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The effects of deposition variables on spray-deposited ZnO thin film prepared from $Zn(C_2H_3O_2)_2$

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Undoped ZnO thin films have been prepared by a modified spray technique under various deposition conditions and the effects of the different deposition variables on the electrical and optical properties of the prepared films have been studied in detail. Substrate temperature has been found to be the most important parameter for the deposition process. To obtain a low resistive highly transparent ZnO film with appreciable Hall mobility and carrier concentration, a post-deposition heat treatment in vacuum is always necessary and is a precondition for undoped films. From the study of the optical transmission spectra in the visible and near-UV regions it was observed that the films are highly transparent (98%) in the visible range. The fundamental absorption edge of the films lies in the UV region. Values of refractive indices of these films were also determined.

1. Introduction

In recent years increase demand of low cost transparent conducting films have been noticed because of their immense application in various energy efficient purposes. As a thin layer non-stoichiometric material ZnO, SnO_2, In_2O_3 etc. have proved useful for these purposes. These layers are easy to deposit and are generally chemically stable in ordinary environmental conditions. Of all the transparent conducting materials ZnO is relatively less expensive and possesses a very sharp UV cut off and are therefore advantageous in many cases. There are many processes [1–4] by which these layers can be prepared on glass substrates but the well known pyrosol process [5, 6] is one of the easy and least expensive methods suitable for the deposition of ZnO thin films. Because of the extreme simplicity in the process itself, the number of deposition variables increases and precise control over all the associated variables becomes rather difficult. The properties of the resulting films therefore vary, as reported by different workers, even when the deposition conditions are kept almost the same. On spray deposited films there is a volume of literature on tin oxide and indium oxide films but for ZnO films the reports are only very limited [7] and work is still needed to understand the various properties of this film.

Very recently we have designed a low cost apparatus [6] for the deposition of thin films by a pyrosol process. By this apparatus the control of deposition variables are comparatively easy and high quality undoped ZnO thin films have been prepared in our laboratory for the application as transparent electrodes. In the present paper we have reported the effects of various deposition parameters on the properties of the deposited ZnO film both in the as-deposited and heat treated conditions. All the experimental samples are undoped in the sense that no intentional dopant has been used during the film deposition process but since the process is a chemical one, the presence of unintentional impurity dopants cannot be ruled out.

2. Experimental details

In the pyrosol process there are very many deposition variables [6] (the parameters of the process) such as substrate temperature, spray rate, composition and concentration of the working solution, time of deposition, substrate to source (mouth of the aerosol supplying tube) distance, etc. Some of these variables are mutually dependent on each other. However to study the effects of any one of these variables the remaining others must be kept reasonably constant.

2.1. Sample preparation

The film deposition process is shown schematically in Fig. 1. To have a sufficient quantity of aerosol supply a number of separate aerosol production units U_1, U_2, U_3 (Fig. 1a) can be used in parallel. For the present purpose we have used three such units (Fig. 1b). The reactor was a 12 cm long vertical pyrex glass cylinder provided with a heater at the bottom. The whole set up was kept in a closed chamber with a suitable exhaust mechanism. A constant aerosol supply rate was maintained throughout the whole experiment by adequately adjusting the air pressure. Microscope glass sides (from Corning glass works, USA) were used as substrates.

Aqueous solution of reagent grade $Zn(C_2H_3O_2)_2$ of various concentrations (0.1 to 0.4 M) were used as the working liquid. No alcohol was used. Substrate temperature, T_s, was controlled by an electronic power controller attached to the heater and measured by a chromel–alumel thermocouple attached to the substrate. An uncertainty in T_s of about $\pm 5^\circ$ C was

