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The Optical Study of ZnO Thin Films at Different Times of Annealing and Varying Temperatures Prepared by Chemical Bath Deposition.

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Abstract: *A research on the Deposition and Characterization of ZnO Thin Films by Chemical Bath Deposition Technique using Ammonia (NH_3) as a complexing agent. Thin films of ZnO are deposited onto glass substrates at room temperature for 5hours. The optical properties of the films were measured using Double Beam UV- Spectrophotometer with serial number UV061514, Rutherford Back Scattering Spectroscopy (RBS) analysis revealed that the thin filmshave percentage ratios of the elements of Zn/O, 47/53 as annealed for 3hours at the temperature of 250 ℃ and Zn/O, 48.8/51.2as annealed for 1hour at the temperature of 150 ℃. The thicknesses are 80nm for 3hours and 150nm for 1hour asannealed samples at 250 ℃ and 150 ℃ respectively. It was found that ZnO thin films exhibits n-type conduction. Optical band gap values of the twosamples are 3.1±0.05eV as annealed for 3hours and 3.3±0.05eV as annealed for 1hour with an average of 3.2±0.05eV. Other optical properties calculated from transmittance using appropriate equations are absorbance, reflectance, band gap , absorption coefficient, optical conductivity, refractive index and extinction coefficient.*
Keywords: *Annealing, absorption coefficient, extinction coefficient, absorbance, band gap substrates.*

I. Introduction

Advances in the area of alternative energy technology will ensure a stable electricity which will lead to smooth transition away from fossil fuels and nuclear energy, that comprise about 93% of the world's energy budget with a negligible contribution from solar energy. ZnO thin films have valued properties such as high optical transparency in the visible and near-infrared region of electromagnetic spectrum [1], chemical stability in hydrogen plasma [2], high refractive index [3], and wide band gap semiconductor [4]. The thin films of the metallic oxide have wide range of applications such as antireflection coating [5], surface acoustic wave devices [6], band pass filter [7], laser deflectors using piezoelectric and piezo-optic properties [8].

ZnO thin films can be produced by different methods such as pulse laser deposition[9], spray pyrolysis[10], sol-gel technique[11],chemical bath deposition[12]. The films in this study are grown by chemical bath deposition (CBD) which creates a thin film on a solid substrate via a reaction in a liquid solution. The CBD method is inexpensive, easy to prepare and its necessary vessels can be found in an ordinary chemistry laboratory [13].

In this work, we report the study of the optical properties of ZnO thin films at varying annealing times and temperatures prepared by chemical bath deposition on glass substrates.

Experiments

ZnO thin films were deposited on glass substrates by chemical bath deposition based on the reaction between $ZnCl_{2(aq)}$,$NaOH_{(aq)}$ and with $NH_{3(aq)}$ as complexing agent according to the equation;

$$ZnCl_2 + 4NH_3 + H_2O \longrightarrow [Zn(NH_3)_4]^{2+} + H_2O + 2Cl^-$$

$$[Zn(NH_3)_4]^{2+} + 2NaOH \longrightarrow ZnO + 4NH_3 + 2Na^- + OH^-$$

An excess aqueous ammonium was added to 20ml of 0.5M solution of $ZnCl_2$ to form a white ($Zn[NH_3]_4^{2+}$) which dissolved completely on stirring to form a clear solution. 10ml of 1M solution of NaOH was finally added for complete formation of ZnO thin films in an alkaline medium. The pH of the final solution was measured to be 9.3 and was done at room temperature. Glass substrates were then immersed vertically into the final solution which were made in 50ml beaker and optimum depositions were obtained after five hours

II. Results and Discussion

Many samples were deposited under different set of conditions of reactant concentrations, temperature, and pH of the solution. Two slides were immersed in each beaker representing a given set of conditions. Optimum results were obtainedon the slides under the stated conditions below:

Concentration and volume of reactants; 20ml of 0.5M $ZnCl_{2(aq)}$ + 4ml of 3M $NH_{3(aq)}$ + 10ml of 1M$NaOH_{(aq)}$

Deposition temperature; 23°C

PH of final solution; 9.3

Deposition time; 5 hours

Annealing temperatures; 250°C and 150°C for each of the two representative samples

Annealing time; 3 hour and 1 hours for, each of the two representative samples.

