

Preparation and Doping of Zinc Oxide Using Spray Pyrolysis

Julie De Merchant and Michael Cocivera*

Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

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ZnO conductive layers were prepared using spray pyrolysis in air, at a substrate temperature of 150 °C. Doping was achieved using B, Al, Ga, In, As, Fe, La, Gd, and Mo. As-sprayed undoped ZnO films had a resistivity of $3.5 (\pm 2) \times 10^4 \Omega \text{ cm}$. Hydrogen anneal at 350 °C for 5 min reduced the resistivity of most films by several orders of magnitude, and resistivities in the $10^{-3} \Omega \text{ cm}$ range were obtained for films doped with Al and In and $10^{-2} \Omega \text{ cm}$ with Ga, Mo, and B. The films have a high degree of transparency, 80–90%, even when doped and annealed in hydrogen. The bandgap was measured to be 3.22 eV and was unaffected by doping with Al and B, by annealing in hydrogen and by substrate temperature. AFM and STM images show crystallinity of the films. Carrier concentration ranged up to 10^{21} cm^{-3} and mobilities up to $30 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$. ZnO was spray deposited on top of CdS films without destroying the CdS films. This film was then annealed in hydrogen and the resulting ZnO/CdS film was measured for conductivity in the range of $10^{-2} \Omega \text{ cm}$.

Introduction

Recently, interest has increased for developing transparent conductive materials for applications as window materials for solar cells. For example, development by ARCO Solar of a 14% high efficiency cell using the ZnO/CdS/CuInSe₂/Mo structure^{1,2} has kindled interest in inexpensive methods of fabrication of transparent conductive ZnO layers. ZnO, with a bandgap of 3.3 eV, is a good candidate. ZnO has been prepared by a variety of methods including chemical beam deposition,³ RF sputtering,⁴ reactive evaporation,⁵ spray pyrolysis,^{6,7,10,11,18–20} and reactive sputtering.⁸

In general, the resistivity of ZnO thin films has been lowered through the use of dopants,^{3,4,7,9} increased temperature of substrate,¹⁰ and hydrogen anneal.^{5,11} Dopants used previously were Al,³ B,⁸ F,⁹ In, and Ga.⁸ The minimum resistivities obtained by some of these methods were $3.4 \times 10^{-4} \Omega \text{ cm}$ by chemical beam deposition³ using aluminum dopant, $5 \times 10^{-3} \Omega \text{ cm}$ using spray pyrolysis of indium in a methanol solution⁷ at temperatures of 400–500 °C, $4 \times 10^{-4} \Omega \text{ cm}$ using boron by chemical vapor deposition,⁸ $0.085 \Omega \text{ cm}$ by reactive evaporation,⁵ and $10 \Omega \text{ cm}$ for RF sputtering.⁸

In the present paper, we report the preparation of ZnO by spray pyrolysis, in air, at relatively low tem-

peratures, using Zn(NO₃)₂ as precursor. In addition to determining the efficiency of the process, we wished to determine its suitability for controlling the electrical properties of the film. A number of reports have stated that spray pyrolysis is suitable for the preparation of large areas,^{7,10,12} simply,^{12,13} rapidly¹⁰ and relatively inexpensively,^{7,13,14,18} without the use of vacuum techniques. Doping was easily accomplished by adding the dopant precursor to the spray solution to produce uniformly doped films. The dopants in the present study were B, Al, Ga, In, As, Fe, La, Gd, and Mo. Among the film properties measured were resistivity, mobility, carrier concentration, bandgap, and transmittance. Using this technique, the films can be made of varying resistivity as a function of dopant type and concentration. The resistivity was lowered by B, Al, In, Mo, and Ga, while As, Fe, La, and Gd had little effect. A hydrogen anneal significantly lowered resistivities in almost all cases. In addition a layer of ZnO was applied to a CdS film, and resistivity and optical properties of the resultant composite film measured. Atomic force and scanning tunneling micrographs are also presented. Because of the low temperature of deposition of ZnO (150 °C), the ZnO film can be sprayed onto a CdS film without destroying the CdS film even though an oxidative atmosphere was employed. For all other reports of the formation of ZnO by spray pyrolysis, the substrate temperatures were substantially higher (300–575 °C)

* Address correspondence to this author.