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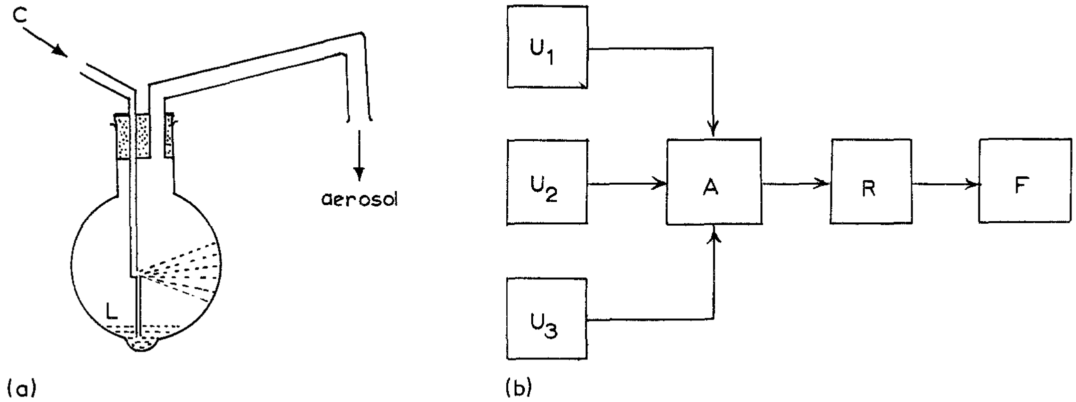

Figure 1 Process of film deposition showing (a) detail of the aerosol production unit (U); C – compressed air inlet and L – working liquid. (b) Schematic diagram showing the arrangement of the apparatuses. U_1, U_2 and U_3 are aerosol production units; A – aerosol accumulator, R – reactor and F – film formation section.

unavoidable. The initial air pressure to produce the aerosol from the working liquid was 20 lbs in^{-2} (137.9 KPa) but the aerosol reaches the substrate at almost normal pressure. When the aerosol passes through the reactor chamber it undergoes a complicated reaction process of pyro-hydrolysis and ZnO films are formed there on a glass substrate placed over the heater. Due to the slow decomposition rate of the acetate solution the film deposition rate is rather slow, about 10 nm min^{-1} at a solution concentrtion of 0.4 M and at 0.8 ml min^{-1} of liquid flow rate. The special aspects of the present approach were that the aerosol supply rate was kept near to its lower limit about 0.8 ml min^{-1}, the solution was not alcoholic and the substrate temperature (~ 300° C) was comparatively low. Also the aerosol production section and the film formation sections were widely separated from each other so that small very uniform droplets can only reach the substrate surface via a virtual filtration process in the aerosol production section. Good quality films are thus obtained.

2.2. Measurements

Film thickness was measured by the Tolansky interferometric method and the resistivity and Hall coefficients were determined by the Van der Pauw four-point probe method with appropriate correction factors. The optical transmissions in the visible and ultraviolet ranges were determined by a double beam spectrophotometer (Shimadzu UV-180). Structural properties were studied by electron microscopic observations. Digital multimeters (Hewlette Packard 3465A, USA) were used for the electrical measurements. Post-deposition heat treatments of the films were performed in a vacuum of the order of ~ 10^{-5} torr for an hour at a constant temperature of 250° C.

3. Results and discussion

3.1. Physical structure

All the films (deposited at $T_s \gtrsim 300°$ C) were found to show a granular polycrystalline structure with a very small grain size uniformly distributed over the enitre film area and the samples have a very smooth surface. The films (about 0.2 μm thick) appear so clear and transparent to a normal eye that it was very hard to distinguish between the coated and uncoated portion of the substrate.

3.2. The effect of substrate temperature

The substrate temperature T_s is the most important parameter in the pyrosol process. Fig. 2 shows the variation of film thickness t with the substrate temperature T_s at a constant deposition time, t_d of 20 min. The solution concentration was 0.4 M. This shows that at about 270 to 300° C the average growth rate is maximum and is about 15 nm min^{-1} which gradually comes down to 4.0 nm min^{-1} at higher substrate temperatures. Above 300° C the growth process is thermally activated. The activation energy E_{act} for the film growth process is found to be 0.35 to 0.4 eV in the temperature range 300 to 420° C. Below 270° C no stable ZnO film has been obtained except a deposit of white powder perhaps of unreacted acetate which was easily removable from the substrate.

