Optical and electrical properties of transparent conducting ZnO films prepared by spray pyrolysis

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Transparent conducting zinc oxide (unintentionally doped) films were prepared by spray pyrolysis using air as the carrier gas. The optical and electrical properties of the films are presented and discussed as a function of the substrate temperature. The optical properties were studied in the ultraviolet (u.v.) visible and near infrared (i.r.) regions. The transmittance data were used to determine the optical constants, the refractive index, *n*, the extinction coefficient, *k*, and the absorption coefficient, α. The reflectivity of the films was calculated and found to be very small in the wavelengths investigated, showing a tendency to increase in the i.r. range in order to act as a host reflector.

1. Introduction

Transparent oxide films with large energy-band gaps and with low electrical resistivities have attracted considerable interest in recent years, because of their potential use as transparent electrodes in optoelectronic devices such as liquid-crystal displays and solar cells [1]. More recently, large-area heat-mirror coatings have been successfully produced on an industrial scale on glass by sputtering and by pyrolytic deposition [2].

ZnO is an inexpensive material with a wide band gap of 3.3 eV. As such, it is potentially suitable for use as a heat-mirror material. The electrical properties of n-type semiconducting ZnO films have been investigated [2, 3]. Their resistivities can be adjusted over several decades by controlling the preparation conditions. In recent years, several groups have studied transparent conductive ZnO films produced by different deposition techniques [4–11]. Solar cells, prepared by depositing ZnO films on CdTe single crystals by spray pyrolysis, have shown conversion efficiencies of 8.8% [12]. ZnO is full of promise for applications in semiconductor gas sensors [13–15]. Therefore, there is sufficient interest to provide the motivation to investigate the effects of film-preparation conditions on the properties of ZnO films, as their constituents are of low cost and are non-toxic.

In this paper, a report is given of the results of an investigation of the electrical and optical properties of the deposited ZnO prepared by spray pyrolysis at different substrate temperatures. It is also intended to demonstrate that this method is more useful than other preparation methods.

2. Experimental procedure

ZnO films were prepared by spray pyrolysis on glass and fused-silica substrates. The spray solution was 0.2 M zinc acetate (99% pure), dissolved in bidistilled water. The air flow rate was $3\,l\,min^{-1}$, and the spraying time was 25 min. The substrate temperature ranged from 380 to 490 °C. The apparatus and details of the deposition have already been reported [16].

Structural analysis was carried out using XRD patterns obtained with a Philip PW 1720 X-ray diffractometer.

Sheet-resistance measurements were performed using a four-point probe. Electrical-resistivity values were derived from knowledge of the film thicknesses, determined from interference extrema of the transmission curve [17].

Hall-effect measurements were carried out using a Newport type electromagnet. The currents through the samples were determined by measuring the voltage across a standard resistor. All the voltages were measured using a Keithley model 610C electrometer. The number of carriers was calculated using the Hall coefficient.

The optical constants, the refractive index, *n*, the extinction coefficient, *k*, and the absorption coefficient, α, were computed from transmittance data measured over the wavelength range $0.25\ \mu m < \lambda < 0.9\ \mu m$, using a spectrophotometer of type PMQ3 from Carl Zeiss.

3. Results and discussion

3.1. Structure results

The unintentionally doped ZnO layers prepared by spray pyrolysis on glass substrates were checked in order to identify and confirm their composition and structure. Typical XRD patterns for the samples are shown in Fig. 1. The position of the main peaks coincided with those given in the ASTM file for ZnO. This shows that the material in the prepared thin films was pure ZnO with a hexagonal wurzite-type structure. The intensity and width of the peaks varied according to the substrate temperature [16].