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(1) Mitchell, K. W.; Liu, H. I. (Arco), publication prepared for 20th IEEE PV Spec. Conf., 1988.

(2) Zweibel, K.; Ullal, H. S.; Mitchell, R. L.; Noufi, R. *Proceedings of the 22nd IEEE Photovoltaic Spec. Conf.*, 1991.

(3) Sato, H.; Minami, T.; Takata, S.; Miyata, T.; Ishii, M. *Thin Solid Films* 1993, 236, 14.

(4) Martinez, M. A.; Herrero, J.; Gutierrez, M. T. *Sol. Energy Mater. Sol. Cells* 1993, 236, 14.

(5) Ma, J.; Li, S. Y. *Thin Solid Films* 1994, 237, 16.

(6) Milosevic, O.; Jordovic, B.; Usdodovic, D. *Mater. Lett.* 1994, 19, 165.

(7) Guillemoles, J. F.; Lincot, D.; Cowache, P.; Vedel, J. C. R. *Acad. Sci. Paris*, 1991, T.312, Serie II, 1273.

(8) Chou, D.-S.; Liu, G.-D. *Mater. Chem. Phys.* 1994, 37, 156.

(9) Hu, J.; Gordon, R. G. *Sol. Cells* 1991, 30, 437.

(10) Afify, H. H.; Nasser, S. A.; Demian, S. E. *J. Mater. Sci.: Mater. Electron.* 1991, 2, 152.

(11) Belghit, K.; Subhan, M. A.; Rulhe, U.; Duchemin, S.; Bougnot, J. *Eur. Photovolt. Sol. Energy Conf.* 1991.

(12) Chopra, K. L.; Major, S.; Pandya, D. K. *Thin Solid Films* 1983, 106, 1.

(13) Acosta, D. R.; Maldonado, A.; Asomoza, R. *J. Mater. Sci.* 1993, 4, 187.

(14) Goyal, D. J.; Agashe, C.; Takwale, M. G.; Marathe, B. R.; Bhide, V. G. *J. Mater. Sci.* 1992, 27, 4705.

(15) Weng, S.; Cocivera, M. *J. Electrochem. Soc.* 1992, 139, 3220.

(16) Weng, S.; Wynands, H.; Cocivera, M. *Chem. Mater.* 1992, 4, 1426.

(17) von Windheim, J. A.; Cocivera, M. *J. Appl. Phys.* 1990, 67, 4167.

(18) Berry, A. K.; Boone, J. L.; Van Doren, T. P. *Mater. Lett.* 1990, 10, 261.

than the one used here. As a result, the substantially higher substrate temperatures used by these procedures could convert CdS to CdO. Our final processing step, annealing in hydrogen at 300 °C, does not adversely affect the CdS thin film, because of the reducing conditions and the protection afforded by the ZnO overlayer.

Experimental Section

Zinc Oxide. Thin film ZnO was prepared by spray pyrolysis of zinc nitrate dissolved in millipore water (18 M Ω resistance) using an apparatus described earlier.¹⁶ The solution was sprayed on a Corning glass 7059 plate, which was maintained at 150 °C. The spray, which was developed by an ultrasonic nebulizer (Sunbeam), was directed toward the substrate through a glass nozzle using a regulated air flow. The spray assembly was mounted on a moving table and was rastered across the substrate using two stepping motors.

The following spray conditions were used: temperature of substrate, 150 °C, pressure inside spray chamber 8 cm/H₂O, distance between the spray nozzle and substrate 1.6 cm, ultrasonic nebulizing rate 8 mL/h, time of spraying 1 h, and zinc nitrate concentration 0.1 M. The nozzle was made from the tip of a disposable pipet.