The variation of resistivity ϱ with T_s is shown in Fig. 3 curve (a) for the as-deposited films of ZnO of thickness about 0.2 μm. The minimum value of ϱ observed in the present case is 12 Ω cm obtained at a substrate temperature of 360° C. The same set of films after a vacuum heat treatment at 250° C for an hour shows the T_s against ϱ variation to be almost similar

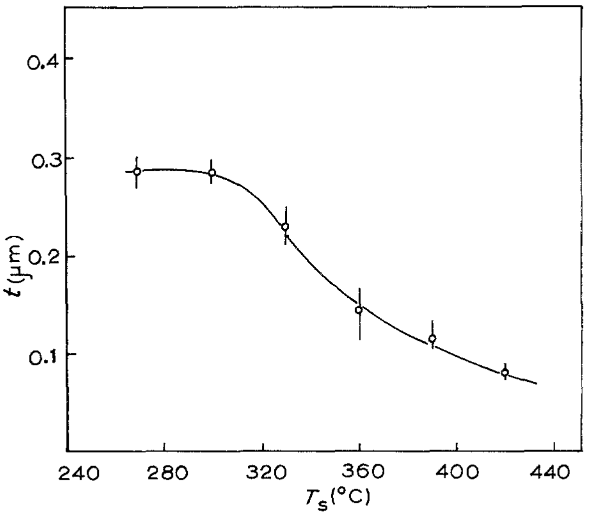

Figure 2 Variation of film thickness t with the substrate temperature T_s.

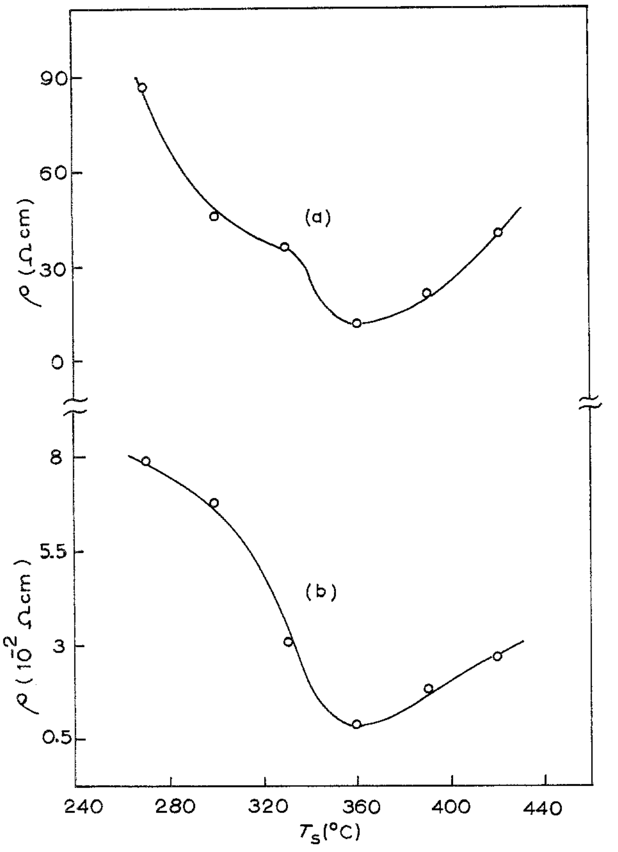

Figure 3 Variation of resistivity ϱ as a function of substrate temperature T_s, (a) for as-deposited films and (b) for the same set of films but after a vacuum heat treatment.

to that of the as-deposited set but with the magnitude of ϱ drastically decreased. The minimum value of ϱ for the heat treated film is $8.3 \times 10^{-3}\,\Omega\,\text{cm}$, shown in Fig. 3 curve (b).

The Hall mobility μ and carrier concentration N of the heat treated films were measured and the variations of μ and N with T_s are shown in Fig. 4 by curves (a) and (b) respectively. It is observed that both μ and N have maxima at $T_s = 360°\,\text{C}$. The carrier concentration and conductivity $(1/\varrho)$ decrease towards either side of this T_s value. Hall mobility varies from ~ 9 to $21\,\text{cm}^2\,\text{V}^{-1}\,\text{sec}^{-1}$ in the carrier concentration range 1×10^{19} to $3.77 \times 10^{19}\,\text{cm}^{-3}$. All of the films were found to show n-type conductivity.

