

## CHEMICAL DEPOSITION OF ZnO FILMS

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A method for the deposition of ZnO thin film from an aqueous solution of a zinc complex has been developed. The resistivity of the film could be varied by two orders of magnitude by doping with  $\text{Sn}^{2+}$  during the deposition process. The resistivity was drastically reduced by annealing in an argon atmosphere. The film obtained using this method showed slow response photoconductivity with a dark-to-light resistivity ratio of  $10^4$ .

## 1. INTRODUCTION

Zinc oxide thin films offer a variety of applications. The low conductivity, highly oriented film can be used as an ultrahigh frequency electroacoustic transducer because of its piezoelectric property<sup>1,2</sup>. The medium conductivity thin film is an n-type semiconductor and can be used with an appropriate p-type semiconductor as a heterojunction in the field of photovoltaic conversion of solar energy<sup>3,4</sup>. The high conductivity ZnO thin film with a high transparency in the visible spectrum can be used as a transparent electrode in the field of optoelectronic displays and in the field of photovoltaic solar energy conversion as well<sup>5,6</sup>. ZnO thin films can be used in electrophotography and also as a gas sensor<sup>5</sup>.

There are numerous methods for the preparation of ZnO thin films, such as sputtering<sup>2,6-8</sup>, vapour deposition<sup>1,7,9</sup> and spray pyrolysis<sup>3,4</sup>. Chemical deposition of thin films from aqueous solutions is a very promising method because of its simplicity and economy. Chemically deposited ZnO thin film was obtained as a byproduct in an attempt to prepare the composite  $\text{Cd}_x\text{Zn}_{1-x}\text{S}^{10}$ .

The method described here enables the deposition of ZnO thin film with a thickness and conductivity which can be controlled during the preparation procedure. The deposition can be performed onto any kind of substrate that is inactive with respect to the chemicals used.

## 2. EXPERIMENTAL DETAILS OF THE FILM PREPARATION

To prepare the ZnO thin films we used a technique of successive immersion of

the substrate into two separate solutions, a technique already employed for  $\text{Cu}_2\text{O}$  thin film preparation<sup>11</sup>. Four different solutions of  $\text{Zn}^{2+}$  complexes were used for this. The first was an aqueous solution of  $(\text{NH}_4)_2\text{ZnO}_2$  prepared in the following way. Concentrated  $\text{NH}_4\text{OH}$  was poured into  $100\text{ cm}^3$  of  $0.5\text{ M}$   $\text{ZnCl}_2$  or  $\text{ZnSO}_4$  until a white precipitate of  $\text{Zn}(\text{OH})_2$  was formed. On the further addition of  $\text{NH}_4\text{OH}$  the precipitate dissolved. The solution was diluted to  $500\text{ cm}^3$  to obtain a  $0.1\text{ M}$  solution of the  $\text{Zn}^{2+}$  complex which was found to be the most convenient concentration to produce a good quality film.

The second solution was an aqueous solution of  $\text{Na}_2\text{ZnO}_2$ , prepared in a similar way to the first, in which  $\text{NH}_4\text{OH}$  was substituted by  $\text{NaOH}$ .

The third solution was a complex solution of  $\text{Zn}(\text{OH})_2$  in  $\text{NaCN}$  obtained by adding granular  $\text{NaCN}$  to the white precipitate of  $\text{Zn}(\text{OH})_2$  and diluting to  $500\text{ cm}^3$  to obtain a  $0.1\text{ M}$  complex solution.

The fourth solution was  $0.1\text{ M}$  aqueous  $\text{ZnCl}_2$ .

A thin film of  $\text{ZnO}$  formed on the substrate on decomposition of the  $\text{Zn}^{2+}$  complex in hot water ( $95\text{--}100^\circ\text{C}$ ).  $\text{ZnO}$  thin films were deposited onto glass, quartz and mica substrates and the physical properties such as crystal structure, optical transmittance, conductivity and photoconductivity were examined.