Dopants. Doped ZnO was prepared by introducing the dopant in the zinc nitrate solution at the spray pyrolysis stage. Except for B and Mo, the dopants Al, Ga, In, As, Fe, La, and Gd were added to the zinc nitrate solution as nitrate salts. The purity was 4–5 N except for H₃BO₃ and Gd(NO₃)₃ which were 3 N. H₃BO₃, Al(NO₃)₃, and La(NO₃)₃ were supplied by Baker, JM, and Fisher, respectively; all others were supplied by Aldrich. Molybdenum was dissolved in HF and nitric acid.

Hydrogen Anneal. The films were annealed in a quartz tube at various temperatures in a hydrogen atmosphere, using a Lindberg tube furnace. The films were heated to the temperature setpoint using a heating rate of 20 °C/min and then after the anneal time had elapsed, allowed to cool slowly while in the furnace. Cooling required 2–3 h.

Characterization. Proton-induced X-ray emission (PIXE) spectroscopy was used to determine the composition of some Ga-doped ZnO films, in the manner described by Weng et al.^{15,16} The PIXE data were analyzed using standard computer software developed by Professor J. S. Campbell (Department of Physics, University of Guelph) and provided elemental analysis with an error of about 1.0%.

Some films were dissolved in nitric acid, and the resultant solutions were analyzed by inductively coupled plasma (ICP) optical emissions spectroscopy using a LECO Plasmarray instrument and photodiode array. Others were analyzed by atomic absorption spectroscopy using a Perkin-Elmer 2380 spectrophotometer. Indium content was determined by differential pulse polarography using an EG&G Princeton Applied Research Model 264A polarographic analyzer. Electron micrographs and energy-dispersive X-ray spectroscopy (EDS) of CdS and ZnO were determined using a Hitachi S570 scanning electron microscope (SEM) equipped with a germanium detector and Norvar window (Voyager, Noran Instruments). Optical absorption spectra were measured using a Shimadzu spectrometer Model UV160U with a blank piece of 7059 glass in the reference beam. Thickness was measured using a Sloan Dektak surface profile measuring system. Typical accuracy of 0.1 μ m can be obtained for smooth films.

For resistivity and Hall effect measurements, contacts were made using colloidal graphite 2-propanol-based paint at the end of each arm of a cross formed in the film as described previously.¹⁷ The Hall effect measurements were performed using a home-built apparatus operating at a magnetic field strength of 0.8 T. Films having resistivity of less than 50 Ω cm were measured by the Van der Pauw method using indium gallium eutectic as contact material. Burleigh instructional scanning tunneling microscope (STM) and Burleigh Personal

atomic force microscope (AFM) were used to study the morphology of some films.

Results and Discussion

Efficiency of Spray Pyrolysis. The efficiency of the spray deposition depends critically on a number of parameters associated with the spray system, and these parameters were found to depend on the spray characteristics of the nozzle. The results described below were obtained using a nozzle that provided a narrow conical spray. It was constructed from the tip of a pipet. The efficiency of deposition went through a maximum as the nozzle was moved toward the substrate, but the optical transparency decreased as the efficiency of material utilization increased. The effect of the distance of the homemade nozzle on the efficiency varies from nozzle to nozzle because of the divergence of the conical spray changes. Consequently, each spray tip must be calibrated. For this reason, a tabulation of efficiency as a function of distance is not very informative. Below 130 °C, evaporation was not sufficiently rapid, and smooth uniform films were difficult to obtain. The spray rate depended on the power applied to the nebulizer and on the air flow through the nebulizing chamber. The air flow was regulated by controlling the air pressure, and the optimum value was found to be 6–8 cm of water at the nozzle, which combined with an applied power of 24 W gave a spray rate of 0.12 mL/min. Under these conditions for 0.1 M Zn(NO₃)₂, a spray duration of 25 min, and a scan rate of 1.5 cm/s gave a ZnO thickness of 0.28 μ m for a substrate surface of 2.5 \times 5.0 cm² and resulted in a deposition efficiency of 36% with an optical transparency of over 85% in most of the visible spectrum. Although many studies of spray pyrolysis deposition have been reported^{6,7,10–12,18–20} few seem to address the issue of deposition efficiency. However, in one paper it was indicated that the deposition without corona discharge assistance usually had efficiencies of only a few percent.²¹ Furthermore it was found that the deposition efficiency could be increased to <80% when the aerosol droplets were loaded in a corona discharge and transported to the substrate by an electric field. Although the efficiency of our procedure was not as high as the one for this more complicated approach, it compares favorably with the simpler methods.