The n-type conductivity in undoped non-stoichiometric ZnO is generally accepted as due to the lattice oxygen deficiency and interstitial zinc atoms which act as donors [8]. The resistivities of the as-deposited films are high and this is probably due to the grain boundary effects since the films are polycrystalline in structure. It is expected that a large number of oxygen (O_2^{1-}) molecular ions are chemisorbed in the film at the time of their deposition and these oxygens are largely incorporated at the grain boundaries and on the surface of the film producing potential barriers which hinder the conduction process. According to a model suggested by Fujita and Kwan [9] when these films are heat treated the chemisorbed O_2^{1-} desorbed from the sample donating an electron to the zinc oxide ($O_2^{1-} \rightarrow O_2 + e$), hence causing the resistivity to decrease drastically. This is due to a cumulative effect of lowering of grain-boundary potentials and increase of carrier concentration in the sample. On the other hand in the crystalline lattice the ions have a closed outer shell and the energy band arise from the filled 2p levels of the O^{2-} ion and the empty 4s levels of the Zn^{2+} ion. If the crystal is now caused to lose oxygen by heat treatment, the ions escape as neutral molecules (O_2) leaving two electrons per atom behind. They, in turn, combine with the Zn^{2+} ion in an interstitial position to produce a neutral zinc atom. One electron is then easily ionized into the conduction band from a zinc atom in this position [10]. Thus the conductivity of the heat treated film may easily increase. In as-deposited films however it was very difficult to observe any appreciable Hall effect.

With the increase of substrate temperature from 270 to 360° C the crystallinity of the films improves and causes the Hall mobility to increase (Fig. 4). When the temperature increases above 360° C (thermally activated growth region), the film tends to attain a

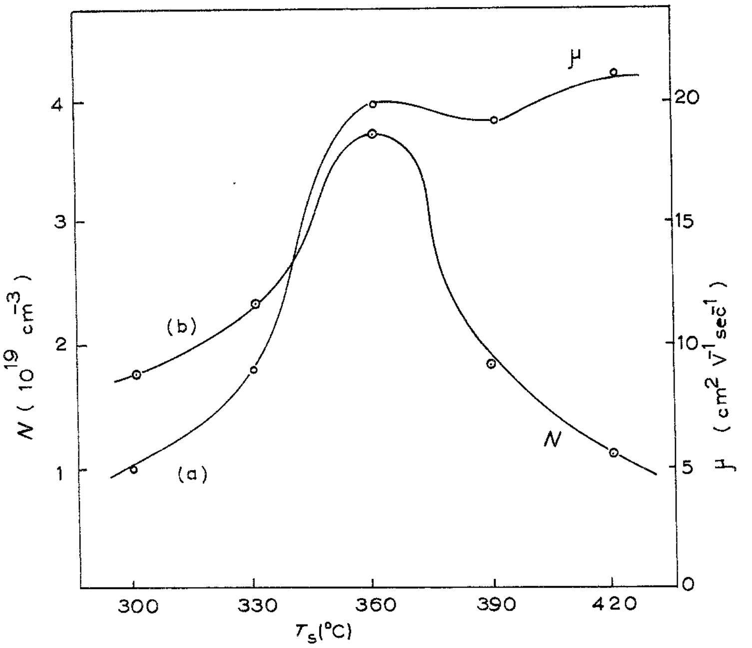

Figure 4 The variation of (a) Hall mobility μ and (b) carrier concentration N of some vacuum heat treated films of ZnO with the substrate temperature T_s. The ϱ against T_s plot for these films are shown in Fig. 3 curve (b).

