Physical Properties of ZnO Thin Films Prepared by Spray Pyrolysis

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Abstract

In this study, ZnO thin films were deposited by the spray pyrolysis technique on glass substrates. Optical properties of the films were also investigated by Ultraviolet-Visible-Near Infrared (UV-VIS-NIR) spectrophotometer. Spray pyrolysis is a useful alternative to traditional methods for obtaining zinc oxide (ZnO) films, because of its simplicity, low cost and minimum waste production. The spray pyrolysis process allows the coating of large surface and it is easy to include in the industrial production line. The optical transmittance at normal incidence was recorded in the wavelength range of 300-1100 nm by using the UV/VIS/NIR spectrophotometer.

Introduction

Zinc oxide is often called a II-VI semiconductor because zinc and oxygen belong to the 2nd and 6th groups of the periodic table [Segawa (1997)], respectively. This semiconductor has several favorable properties: good transparency, high electron mobility, wide band gap, strong room temperature luminescence, etc. Those properties are already used in emerging applications for transparent electrodes in liquid crystal displays and in energy-saving or heat-protecting windows, and electronic applications of ZnO as thin-film transistor and light-emitting diode [Segawa, 1997; Huang, 2001].

The material ZnO has gained substantial interest in the field of semiconductor research because of its large excitation binding energy (60 MeV) compared with other semiconductor materials, ZnO has a high potential for room temperature light emission, and more resistant to radiation, and is multifunctional as it has piezoelectric, ferroelectric, and ferromagnetic properties [L. M. Levinson and H. R. Philipp, 1986]. ZnO has a direct band gap of 3.37 eV at 300 K. The crystal structures shared by ZnO are wurtzite. Each sublattice includes four atoms per unit cell and every atom of one kind (group-II atom) is surrounded by four atoms of the other kind (group VI), or vice versa.
Fig 1  Schematic representation of a wurtzitic ZnO structure having lattice constants $a$ in the basal plane and $c$ in the basal direction; $u$ parameter is expressed as the bond length or the nearest-neighbor distance $b$ divided by $c$ which are coordinated at the edges of a tetrahedron [Look, 1998] In a real ZnO crystal, the wurtzite structure deviates from the ideal arrangement, by changing the $c/a$ ratio or the $u$ value fig. (1)

**Optical Constants**

The optical energy gap $E_g$ determined by using Tauc equation:

$$(\alpha hv) = B(hv-E_g)^{r}$$

where $B$ is Tauc constant and $(hv)$ is the photon energy, $\alpha$ is the absorption coefficient. For $r=1/2$ yields linear dependence, which describes the allowed direct transition. The optical behavior of a material is generally utilized to determine its optical constant [refractive index($n$), extinction coefficient ($k$), real and imaginary parts of dielectric constant ($\varepsilon_1$ and $\varepsilon_2$)].

The complex index of refraction ($n_c$) is defined as [D. C. Look, (1998).] 

$$n_c = n + ik = \varepsilon^{1/2} = [\varepsilon_1 + i\varepsilon_2]^{1/2}$$

where $n$ is the real refractive index and $k$ is the extinction coefficient. The optical constants, $n$ and $k$, are real and positive numbers, and can be determined from optical measurements.

From Equation 2, it follows that [ J. R. Sizelove, 1998],

$$\varepsilon_2 = n^2 - k^2$$

$$\varepsilon_1 = 2nk$$

The extinction coefficient characterizes absorption of the electromagnetic wave energy in the process of propagation of a wave through a material. The wave intensity $I$ after it passes a distance $x$ in an isotropic medium is equal to:

$$I = I_0 \exp(-\alpha x)$$

Where $I_0$ is the intensity at $x = 0$ and $\alpha$ is called the absorption coefficient. For many applications, the extinction coefficient, $k$, this is equal to:

$$k = \frac{\alpha \lambda}{4\pi}$$

Where $\lambda$, is the wavelength of light in vacuum.

The normal-incidence reflectivity $R$ can also be given by:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$
Then the refraction index value can be calculated from the formula [D. M. Bagnall, 1997]:

\[
    n = \sqrt{\frac{4R}{(R+1)} - k^2} - \frac{(R+1)}{(R-1)}
\]

………………..(7)

**Experimental procedure**

Various techniques have been used to synthesize ZnO. Low temperature deposition methods for thin film photovoltaic devices are of interest to enable the use of lightweight, flexible substrates. Such devices provide a higher power-to-weight ratio and significant cost savings compared to current technologies.

The spray pyrolysis method is a well-known nanostructured thin-film preparation method with excellent features such as the need for no sophisticated equipment, and quality targets or substrates; also, film thickness and stoichiometry are easy to control and the resulting films are well compacted.