A clean substrate was immersed first in a cold solution of the complex and then in boiling water for  $1\text{--}2\text{ s}$ . In this way the substrate was covered with a thin layer of the complex solution which decomposed to  $\text{ZnO}$  when placed in boiling water. Part of the  $\text{ZnO}$  so formed was deposited onto the substrate as a strongly adherent film and part of it formed a precipitate.

The technique of immersion of the substrate into separated chemicals (a cold solution of the  $\text{Zn}^{2+}$  complex first and hot water second) effected a constant increase in the thickness for each immersion, so that the final thickness of the film was determined by the number of immersions. Using the concentrations mentioned a yellow interference appeared after  $24\text{--}25$  immersions. Continuing with successive immersions, the interference colour changed to red, violet, green and yellow again. In this way, it was possible to monitor the film growth visually. The thickness of the film was calculated from the mass of equally coloured parts of the film and it was found that the change in the interference colour from red to red corresponded to an increase of  $0.17\text{ }\mu\text{m}$  in the film thickness. The rate of increase in the thickness was constant because the concentration of the solutions was constant during the growing procedure. This is because immersion of the substrate does not change the concentration, and because the chemical reaction, namely the decomposition of the ammonia complex occurs at the interface between the substrate and the hot water.

The higher  $\text{Zn}^{2+}$  complex concentration gave a higher growth rate but the quality of the film was poor since it contained a powder-like deposit. In order to obtain a highly transparent film it was necessary to rub down the film with a piece of cotton after the first immersion. In this way the weakly adherent microcrystals were removed while the strongly adherent microcrystals remained on the surface. These crystals then serve as nuclei for further growth and therefore if the first layer is of good quality further growth will continue with the same quality.

The highest growth rate was obtained in the case of preparation using the ammonia complex solution and the lowest growth rate was obtained from pure

ZnCl<sub>2</sub> solution, which was about five times slower. The best film quality (high transparency) was obtained from the ammonia complex solution. For this reason, all the films used for examination of the physical properties were prepared from the ammonia complex solution.

### 3. PHYSICAL PROPERTIES OF ZnO FILMS

X-ray diffraction spectra and optical transmission spectra were obtained and the temperature variations in the resistivity and in the photoconductivity of the ZnO films were measured for films of thickness 0.85 μm by monitoring the fifth appearance of the red interference colour. A scanning electron micrograph of the film surface is given in Fig. 1 with a magnification of 4500×. The X-ray spectrum obtained using the Debye–Scherrer method is presented in Fig. 2. For comparison the diffraction spectrum of a ZnO standard is presented in the same figure (lower spectrum).



Fig. 1. Scanning electron micrograph of a ZnO thin film. (Magnification 4500 ×.)

From this it can be concluded that the deposited film is pure ZnO and that any impurities are present in concentrations below the limit of detection. The pronounced peak at  $2\theta = 34.4^\circ$  in Fig. 2 with respect to the same peak of the standard shows that the preferred orientation of the microcrystals of the film is along the *c* axis normal to the substrate surface. The same preferred orientation of the microcrystals was found in the case of ZnO films prepared using other methods<sup>1,6,12</sup>.

The film obtained using this method showed slow response photoconductivity and a dark resistivity as high as  $10^7 \Omega \text{ cm}$ . This indicates that the film has fairly good stoichiometry. Under ordinary daylight illumination the resistivity decreased to  $10^6 \Omega \text{ cm}$ . Doping of the film with Sn<sup>2+</sup> during the growth procedure by adding  $10 \text{ cm}^3$  of 0.1 M Na<sub>2</sub>SnO<sub>2</sub> or SnCl<sub>2</sub> decreased the dark resistivity by two orders of magnitude. Annealing of the undoped film in an open atmosphere decreased the