Volume ratio; 20:4:10 which gave the desired depositions.

Composition and thickness measurements

Two representative samples were selected out of the four samples deposited under the same conditions at room temperature of 23°C. The two samples were subjected to **Rutherford Back Scatteringspectroscopy analysis (RBS)**. The presence of Zn^{2+} and O^{-2} were confirmed in the ratio of 0.47:0.53 by number of atoms. This implies that 47% of Zn^{2+} and 53% of O^{2-} are present in the sample annealed for 3hours at 250°C as shown in Fig.3. Also, the percentage compositions of the sample annealed for 1hour at the temperature of 150°C are 48.8% Zinc and 51.2% oxygen as shown in Fig.2. The thicknesses of the films were also determined to be 150nm and 80nm for the samples annealed for one hour and three hours respectively from the **RBS** test as shown in Figs. 2 and 3.

Fig.1, is the RBS of the uncoated glass slide.

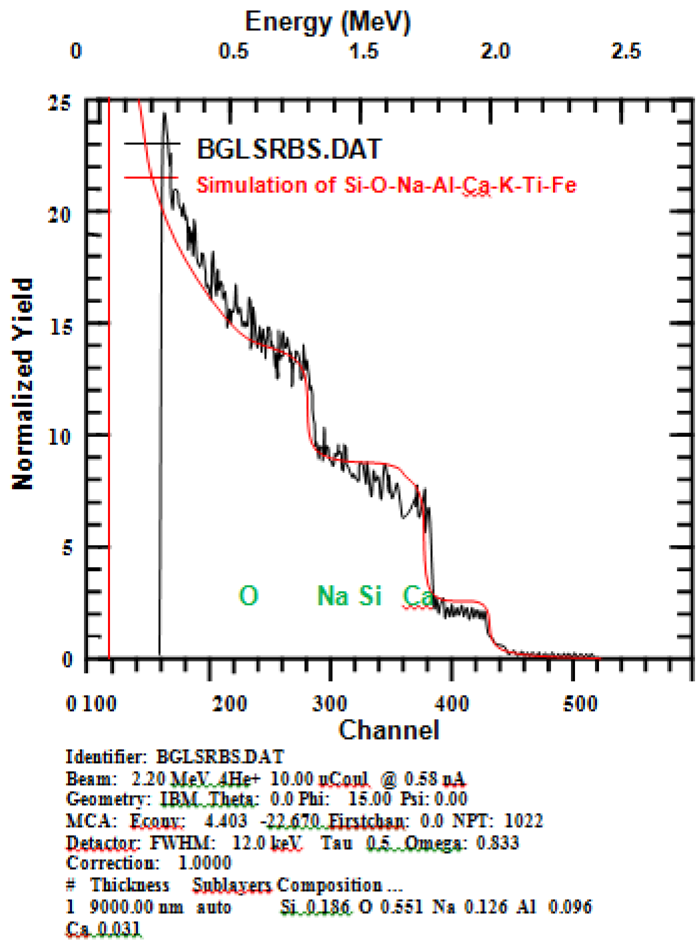
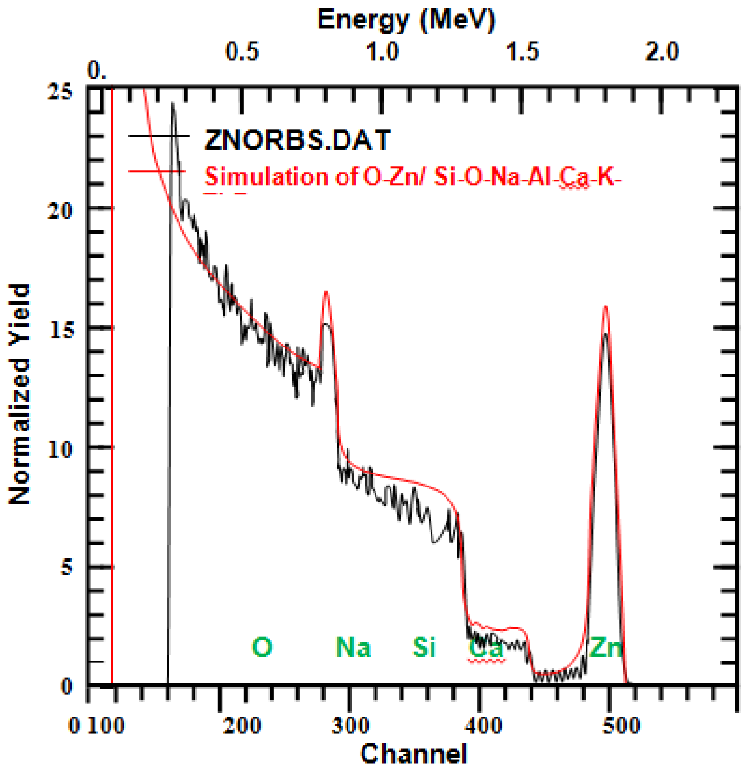
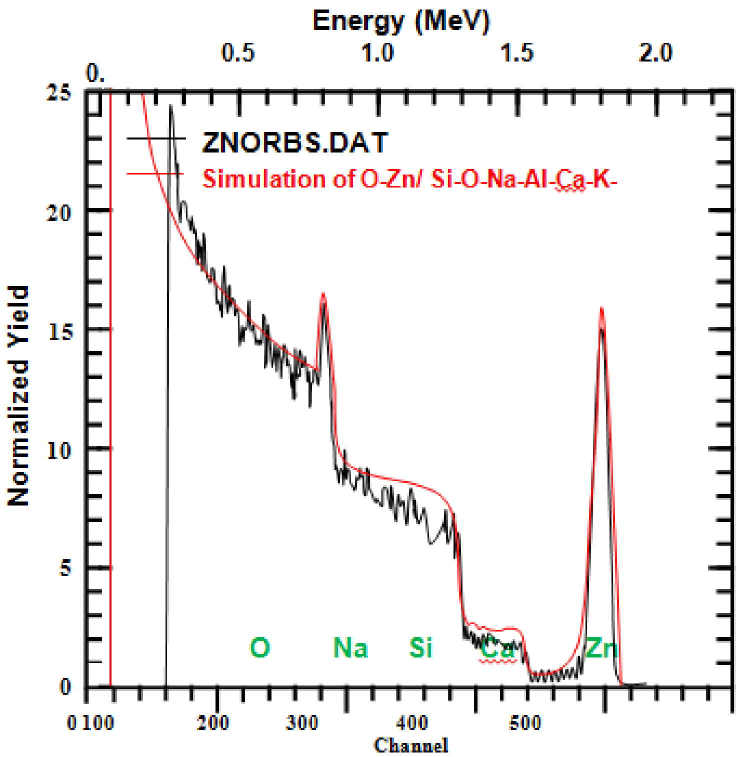