Undoped and Al-Doped ZnO Films. The average resistivity of four undoped ZnO films was 3.5 (\pm 2) \times 10⁴ Ω -cm. ZnO films were then doped by adding dopants to the spray solution in increments of 0.5 atomic % or 1% up to 4 or 6% relative to the Zn content. Aluminum dopant was used to optimize the doping and annealing procedures and will be presented first. Figure 1, which shows the resistivity of three series of ZnO films as a function of Al dopant concentration, indicates that the resistivity reached a minimum value at 2% Al content. The results of the earliest series were not consistent and are not presented. Although the minimum value varied between the three series, the July and August series, which were the last to be prepared, exhibited a substantially narrower range of variation.

(19) Eberspacher, C.; Fahrenburch, A. L.; Bube, R. H. *Thin Solid Films* **1986**, *136*, 1.

(20) Aktaruzzaman, A. F.; Sharma, G. L.; Malhotra, L. K. *Thin Solid Films* **1991**, *198*, 67.

(21) Siefert, W. *Thin Solid Films* **1984**, *120*, 267.

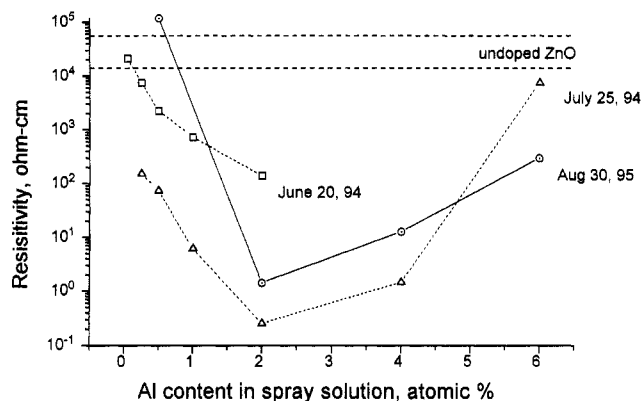


Figure 1. Resistivity of unannealed ZnO films as a function of Al content relative to the zinc nitrate concentration in the spray pyrolysis solution. The dates at which the films were sprayed are noted for three series of Al-doped ZnO. The dotted lines represent the upper and lower limits of resistivity of undoped ZnO. Film thickness vary from 0.3 to 0.7 μm .

These two series probably indicate the degree of consistency that can be achieved by this process. Comparison of these values with the average resistivity of undoped ZnO in Figure 1 illustrates that a substantial decrease of at least 4 orders of magnitude can be achieved using Al as the dopant. The increase in resistivity at higher dopant concentration indicates that the increase in scattering centers probably offsets the increase in carrier concentration.