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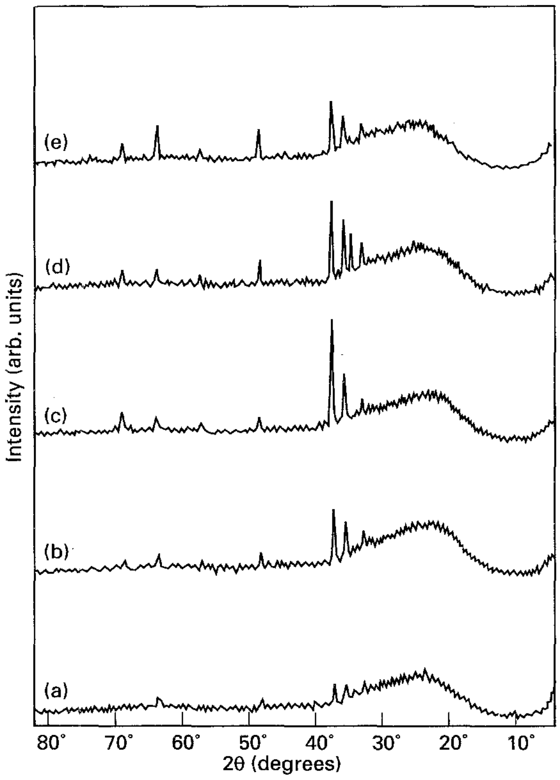

Figure 1 XRD patterns for the ZnO prepared by spray pyrolysis at substrate temperatures: (a) 650 K, (b) 680 K, (c) 700 K, (d) 720 K, and (e) 760 K.

3.2. Electrical properties

Room-temperature sheet-resistance measurements for the as-prepared ZnO films were obtained using four contacts made with silver-paste strips. The electrical resistivity was then calculated for each film, from their thicknesses, t. The resistivity of the films changed from $5 \times 10^{-2}\ \Omega$ cm to $2 \times 10^{-1}\ \Omega$ cm according to the substrate temperature, which was changed from 380 to 490 °C.

The usual preparation conditions for crystals and thin films do not lead to intrinsic ZnO; they lead to an n-type-doped material, even in the absence of foreign dopants [18, 19]. The point defects can be zinc interstitials or oxygen vacancies [17]. The conductivity in the unintentionally doped ZnO prepared by spray pyrolysis was confirmed to be n-type (by Hall-coefficient measurements). The electrical parameters for ZnO prepared at different substrate temperatures are shown in Table I. These results are quite close to previously measured parameters [2].

3.3. Optical properties

The room-temperature transmission, T, of unintentionally doped films of ZnO in the wavelength range 0.25–0.9 μm is shown in Fig. 2. For most of the samples, the transmission was higher than 85%. At shorter wavelengths, T decreased steeply, and it dropped to zero within 3.0 nm. From the intersection of the curve with the $T = 0$ °C axis, the cut-off wavelength, λ_t, was determined, and the energy gap was calculated. For all the samples, the optical energy gap was found to be 3.3 eV. This value is in good agreement with previously reported data [21]. It can be observed that the average optical transmission is independent of the substrate temperature.

TABLE I Room temperature electrical parameters of ZnO films prepared by spray pyrolysis at different substrate temperatures

	T_{subs} (K)	t (nm)	ρ (Ω cm)	R_H ($cm^3\,°C^{-1}$)	n ($\times 10^{18}\ cm^{-3}$)	μ ($cm^{2\mu}\,V^{-1}\,s^{-1}$)
ZnO1	650	200	0.17	476	1.3	28
ZnO5	760	700	0.047	155	4.0	33

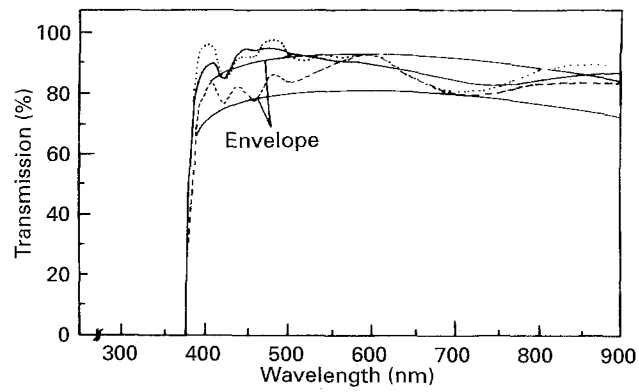

Figure 2 Transmission spectra of ZnO films at substrate temperatures of: (– – –) 380 °C, (——) 420 °C, and (···) 490 °C. It is possible to compute the optical constants from the envelope.