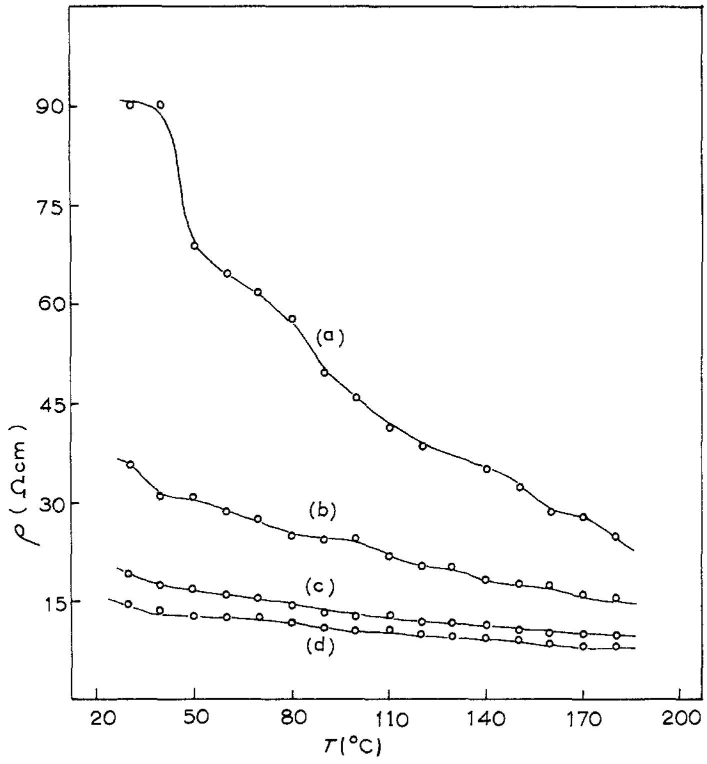

Figure 5 Variation of resistivity ϱ as a function of temperature T for some as-deposited films of ZnO when they are heat treated in normal atmosphere. Different curves are for films having different deposition temperatures T_s. (a) T_s = 270° C; (b) T_s = 330° C; (c) T_s = 390° C and (d) T_s = 360° C.

relatively better stoichiometry and the carrier concentration decreases. This, in turn, increases the resistivity [8] (Fig. 3).

3.3. The effect of heat treatment in normal atmosphere

Some of the as-deposited samples having various deposition temperatures were subjected to a heat treatment in normal atmosphere and their temperature dependence of resistivity were studied in the temperature range 30 to 180° C. Fig. 5 shows the variation of resistivity as a function of temperature T. It is observed that the resistivity decreases almost linearly with the increasing temperature. The values of thermal activation energy for the ionization of donors have been calculated from the ln σ against T^{-1} plot using an uncompensated extrinsic semiconductor model for the samples, and are shown in Table I. It can be noticed from this table that the film deposited at 360° C has the lowest activation energy as expected, and there exists a single activation energy in the temperature range investigated. These activation energies may correspond to donor levels of various depths and origins [11–13], and are not clearly known at present for our as-deposited ZnO samples. The values of temperature coefficient of resistivity (TCR) are all negative which shows the semiconducting nature of the samples.

TABLE I Values of thermal activation energy ΔE and *TCR* of some as-deposited films of ZnO prepared at different substrate temperatures

Substrate temperature (° C)	Investigated temperature range (° C)	Activation energy ΔE (eV)	*TCR* (10^{-3} °C^{-1})
270	30–150	0.174	−5.71
330	30–150	0.133	−4.26
360	30–150	0.084	−3.12
390	30–150	0.114	−3.69

3.4. The thermoelectric power

The thermoelectric power (TEP), Q, of some as-deposited samples were measured in the temperature range 27 to 150° C by taking pure metallic lead (Pb) as reference metal. The details of the method of

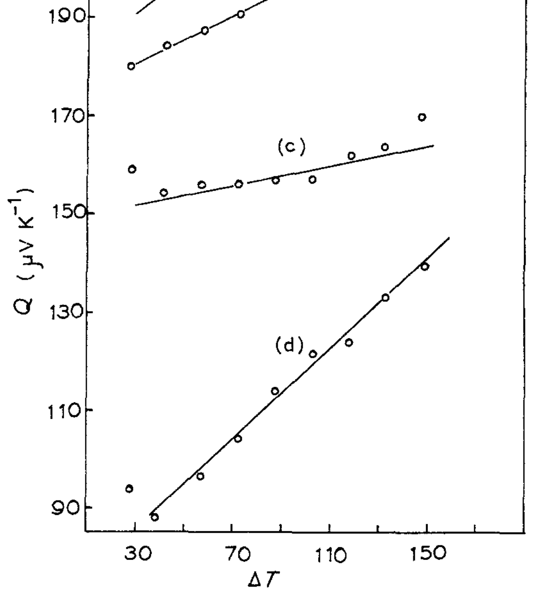

Figure 6 Variation of the thermoelectric power Q as a function of temperature ΔT. Different curves are for samples having different deposition temperatures T_s. (a) T_s = 300° C; (b) T_s = 330° C; (c) T_s = 390° C and (d) T_s = 360° C.

