolet (UV) regions to near infra-red (NIR) regions of the electromagnetic spectrum using the spectrophotometer and then deducing the reflectance value from the measurements. The UNICAM UV1 061408 double beam spectrophotometer was used to measure the spectral transmittance and absorbance of the film samples. It has a spectral range of 190nm to 1100nm. The T-R-A spectra were obtained in the UV/ visible regions and in the near-infrared region up to 1.0µm. Uncoated glass slide was used as reference. Six samples were selected from the ZnO thin films for characterization. Sample A₀ was used as a representative sample.

The optical properties, which we measured and calculated in this work are the transmittance (T), absorbance (A), reflection (R), reflective index (n) extinction coefficient (k), complex dielectric constant (ε) and optical conductivity (σₒ). The solid state properties under consideration are the compositions of the films and the thickness computations. These properties are important for the characterization of this work and they are briefly explained below.

Composition and Thickness Measurements

It is often necessary to determine the elements that make up the thin film samples. In this work, atomic compositions were determined by X-ray fluorescence (XRF) analysis, Rutherford back scattering (RBS) analysis. The Rutherford backscattering analysis shows that the thickness sub-layers composition of the ZnO sample annealed at 300°C are 94% of oxygen and 6% of zinc. This shows oxygen-rich films, which may be as a result of exposure to air and surface hydroxide. This is shown in Fig.2.3

The thickness of the films in this work was calculated by gravimetric method by assuming the density of the bulk material and then using mass-volume-density relationship. The thickness of ZnO sample annealed at 300ºC is 0.082μm.

The X-ray fluorescence (XRF) analysis shows the various elements that make up the plane glass slide with different peaks as shown in Fig.2.1 with the analyzed results in Table 2.1. It also revealed the presence of Zn²⁺ as the main constituents of the deposited film sample. This is shown in Fig. 2.2 with the analyzed results in Table 2.2.

Quantitative Analysis Report on Sample A₀

Tube Excitation: AG – ANODE operating at 25.0 KV

Live time: 1000 Sec

Tube Current: 0.50 Ma

Method is Direct Comparison of Count rates

### Table 2.1: XRF data on uncoated glass slide showing presence of active elements

<table>
<thead>
<tr>
<th>E₁</th>
<th>Counts</th>
<th>Compound</th>
<th>Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>1327 ± 45</td>
<td>Cl</td>
<td>748.238 ± 147.763 ppm</td>
</tr>
<tr>
<td>K</td>
<td>2960 ± 62</td>
<td>K</td>
<td>7516.506 ± 1700.806 ppm</td>
</tr>
<tr>
<td>Ca</td>
<td>18947 ± 135</td>
<td>Ca</td>
<td>5.830 ± 1.073 %w</td>
</tr>
<tr>
<td>Ti</td>
<td>261 ± 34</td>
<td>Ti</td>
<td>559.846 ± 130.188 ppm</td>
</tr>
<tr>
<td>Mn</td>
<td>573 ± 49</td>
<td>Mn</td>
<td>343.938 ± 78.028 ppm</td>
</tr>
<tr>
<td>Fe</td>
<td>4104 ± 84</td>
<td>Fe</td>
<td>1790.967 ± 334.382 ppm</td>
</tr>
<tr>
<td>Ni</td>
<td>356 ± 55</td>
<td>Ni</td>
<td>151.136 ± 37.216 ppm</td>
</tr>
<tr>
<td>Cu</td>
<td>751 ± 61</td>
<td>Cu</td>
<td>496.037 ± 110.707 ppm</td>
</tr>
<tr>
<td>Zn</td>
<td>465 ± 59</td>
<td>Zn</td>
<td>715.935 ± 188.640 ppm</td>
</tr>
</tbody>
</table>