The optical parameters, the refractive index, n, the extinction coefficient, k, and the thickness of the film, t, were calculated from the interference extrema of the T–λ spectra. The method is based on an analysis of the transmittance spectrum of a weakly-absorbing-film/non-absorbing-substrate system [17]. The reciprocal of the transmittance can be decomposed into two components

$$1/T = u(\lambda) - c(\lambda)\,v(\lambda)$$

where $u(\lambda)$ and $v(\lambda)$ consist of exponential and sinusoidal terms, respectively. $u(\lambda)$ and $v(\lambda)$ can be calculated as follows:

$$u(\lambda) = \frac{T^+(\lambda) + T^-(\lambda)}{2T^+(\lambda)\,T^-(\lambda)}$$

$$c(\lambda) = \frac{T^+(\lambda) - T^-(\lambda)}{2T^+(\lambda)\,T^-(\lambda)}$$

where $T^+(\lambda)$ and $T^-(\lambda)$ are the values of T, deduced from the experimentally traced envelope curves of the transmission spectrum, shown on a representative sample in Fig. 2.

The refractive index, n, the extinction coefficient, k, and the thickness, t, are given by

$$n(\lambda) = 1/2\{[8n_s c(\lambda) + (n_s + 1)^2]^{1/2} - [8n_s c(\lambda) + (n_s - 1)^2]^{1/2}\}$$

$$t = \left\{2\left[\frac{n(\lambda_i)}{i} - \frac{n(\lambda_{i+1})}{i+1}\right]\right\}^{-1}$$

$$K(\lambda) = \frac{\lambda}{4\Pi t}\ln\frac{u - (u^2 - c^2 + \sigma)^{1/2}}{2a_+}$$

where

$$\sigma = \left(\frac{n_s^2 - 1}{8n_s}\right)^2 \left(n - \frac{1}{n}\right)^2$$

$$a_+ = \frac{(n+1)^3(n+n_s^2)}{16n_s n^2}$$

where n_s is the refractive index of the substrate, i is the order of the interference maximum, and λ is the wavelength at the ith maximum. The film thickness was found to increase as the substrate temperature increased. Table I shows the results of the calculations.

The variation of the refractive index with the wavelength, as calculated from the above method, is shown in Fig. 3. It is interesting to note that each curve showed a minimum; no systematic variation in the position of the minimum could be detected. These irregularities may be attributable to the defect concentration [2].

Fig. 4 presents the variation of the calculated values of the extinction coefficient, k, with the wavelength, λ. Calculations were carried out for more than one thickness. The common feature of the graphs is an increase in k as λ increased; this can be attributed to an approach to the plasma wavelength λ_p, where λ_p, defined when $n^2 - k^2 = 0$, characterizes a free-electron plasma. For wavelengths $\lambda > \lambda_p$, collective oscillations of electrons create a strongly reflective plasma; this is commonly observed in the high reflectivity of metals to visible light. For ZnO films, $\lambda_p = 2.8$ µm [6], and therefore a reflection should be observed in the i.r. Accordingly, k is expected to increase with wavelength until it eventually equals n in the i.r. region. Fig. 5 shows the variation of k with the film thickness, t. Fig. 5 shows that k decreased as t increased.

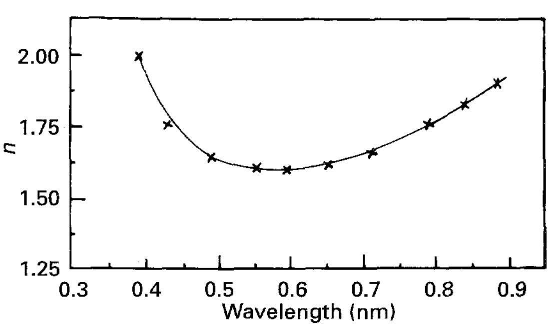

Figure 3 The spectral variation of the refractive index, n, at room temperature for the ZnO films.