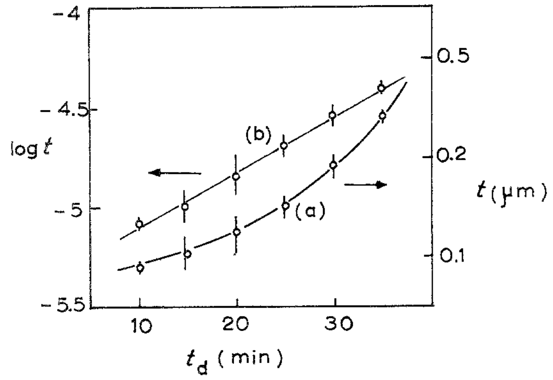

Figure 7 (a) Variation of film thickness t with the deposition time t_d, and (b) a plot of log t against t_d.

measuring the TEP values may be obtained elsewhere [14]. The variation of TEP with temperature is shown in Fig. 6. It is observed that TEP increases linearly with the increasing temperature. Here different curves represent samples having different deposition temperatures. At room temperature the TEP is a minimum for films deposited at 360° C and maximum for films deposited at ~300° C.

3.5. The effect of deposition time on film thickness

ZnO films were deposited at a constant temperature of 360° C taking deposition time as a parameter. In Fig. 7 curve (a) shows that the film thickness t increases non-linearly with the deposition time t_d. It has been observed that log t varies approximately linearly with t_d as shown by curve (b) of the same figure. It is evident from these curves that the rate of deposition gradually increases with the increasing deposition time. This is probably due to the fact that, after deposition of a certain thickness of the film it becomes energetically more favourable for the rest of the film to grow more easily on the deposited layer. Similar behaviour was also noticed [6] in the case of SnO_2 film when deposition was carried out by the same apparatus.

3.6. Effect of solution concentration

Fig. 8 shows the variation of film thickness with the working solution concentration. This shows a linear relationship between these two parameters in the concentration range 0.1 to 0.4 M. This is quite natural, of course up to a certain maximum limit, since an increasing supply of reactant should increase the product accordingly. It can be said here at least that, this maximum has not been reached up to 0.4 M solution.

3.7. Effects on optical properties

The optical transmission spectra of the films prepared at various substrate temperatures are shown in Fig. 9. Measurements have been taken in the wavelength range 280 to 900 nm on the as-deposited as well as on the heat treated films of almost equal thicknesses. No detectable change in the optical transmission has been noticed due to heat treatment. The transmission coefficient (T%) of the film prepared at 390° C is found more than 97% at about 550 nm. All the samples were found to show a sharp UV cut-off at about 370 nm. The visible transmission decreases with the decrease of substrate temperature. At lower temperatures $T_s \lesssim 300°$ C the films become slightly hazy and optical transmission falls. It is probably due to incorporation of some white powdery precipitate in the film formed at lower substrate temperature because of incomplete reaction system.

The refractive index was calculated from these transmission data was found to lie within 1.54 to 2.02 in the visible region for films deposited at $330° \text{C} \leqslant T_s \leqslant 390°$ C. Also the optical band gap E_g has been graphically determined from the same data. It was found that for both the transitions, direct allowed and forbidden, the band gap is almost the same and is about 3.26 eV at room temperature. This value of E_g is in excellent agreement with the reported value of 3.3 eV for bulk zinc oxide crystal [8, 15].