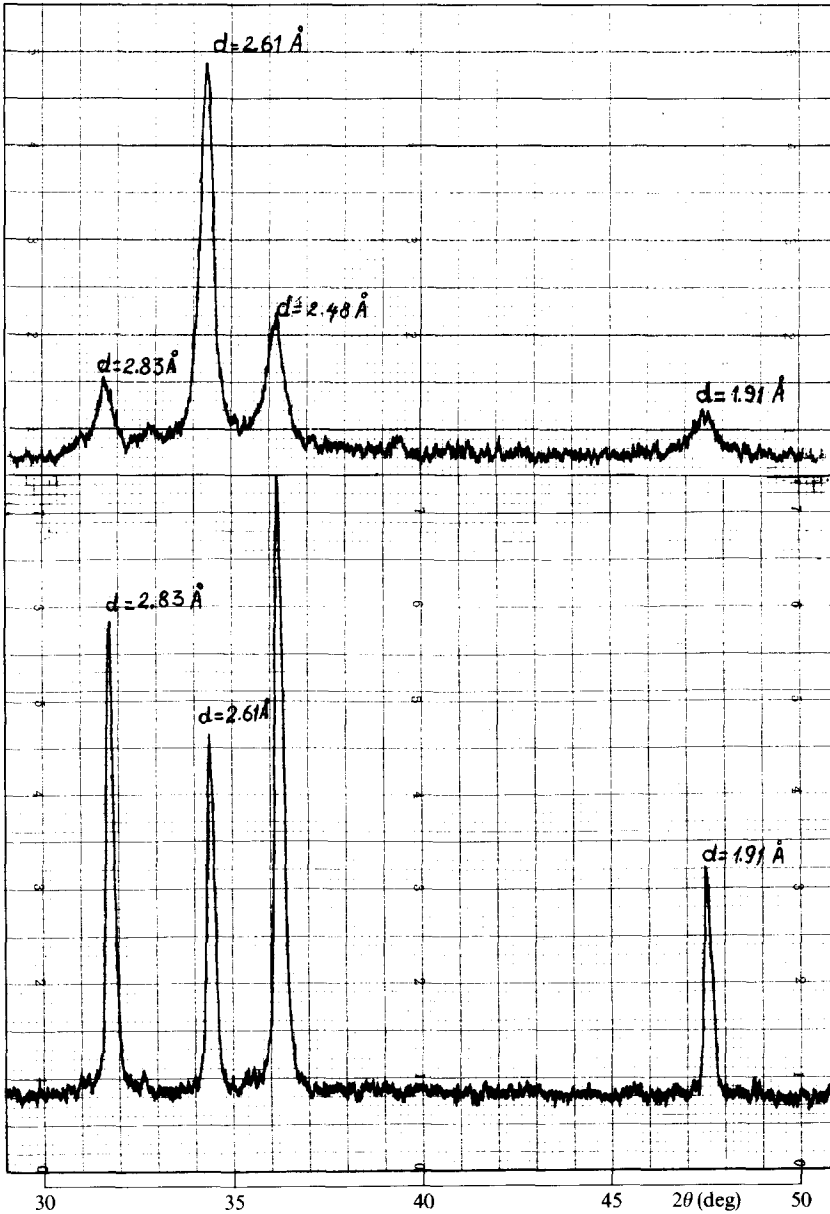


Fig. 2. X-ray diffraction spectra of a ZnO thin film (upper spectrum) and of a ZnO standard (lower spectrum) (wavelength  $\lambda = 1.54050 \times 10^{-10}$  m, nickel-filtered  $K\alpha$  radiation).

resistivity by two orders of magnitude. The resistivity of both undoped and doped films was drastically reduced by  $100 \Omega \text{ cm}$  on annealing the films in an argon atmosphere at  $400^\circ \text{C}$ , which was found previously for films obtained using other methods<sup>4,10</sup>. It was also found that the resistivity can be decreased by diffusion of cadmium after immersion of the film in molten cadmium.

The transmission spectrum of a ZnO film with a thickness of 0.85  $\mu\text{m}$  measured using a Pye–Uvicam spectrophotometer is presented in Fig. 3, in which it can be seen that there is a high transmission region (over 90%) with a sharply defined absorption edge at 360 nm which corresponds to an energy band gap of 3.2 eV. The transmission spectrum of tin-doped ZnO film, presented in the same figure (curve b) shows the same fundamental absorption edge but not so sharply defined. The undulating shape of the transmission curves is caused by interference of the light in the film itself.