### Table 2.2: XRF Data indicating the presence of Zn²⁺ in the ZnO thin films of sample: A₀

<table>
<thead>
<tr>
<th>E₁</th>
<th>Counts</th>
<th>Compound</th>
<th>Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>1237 ± 44</td>
<td>Cl</td>
<td>697.491 ± 138.123 ppm</td>
</tr>
<tr>
<td>K</td>
<td>3387 ± 66</td>
<td>K</td>
<td>8600.812 ± 1927.410 ppm</td>
</tr>
<tr>
<td>Ca</td>
<td>21226 ± 142</td>
<td>Ca</td>
<td>6.531 ± 1.202 %w</td>
</tr>
<tr>
<td>Ti</td>
<td>155 ± 32</td>
<td>Ti</td>
<td>332.475 ± 109.588 ppm</td>
</tr>
<tr>
<td>Mn</td>
<td>261 ± 45</td>
<td>Mn</td>
<td>158.463 ± 40.446 ppm</td>
</tr>
<tr>
<td>Fe</td>
<td>3791 ± 80</td>
<td>Fe</td>
<td>1654.375 ± 306.496 ppm</td>
</tr>
<tr>
<td>Ni</td>
<td>318 ± 56</td>
<td>Ni</td>
<td>135.003 ± 34.206 ppm</td>
</tr>
<tr>
<td>Cu</td>
<td>615 ± 60</td>
<td>Cu</td>
<td>406.209 ± 83.942 ppm</td>
</tr>
<tr>
<td>Zn</td>
<td>2035 ± 75</td>
<td>Zn</td>
<td>3133.179 ± 188.640 ppm</td>
</tr>
</tbody>
</table>
Fig. 2.1: X-ray fluorescence spectrum for uncoated glass slide.

Fig. 2.2: X-ray fluorescence analysis of ZnO thin film, indicating the presence of Zn$^{2+}$ as well as other elements in the glass slide material of sample $A_0$. 
Observation

It was observed that when 5ml of 1M solution of NH$_3$ was allowed to react with 20ml of 0.5M solution of ZnCl$_2$, a white precipitate was initially formed, which dissolved in excess NH$_3$ solution forming a colourless transparent solution of [Zn(NH$_3$)$_4$]$^{2+}$ (tetra-ammine complex zinc ion).

When 15ml of 1M solution of NaOH varied from 60°C – 100°C was added to the solution of [Zn(NH$_3$)$_4$]$^{2+}$, the white precipitate reappeared.

When the substrates were inserted into the mixture, it took between 4-12 hours for optimum deposition to occur depending on the operating temperatures of NaOH solution, volume of reactants and the concentration. This was not achieved under the same conditions at room temperature. It took 48hrs to have non-uniform films to deposit on the substrates which were almost removed when rinsed in distilled water. At times, no deposition was formed.

It must be stated clearly here that the chosen parameters (i.e. concentration, volume temperature, pH and time of deposition) were found largely by trial and error and we have no means of guaranteeing that they lead to the best possible optical and electrical properties (Eze, 1998).

From literature, zinc salts, have the capability of forming complex solutions of tetra-ammine zinc complex ion [Zn(NH$_3$)$_4$]$^{2+}$.

This makes ammonia solution a suitable complexing agent for the deposition of zinc oxide thin films.

The concentration of Zn$^{2+}$ ions decrease with increasing concentration of complexing ions.

Thus, the rates of reaction and the formation of precipitates are reduced, leading to a larger terminal thickness of the films.

It was observed that the deposition of ZnO thin films is pH-dependent. OH$^-$ ions from NaOH, did not take part in the complex formation therefore, the addition of OH$^-$ precipitated the corresponding hydrous oxides of zinc ion which were deposited on the substrates.

In the case of OH$^-$ ions taking part in the complex formation, the addition of OH$^-$ ions increase the pH value, making the complex more stable, thereby reducing the concentration of free cations. The suitable pH value for this work is between 9 to 11 as detected by the piston pH meter.

By raising the temperature of NaOH solution varied from 60°C-100°C, there occurs the dissociation of the ions of NaOH to Na$^+$ and OH$^-$. These ions are unstable and are ready to accept opposite ions. When added to the zinc complex, the complex acquired thermal energy and further dissociates to Zn$^{2+}$ precipitating their hydrous instead of their hydroxides which were deposited on the substrates.