When the films were subsequently annealed in hydrogen, the resistivity was further reduced. Temperatures of 300, 350, and 400 $^{\circ}\text{C}$ were all successful in lowering resistivity of undoped and Al-doped ZnO films by several orders of magnitude. The extent of the decrease depended on the amount of Al incorporated, with the biggest change observed for the undoped film as might be expected since it had the largest resistivity. The greatest change occurred at about 300 $^{\circ}\text{C}$ for all films. Above 300 $^{\circ}\text{C}$, the resistivity appeared to level off, although there was some scatter of about a factor of 2–5 about the minimum value. The effect of annealing duration was also explored for undoped and Al doped films at 350 $^{\circ}\text{C}$. Figure 2 shows the resistivity of doped and undoped ZnO films annealed for 5, 30, 75, and 240 min. The largest change in resistivity occurred in the first 5 min of the anneal. After this period, the change for the undoped film was not large. The relative change for the Al-doped film was larger. As the time of anneal increased, the resistivity decreased steadily from $1.30 \times 10^{-2} \Omega \text{ cm}$ after a 5 min anneal to $2.85 \times 10^{-3} \Omega \text{ cm}$ for 240 min. As a result of these observations, the hydrogen annealing conditions for all subsequent films were chosen to be 350 $^{\circ}\text{C}$ at 5 min. The intent was to minimize the time of the anneal so that this procedure could be applied to the deposition of ZnO as the top layer in the solar cells without damaging the absorber layer and contacts. This heating step may be detrimental to the cells' efficiency, and so minimum effective annealing conditions were sought.

The effect of hydrogen annealing on resistivity is presented in Figure 3 for undoped and Al-doped films. The results for the doped films in this figure are averages for the July and August series presented in Figure 1. Hydrogen annealing reduced the resistivity of undoped ZnO from to $3.54 (\pm 2.1) \times 10^4$ to 8.84×10^{-2}

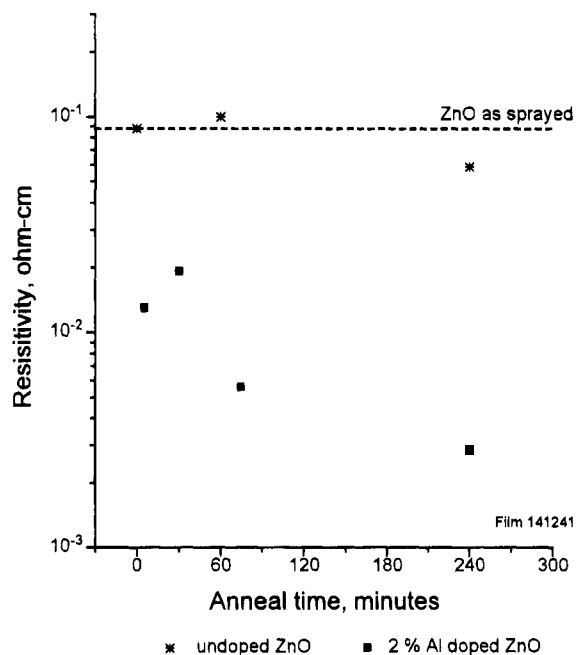


Figure 2. Resistivity of undoped and 2% Al-doped ZnO films as a function of hydrogen anneal duration. These films were annealed at 350 $^{\circ}\text{C}$ for periods ranging from 5 to 240 min. Film thickness was 0.3 μm .

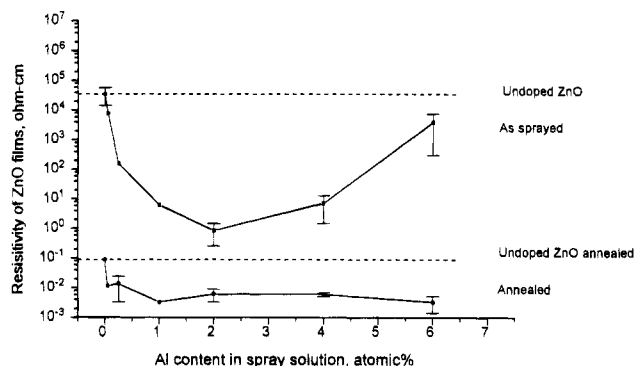


Figure 3. Resistivity of ZnO films, unannealed and annealed, as a function of Al concentration. The Al content is presented as a percentage of the Zn molarity in the spray pyrolysis solution. The upper and lower dashed lines represent the resistivities of undoped ZnO, unannealed and annealed, respectively. Film thickness vary from 0.3 to 0.6 μm .