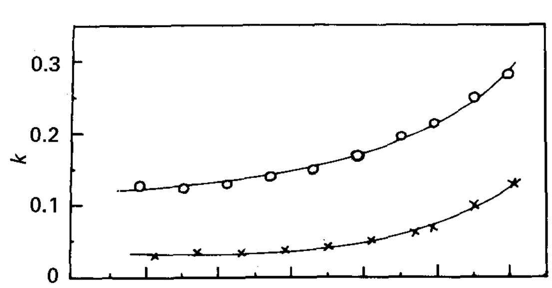

Figure 4 The variation of the calculated extinction coefficient, k, with the wavelength for ZnO films, for thicknesses, t, of: (×) 200 nm, and (○) 700 nm.

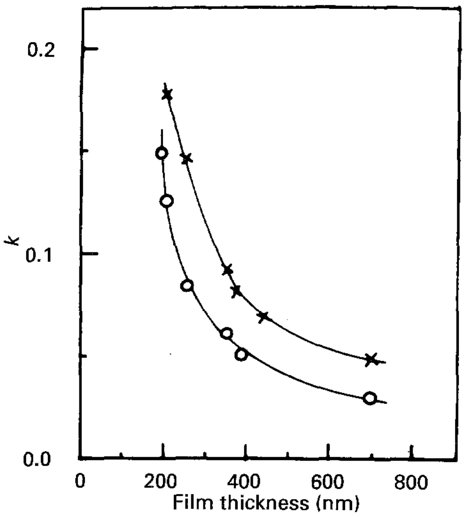

Figure 5 The variation of k with t for ZnO films prepared by spray pyrolysis, for wavelengths, λ, of: (×) 0.7 µm, and (○) 0.5 µm.

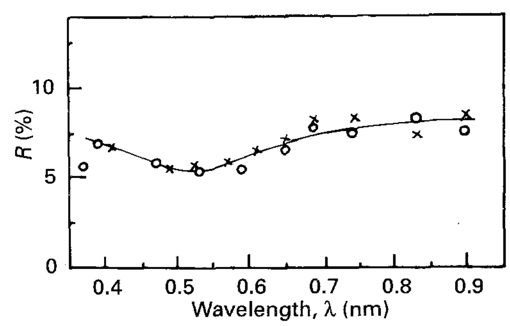

Figure 6 The reflectivity computed as a function of the wavelength for the ZnO films: (×) t = 200 nm, and (○) t = 700 nm. The reflectivity was independent of the film thickness.

The reflectivity of the ZnO samples, in the present investigations, was not measured experimentally. After having obtained values for n and k, it was thought worthwhile to calculate the value of R at different wavelengths from the classical relation

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

Fig. 6, shows R calculated for $0.25 < \lambda < 0.9$ µm. The values of R go through a minimum in the green region of the spectrum. R was found to be independent of the sample thickness; its values are within the range reported in [2].

The small values of n ($\simeq 1.7$) for ZnO in the visible range are a desirable property, since they result in a low reflectivity and accordingly in a high transmissivity in this wavelength range as

$$R = \frac{(1.7-1)^2}{(1.7+1)^2} \simeq 7\%$$

while for Si, where $n = 3$

$$R \simeq 25\%$$

Thus ZnO films can be used as antireflective layers in Si solar cells.

4. Conclusion

ZnO films with high spectral selectivities and low electrical resistivities were prepared by the spray-pyrolysis technique. The coated material has potential applications to energy efficiency, among other possible applications. The optical and electrical properties were studied by measuring optical transmission spectra, the electrical resistivity, the carrier concentration and the Hall mobility. It should be noted that the present coatings are based on a cheap and abundant base metal which avoids potential problems related to toxicity, and it can have a short-wavelength transmittance which is higher than in noble-metal-based coatings.

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