Optical Measurements

The transmittance was measured directly from the UNICAM UV1 061408 double beam spectrophotometer. The absorbance, reflectance, absorption coefficient, refractive index $n$, extinction coefficient, real dielectric constant $\varepsilon_1$, imaginary dielectric constant $\varepsilon_2$, optical
The optical transmittance spectrum of the ZnO thin films grown under the optimum condition of 60°C-100°C of 1M NaOH solution and annealed at the temperature of 300°C on the glass substrate is reported in Fig. 2.4. The calculated film thickness is 0.082μm. The transmittance spectrum shows that the film has good transparency in the UV and high transmittance (65.6%-79.4%) in the visible and high transmittance (79.5%-81.6%) in the near-infrared.

The films have low reflectance of 9.6% to 20.2% from the UV, visible and near infrared regions of electromagnetic spectrum as depicted in Fig. 2.6, This makes ZnO thin films useful in the area of multilayer solar control coating. The coating lets the visible part of the spectrum in but either reflects the infrared (IR) radiation back into the room (energy saving) or does not allow the infrared-radiation into the room (heat-protection), depending on which side of the window has the coating (Ndukuwe, 1996).

ZnO thin films can be used in the production of transparent thin film transistors (TFT) (Nomura et al., 2003). If the films are doped with Al, Ga or nitrogen, a transparent (transparency ~90%) and conductive material could be achieved. It serves as front contact for solar cells or liquid crystal (flat panel) displays for optoelectronic applications.

The optical energy band gap was obtained in k-space using the relation,

\[(zhv)^2 = A(hv-E_g)\]  

(2.1)

where \(A\) is a constant, the inverse of which gives the disorder potential \(\Delta^4\).

The optical band gap \(E_g\) was evaluated by extrapolating the linear portion of the plot \((zhv)^2\) against \(hν\) at \(zhv=0\), where \(α\) is the absorption coefficient and \(h\nu\) is photon energy. This is shown in Fig.2.13.

The value of \(A^4\) is obtained from the gradient of the linear portion of the curve in Fig.2.13, (Eze and Okeke, 1993). In this work, the value of the disorder potential \(A^4=2.5x10^{-17}(\text{eV})^4\text{m}^2\).

A direct allowed band gap of 3.31±0.05eV is obtained. The result is in close agreement with the literature value of 3.3eV (Sun and Kwok, 1999).

This wide band gap obtained in this work, makes ZnO thin film a good material for the production of laser diodes and light emitting diodes (LEDs) (Look, 2001).

It can also be used to produce field-effect transistors where p-n junction may not be required thus avoiding the p-type doping problem of ZnO (Look, 2001).

The absorption coefficient of the film was calculated using the equation,

\[α=1/x \ln(1/T)\]  

(2.2)

where \(x\) is the thickness of the film and \(T\) is the transmittance.

The values of the absorption coefficient range from 2.48x10^6m^-1 to 1.44x10^7m^-1 as the wavelength decreases. Fig. 2.7, shows the semi-log plot of \(α(ν)\) against photon energy, \(h\nu\). The plot indicates an Urbach exponential dependence of the absorption coefficient on the photon energy (De Wit and Crevecoeur, 1972) in the form

\[α(ν) = α_e \exp(hν/W_c)\]  

(2.3)

where \(W_c\) is interpreted as the width of the tail of localized energy states in the band gap. The value of \(W_c\) as calculated from Eqn. (2.3) using Fig. 2.7, is equal to \(W_c=0.12\text{eV}\).

The films exhibited wide band gap of 3.31±0.05eV and low value of \(W_c=0.12\text{eV}\) showing that the films have low amount of impurities which must have been introduced into the film during deposition.

The refractive index of the film rises from 2.47 at \(λ=360nm\) up to 2.64 at \(λ=364nm\) and falls as the wavelength increases to 994nm. This is shown in Fig.2.8. This is in close agreement with the work of Sun & Kwok (Sun and Kwok, 1991). The dependency of refractive index on the reflectance, resulted in decrease of \(n\) from 2.64 to a minimum value of 1.89 as the wavelength increases. This feature, makes the film a useful material for multilayer solar control coating applications.