$\Omega \text{ cm}$. As can be seen from these results, hydrogen annealing alone effectively reduced the resistivity of the undoped film to a value that was lower than values for the Al-doped films that were not annealed. On the other hand, comparison of the values for both doped and undoped films after the hydrogen anneal indicates that the resistivities of the doped films were lower by at least 1 order of magnitude. The lowest resistivity value of $1.38 \times 10^{-3} \Omega \text{ cm}$ was achieved with 6% aluminum solution. It is interesting that the resistivity of the doped films exhibited a smaller variation with Al content after the hydrogen anneal. The reason for this leveling effect of the hydrogen anneal is not obvious. These results indicate that Al is, indeed, an effective dopant for lowering the resistivity of ZnO prepared by our procedure.

To test the stability of these films, one set of annealed ZnO films containing Al was left in ambient air for 3 weeks, and the electrical parameters were remeasured. The resistivity increased by approximately a factor of

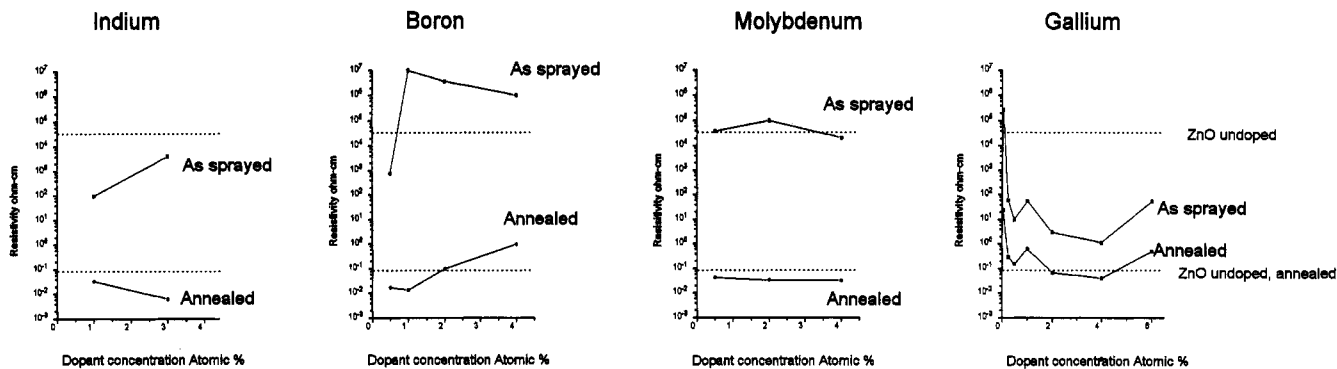


Figure 4. Resistivity of doped ZnO films, as sprayed and annealed, vs dopant concentration, for In, B, Mo, and Ga. The dopant content is presented as a percentage of the Zn molarity in the spray pyrolysis solution. The upper and lower dashed lines represent the resistivities of undoped ZnO, unannealed and annealed in hydrogen, respectively. The anneal conditions for all films were 350 °C, 5 min, hydrogen atmosphere. Film thickness vary from 0.3 to 1.0 μm .

2. As a result, there will be a need to encapsulate the solar cells to avoid this degradation of the ZnO film.

Other Dopants. The effect of other elements on the resistivity of unannealed ZnO films varied. Figure 4 illustrates that Ga, In, and B decreased the resistivity from 2 to 4 orders of magnitude. Gallium, which exhibited the biggest reduction, is almost as effective as Al. On the other hand, Fe, La, Gd, Mo, and As were not effective in lowering the resistivity of the ZnO films (Figures 4 and 5). In fact, Fe, La, and Gd increased resistivity with respect to undoped ZnO films.