4. Conclusion

Various deposition parameters have remarkable effects on spray-deposited ZnO thin film on glass substrates when prepared by the technique described in this article. Aqueous solution of zinc acetate with concentration of about 0.4 M and a spray rate of about 0.8 ml min^{-1} lead to an appreciable film growth rate at 300° C of substrate temperature. To obtain low resistive undoped ZnO film, a substrate temperature of 360° C is found to be adequate and then the deposited films reveal a polycrystalline structure. In the as-deposited condition no appreciable Hall effect has been observed in these samples and the minimum value of film resistivity is of the order of several Ω cm. A post-deposition heat treatment in vacuum causes

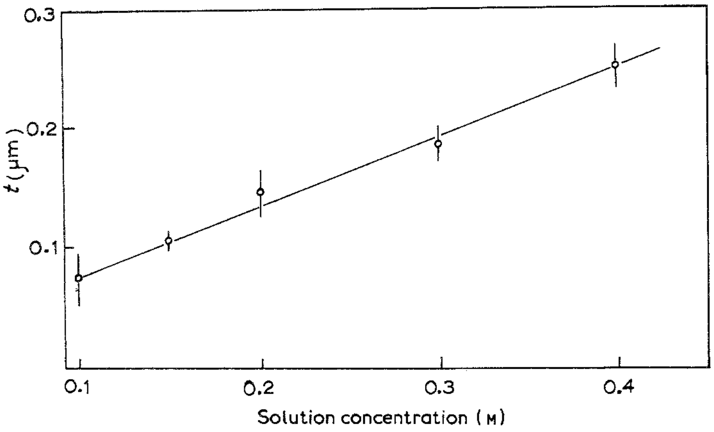

Figure 8 Linear dependence of film thickness t on the concentration of the working solution.

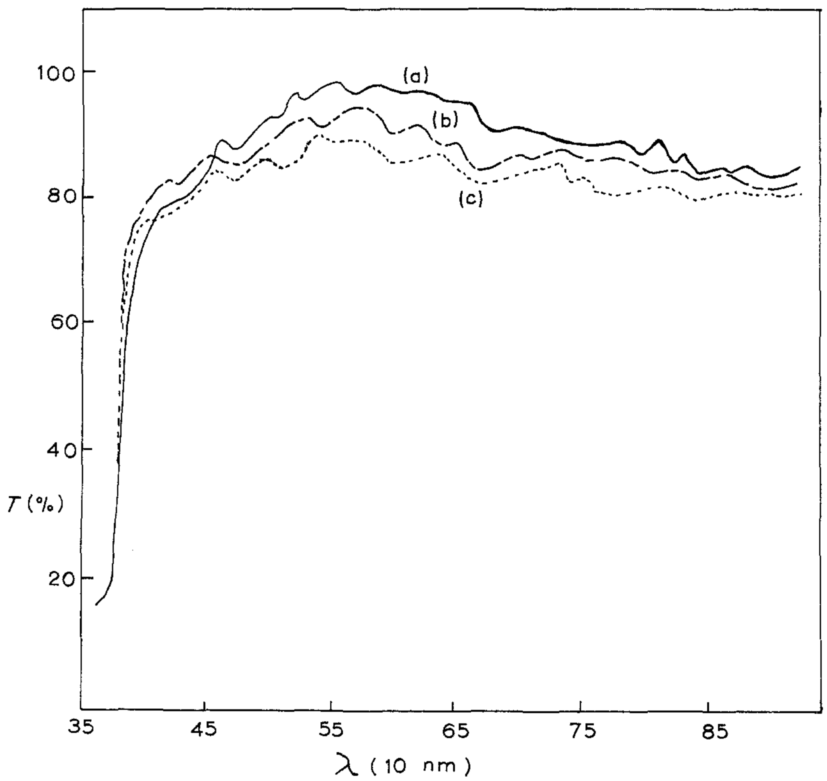

Figure 9 Transmission spectra of spray-deposited ZnO thin film. Deposition temperature of the samples are (a) T_s = 390° C; (b) T_s = 330° C and (c) T_s = 270° C.

the resistivity to decrease drastically and only then appreciable Hall mobility is observed. The carrier concentration of the heat treated film is of the order of $\sim 10^{19}\,\mathrm{cm}^{-3}$. The films are highly transparent in the visible range of wavelengths and possess a very sharp UV cut-off at about 370 nm at room temperature. The calculated band gap of the specimen is found about 3.26 eV. The value of film refractive index varies from 1.54 to 2.02 in the visible wavelengths.

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