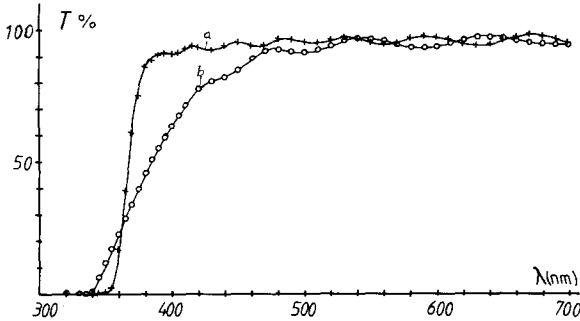


Fig. 3. Optical transmission spectrum of ZnO thin films: curve a, undoped; curve b, doped.

Both the undoped and doped films were provided with silver electrodes 0.5 cm apart painted on one face of the substrate using silver paste. The ZnO film deposited onto the other side was removed by dissolution in HCl. Although the silver electrodes were non-ohmic they were used for high temperature examinations. The ohmic contact was obtained by depositing a thin layer of HgS on the surface prior to painting with silver paste. The film prepared in this manner was placed in a thermostat in the dark in order to eliminate photoconductivity. The resistivity  $R$  was measured at elevated temperatures  $T$  from 100 to 300  $^{\circ}\text{C}$ . The measurements showed that the behaviour of the film was typical of a semiconductor, *i.e.* the resistivity followed the relation  $R = R_0 \exp(E/kT)$  where  $R_0$  is the initial resistivity,  $E$  is the energy and  $k$  is Boltzmann's constant. A plot of  $\ln R$  vs.  $1/T$  is presented in Fig. 4 for an undoped film and straight lines were obtained with activation energies of 0.50 and 1.69 eV. These values agree with those previously found for sintered ZnO samples<sup>13</sup>.

The resistivity of ZnO films obtained using this method was very high (as high as  $10^7 \Omega \text{ cm}$ ) and decreased slowly under illumination, reaching a steady value after 2–3 h. The steady state conductivity, which was measured for illumination up to  $80 \text{ mW cm}^{-2}$ , was found to be proportional to the light intensity. The variation in the dynamic conductivity was followed by switching the illumination on and off and measuring the resistivity at 1 min intervals after the illumination was switched off initially, and at 5–10 min intervals later. The rise and fall of the photoconductance  $Y$  for tin-doped ZnO film is presented in Fig. 5 for monochromatic illumination at  $\lambda = 390 \text{ nm}$ . As shown, the conductance did not reach a stationary value even after 1 h. Although the decay of the conductance resembles an exponential fall, it is not truly exponential since  $\ln(R/R_0)$  vs.  $t$  where  $t$  is the time is not a straight line. The plot

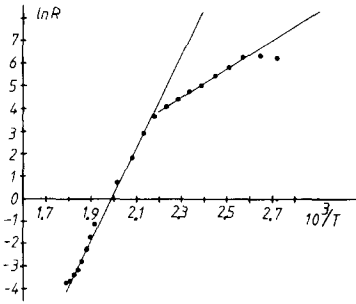


Fig. 4. Temperature dependence of the resistivity plotted as  $\ln R$  vs.  $1/T$ .

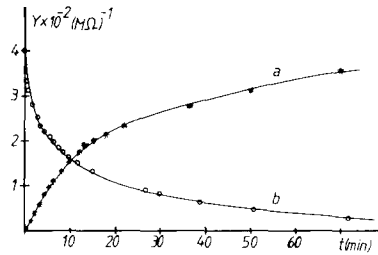


Fig. 5. Curve a, the rise in the conductance after the illumination is switched on; curve b, the fall in the conductance after the illumination is turned off.