Fig.2.12, shows the decreased of optical conductivity from the peak value of 8.52x10^14Ω^-1m^-1 at 360nm to a minimum value of 1.12x10^14Ω^-1m^-1 at 994nm. The behaviour is caused by the dependency of optical conductivity on the nature of refractive index and absorption coefficient because at the UV region, \(α\) and \(n\) are greatest and diminishes as the wavelength increases.

The absorption coefficient dropped from the peak value of 1.44x10^7m^-1 at 360nm to a minimum value of 2.48x10^6m^-1 at 994nm. The behaviour of \(α\) depends on the transmittance and the thickness of the film.

From Fig.2.10, the real dielectric constant rises from 5.98 at 360nm to the maximum value of 6.87 at 364nm and then decreases as the wavelength increases. This is as a result of long deposition time, which modifies the dielectric features of mainly dielectric thin films (Ndukuwe, 1996).
Fig. 2.4: Graph of transmittance against wavelength for ZnO thin film of sample A9.

Fig. 2.5: Graph of absorbance against wavelength for ZnO thin film of sample A9.
Fig. 2.6: Graph of reflectance against wavelength for ZnO thin film of sample A9.

Fig. 2.7: Semi-log plot of absorption coefficient against photon energy for ZnO thin film of sample A9, showing Urbach exponential dependence of $\alpha(v)$ on photon energy.
Fig. 2.8: Graph of refractive index against wavelength for ZnO thin film of sample A9.

Fig. 2.9: Graph extinction coefficient against wavelength for ZnO thin film of sample A9.
Fig. 2.10: Graph of real dielectric constant against wavelength for ZnO thin film of sample A9.

Fig. 2.11: Graph of imaginary dielectric constant against wavelength for ZnO thin film of sample A9.

Fig. 2.12: Graph of optical conductivity against wavelength for ZnO thin film of sample A9.
Zinc oxide films were prepared on glass substrates by solution growth technique from 1M solution of NaOH varied from 60°C-100°C while zinc complex was kept at room temperature. NH₃ solution was used as complexing agent.

The zinc oxide film exhibited appreciable good transmittance in UV, visible and near-infrared regions of the electromagnetic spectrum. ZnO thin films showed relatively high absorbance in the UV at certain wavelength region which decreases as the wavelength increases. It has low reflectance in the UV, visible and near-infrared regions of electromagnetic spectrum.

The other properties investigated were the optical conductivity, optical constants and absorption coefficient.

The ZnO thin film prepared under this condition with a large direct band gap of 3.31±0.05eV has advantages associated with it. These include higher breakdown voltage, ability to sustain large electric field, low electronic noise, stable at high temperature and high power operation. Due to the thermal stability of ZnO film, it can be found useful in the area of ceramics production, anti-corrosion material in iron and other metallic materials.

As a result of its high transmittance, low absorbance and low reflectance, the ZnO film can be used as multilayer solar control coating on windows. The deposited ZnO film with wide direct band gap of 3.31±0.05eV could be a good material for fabrication of laser diodes and light emitting diodes (LEDs). If this material is doped with aluminium (ZnO:Al), a transparent conducting electrode could be produced, which can be used in flat panel displays for electronic applications. Transparent thin film transistors (TTFT) can be produced with the deposited ZnO film because as a field effect transistor, it may not need p-n junction thus avoiding the p-type doping problem of ZnO. It can be considered for spintronics applications. If doped with magnetic ions (Fe, Mn, V, Co etc) it could become ferromagnetic even at room temperature.

IV. CONCLUSION

We are grateful to the laboratory officials of Obafemi Awolowo University Ile-Ife in the persons of Prof. I.E. Obiajunwa of Centre for Energy Research and Development and Mr. E.A. Akinola of Central Science Laboratory for their assistance in successful realization of this work.

ACKNOWLEDGMENT

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