ZnO films have been produced by spraying the aqueous solution of (0.1)M of Zinc acetate \( (CH_3 COO)_2 Zn_2H_2O = 219.5 \text{g/mol} \) onto the microscope glass substrates \((1 \times 25 \times 75 \text{mm}^3)\) at substrate temperature of 370 °C. The substrate temperature was maintained to within ±10°C. 50 ml alcohol was used for preparing the solutions. Used Zinc acetate mass was calculated using the following equation:

\[
    \text{Weight(g)} = \text{Molarity(mol/l)} \times \text{Volume(l)} \times \text{Molecular weight (g/mol)}
\]

………..(8)

Prior to deposition, the substrates were cleaned in with cleaner solution, distilled water and followed by alcohol using ultrasonic bath.

The schematic arrangement of spray pyrolysis set-up is shown in Fig. (2). Spray pyrolysis is basically a chemical process, that is the spraying of the solution onto a substrate held at high temperature, where the solution reacts forming the desired film.

The spray rate of the solution was adjusted to be five sprinkling in minute, the sprinkling time about ten second. The normalized distance between the spray nozzle and the substrate is 29cm. Nitrogen was used as the carrier gas. The temperature of the substrate was controlled by an Iron-Constantan thermocouple.
Fig (2). Schematic of the spray pyrolysis system.

The thickness of the films (t) was determined using the weighing-method.

\[ t = \frac{\Delta m}{A \rho} \] ..........................(9)

Where \( \Delta m \) = the mass difference of slide after and before the deposition, \( A \) = area = 2.5×7.5 cm² and ZnO mass density \( \rho \) = 5.6 g/cm³.

The absorbance and the reflectance have been measured for the scanning of electromagnetic spectrum from the range (300-1100nm) by the UV visible, to calculate from these measurements the energy gap and the other optical constants such as refractive index (n), extinction coefficient (k), real and imaginary parts of dielectric constant (\( \varepsilon_1 \) and \( \varepsilon_2 \)).

Results and Discussion

Optical studies:

Optical study of ZnO films was carried out in the wavelength range 200–900 nm at room temperature for the film deposited on glass substrate.

Figures (3) and (4) shows the room-temperature absorbance and transmittance spectra of three samples at different thicknesses 900, 1400, and 4000 nm.
Fig. (3) The absorbance variation with the wave length for different thicknesses films

Fig. (4) The transmittance variation with the wave length for different thicknesses films

Optical Energy Gap

The optical energy gap values \((E_{g\text{opt}})\) for ZnO films have been determined by using Tauc equation. This is used to find the type of the optical transition by plotting the relations \((\alpha h \nu)^{1/2}\), \((\alpha h \nu)^{1/3}\), \((\alpha h \nu)^{2/3}\), and \((\alpha h \nu)^2\) versus photon energy \((h \nu)\). This equation also selects the optimum linear part. It is found that the relation for \(r=1/2\) yields linear dependence, which describes the allowed direct transition. \(E_{g\text{opt}}\) is then determined by the extrapolation of the portion at \((\alpha =0)\) as shown in figures (5), (6) and (7).
Fig. (5) The variation of $(\alpha h \nu)^2$ versus photon energy $(h \nu)$ for 900 nm ZnO film.

Fig. (6) The variation of $(\alpha h \nu)^2$ versus photon energy $(h \nu)$ for 1400 nm ZnO film.

Fig. (7) The variation of $(\alpha h \nu)^2$ versus photon energy $(h \nu)$ for 4000 nm ZnO film.

From the above figures we can see that the increasing of thickness shifts the optical band gap from approximately 3.25 eV at $t=900$ nm to 3.2 eV at $t=1400$ nm then to 3 eV at $t=4000$ nm this can be attributed to a reduction of the defects in the grains and especially at the grain boundaries.
Extinction Coefficient and the refractive index

Fig. (8) shows the variation of extinction coefficient (k) with wave length at different thicknesses. We know that the extinction coefficient depends mainly on absorption coefficient according to the relation (5) for this reason, we notice the increasing of extinction coefficient with increasing photon energy because the absorption coefficient is increased. This means that direct electronic transition happens.

![Graph showing variation of extinction coefficient (k) with wave length for different thicknesses films](image)

Variation of the refractive index versus wavelength in the range 400–900 nm, for different thicknesses are shown in Fig. (9). We can notice from this figure that the refractive index, in general decreases slightly with increasing thickness.

![Graph showing variation of the refractive index n versus wavelength for different thicknesses films](image)
References
A. Ohtomo, K. Tamura, M. Kawasaki, (2001)“Room-temperature stimulated emission of excitons in ZnO/(Mg, Zn)O superlattices”, *Appl. Phys. Lett. 77*