$\ln\{\ln(R/R_0)\}$  vs.  $\ln t$  is a straight line with a slope of  $2/3$  so the fall in the photoconductivity can be expressed as

$$Y = Y_0 \exp(-at^{2/3})$$

where  $Y_0$  is the initial photoconductance and  $a$  is a constant. This relation was found to be valid for undoped and doped films illuminated with daylight and with monochromatic light in the region of 200–400 nm, and for the variations in the conductivity of over four decades. The spectral sensitivity of the slow response photoconductivity was measured for a tin-doped ZnO film with a thickness of 0.85  $\mu\text{m}$  with an electrode spacing of 0.25 cm. The sample was illuminated with monochromatic light (with a spectral width of 4 nm) from a Pye–Unicam spectrophotometer. The intensity of the monochromatic light was measured using an International Light spectrum radiometer and it ranged from 1 to  $3 \times 10^{-5} \text{ W cm}^{-2}$  in the spectral range from 340 to 800 nm. The conductance was measured using a megaohmmeter. The rise of the conductance was measured initially every 15 s and later every minute with the illumination switched on. The saturation value of the conductance was used to calculate the spectral sensitivity. After 3 h the illumination was turned off and the photoconductance was allowed to relax to its dark value. The measurement was repeated the following day using monochromatic illumination at other wavelengths. The results of the measurements are presented in Fig. 6 from which it becomes obvious that the main yield of photoelectrons is from

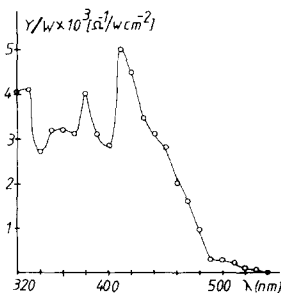


Fig. 6. Spectral sensitivity of the slow response photoconductance of  $\text{Sn}^{2+}$ -doped ZnO thin films.

impurity levels. The peak at 380 nm corresponds to an optical band gap of 3.27 eV and the main peak at 410 nm corresponds to 3.03 eV.

#### 4. CONCLUSION

Very low conductivity ZnO thin film with a high light-to-dark conductivity ratio can be easily deposited by successive immersions of the substrate in a cold ammonia complex solution and then in hot water. The thickness of the film can be controlled by varying the number of successive immersions and it can be monitored by observation of the interference colour. The conductivity of the film can be controlled either by doping with SnCl<sub>2</sub> or by annealing.

Slow response photoconductivity was exhibited by undoped and by Sn<sup>2+</sup>-doped films. Films annealed in argon did not exhibit photoconductivity and behave as degenerate semiconductors.

The proposed method for the preparation of ZnO thin films is very economic and the chemicals used are non-toxic; therefore it could be attractive for industrial production.

#### REFERENCES

- 1 R. F. Belt and G. G. Florio, *J. Appl. Phys.*, **39** (11) (1968) 5251–5223.
- 2 H. W. Lehman and R. Widmer, *J. Appl. Phys.*, **44** (9) (1973) 3868–3879.
- 3 M. S. Tomar and F. G. Garcia, *Thin Solid Films*, **90** (1982) 419–432.
- 4 M. S. Tomar and F. G. Garcia, *Sol. Wind Technol.*, **1** (2) (1984) 71–74.
- 5 K. L. Chopra, S. Major and D. K. Pandya, *Thin Solid Films*, **102** (1983) 1–46.
- 6 H. Nanto, T. Minami, S. Shooji and S. Tanaka, *J. Appl. Phys.*, **55** (4) (1984) 1029–1034.
- 7 T. Shiosaki, M. Adachi and A. Kawabati, *Thin Solid Films*, **96** (1982) 129–140.
- 8 K. B. Sandaram and B. K. Garside, *J. Phys. D*, **17** (1984) 147–153.
- 9 T. Hata, K. Toriyama, J. Kawahara and M. Ozaki, *Thin Solid Films*, **108** (1983) 325–332.
- 10 R. L. Call, N. K. Jaber, K. Seshan and Whyte, *Sol. Energy Mater.*, **2** (1980) 373–380.
- 11 M. Ristov, Gj. Sinadinovski and I. Grozdanov, *Thin Solid Films*, **123** (1985) 63–67.
- 12 S. Sen, D. J. Leary and C. L. Bauer, *Thin Solid Films*, **9** (1982) 7–14.
- 13 F. Seitz and D. Turnbull, *Solid State Physics (Advances in Research and Applications)*, Vol. 8, Academic Press, New York, 1959.