Fig. 1: RBS result for blank glass substrate



LAYER Thickness Sublayers Composition ...
1 150.00 nm auto Zn 0.488 O 0.512
2 9000.00 nm auto Si 0.186 O 0.551 Na 0.126 Al 0.096
Ca 0.031 K 0.005 Ti 0.002 Fe 0.003

Fig. 2: RBS result for sample annealed at 150°C for 1 hour.



LAYER Thickness Sublayers Composition ...
1 80.00 nm auto Zn 0.47 O 0.53
2 9000.00 nm auto Si 0.186 O 0.551 Na 0.126 Al 0.096
Ca 0.031 K 0.005 Ti 0.002 Fe 0.003

Fig.3: RBS result for sample annealed at 250°C for 3 hours.

Optical properties

Transmittance

The transmittance, which is the ratio of the incident intensity to the transmitted intensity of the radiation was measured **using UVI double beam Spectrophotometer with serial number 061514.**

Absorbance, reflectance and other optical properties were calculated from the values obtained from the transmittance values using appropriate equations.

For the sample annealed at 250^0C for 3hours transmittance decreased from 0.70 to 0.66 as the wavelength increased from 368nm to 940nm. For the other sample annealed at 150^0C for 1hour, transmittance decreased from 0.819 to 0.804 as the wavelength increased from 366nm to 940nm. This means that ZnO can be used as window in UV optics, since it has higher transmittance in UV region. Also it can be used as infrared shield. The graphs for the two samples are shown in **Figs.4.**.

Band gap

The energy gap of 3.1±0.05eV and 3.3±0.05eV for the sample annealed at 250˚C for 3hour and 150˚C for 1hour respectively as shown in **Fig.5**were achieved**.**

ZnO have a relatively large direct band gap of 3.3±0.05eV at room temperature. Advantages associated with a large band gap include higher breakdown voltage ability to sustain large electric current, lower electronic noise, high temperature and high power operation. While those with lower band gap (i.e. below 3.3eV) can be use as absorber layers in solar cells.

TheZnO thin films have average band gap of 3.2±0.05eV which is approximately a direct band gap of ZnO thin films [4].

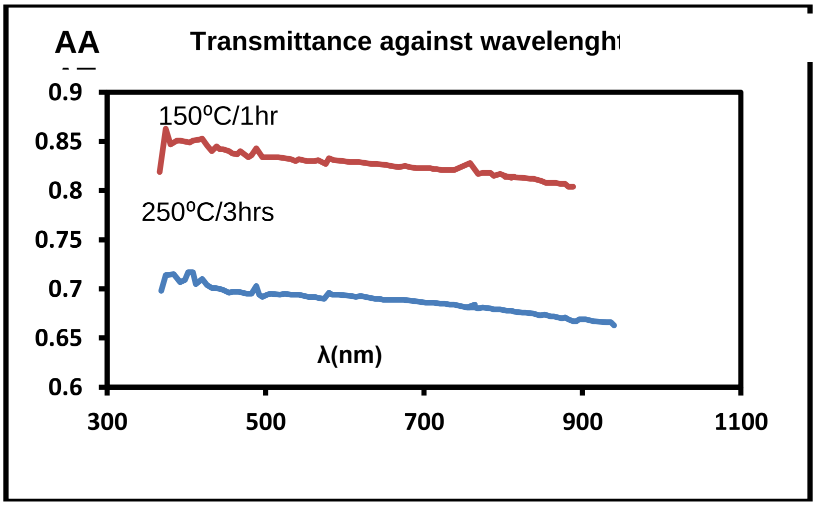


Fig 4: Graph of Transmittance against Wavelength

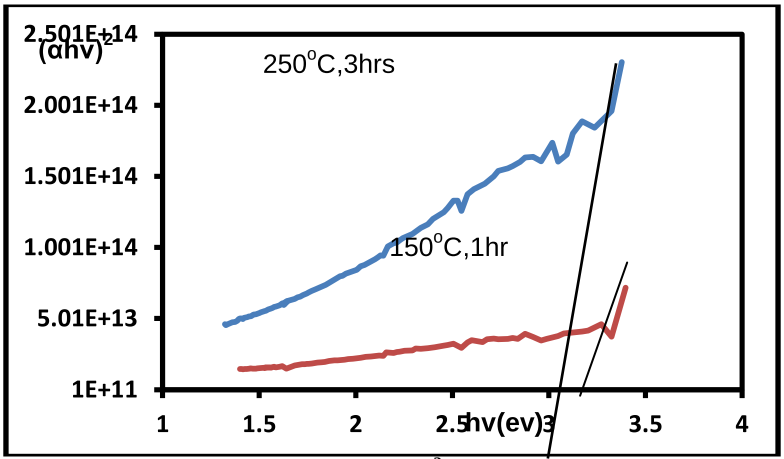


Fig 5: A graph of $(\alpha hv)^2$ against hv(ev)

III. Conclusion

ZnO thin films were deposited onto glass substrates using chemical bath method (CBD). CBD is known to be simple, low temperature and inexpensive large area deposition technique. It is one of the preparation of compound semiconductors from aqueous solutions such as Cds, CdSe, CdO, ZnS, ZnSe and ZnO.It gives good deposits on suitable substrates by controlled precipitation of the compound from the solution. Thin films are made for different purposes both for optical, electronics, electrical and other passive applications.

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