When a hydrogen anneal was employed, In, B, and Mo clearly exhibited lower resistivity than the undoped annealed film by at least a factor of 4. Gallium was comparable to the undoped film. Although a hydrogen anneal was successful in lowering resistivity of films doped with La, Gd, and Fe, the resulting values were not lower than those for the undoped film. For As, a hydrogen anneal had no effect. These results are summarized Table 1, which presents the lowest values achieved for each element. As can be seen, the most conductive films were obtained using the hydrogen anneal. Resistivities below the undoped value were obtained for films doped with Al, Ga, B, In, and Mo. The dopants La, Gd, and Fe had no effect in lowering resistivity as sprayed but when annealed in hydrogen, reduced it by 2–4 orders of magnitude. In this case, the lowered resistivity is attributed to the anneal and not to dopant incorporation since the resistivity values of annealed films were higher than that of undoped annealed ZnO. In the case of As and Gd, resistivity values remained high even after hydrogen anneal. In summary, only Al-, In-, Ga-, Mo-, and B-doped films annealed in hydrogen yielded films with lower resistivity values than annealed, undoped ZnO. Aluminum and In were the most effective.

Mobility, Carrier Type, and Carrier Concentration. Hall effect measurements were carried out on undoped, doped, and annealed ZnO films. It was not always possible to measure the Hall effect because some of the films had very low carrier mobility. In all cases where a carrier type could be determined, the undoped and doped films were n-type films for B-, Al-, Ga-, In-, As-, Fe-, Mo-, and Gd-doped films. The only exception was La, which was n-type as sprayed and p-type after the hydrogen anneal. The reason for this change is not clear at this time. The mobile electron density increased from 10^{13} cm^{-3} for resistive films to 10^{21} cm^{-3} for the

most conductive films. This change of a factor of 10^7 in the electron density was mirrored by a corresponding decreased resistivity, indicating that the decrease in resistivity was due mainly to the increase in carrier density. These findings are consistent with the findings of Belghit et al.¹¹

Because the mobility of majority carriers μ , carrier concentration n , and resistivity ρ , are related through the equation $\mu = 1/(\rho n q)$, where q is the electronic charge, the mobility is calculated from n and ρ . Consequently, the mobility did not show as large a variation as the resistivity. In general, the mobilities ranged from the limit of detection of instrument, 0.05, to $30 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ with most of the values around $4 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$. The resistivity was thus mainly lowered though an increase in carrier concentration as discussed above. Other workers^{5,7,8,11} reported similar values, i.e., mobilities of $2.5\text{--}40 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ and carrier density of $10^{19}\text{--}10^{21} \text{ cm}^{-3}$ for similar film thickness when reported (0.1–1.0 μm).

Other workers successfully prepared ZnO films by spray pyrolysis of water/alcohol solutions at temperatures between 400 and 500 °C to give resistivity of $5 \times 10^{-3} \Omega \text{ cm}$.⁷ For comparison with our approach, a 50% methanol solution was used to prepare ZnO films at 150 °C. The resulting films had resistivities a factor of 10 higher than those prepared with water-based solutions, and addition of Al as a dopant caused an increase in resistivity up to $10^{10} \Omega \text{ cm}$. It would appear that substrate temperatures substantially higher than 150 °C are required for formation of good-quality ZnO from aqueous alcohol solutions.

Other techniques provide a variety of resistivity values for ZnO films. Values as low as $2 \times 10^{-2} \Omega \text{ cm}$ were obtained by spray pyrolysis after a hydrogen anneal at 360 °C.¹⁰ Chemical beam deposition at 150 °C provided films with a resistivity as low as $3 \times 10^{-4} \Omega \text{ cm}$ and a transmittance above 85%.³ RF sputtering between 200 and 380 °C gave resistivities between 5×10^{-4} and $1 \times 10^{-3} \Omega \text{ cm}$ for Al-doped films.⁴ Reactive evaporation of zinc chloride between 360 and 460 °C gave films with resistivities as low as $3.5 \times 10^{-3} \Omega \text{ cm}$ after a hydrogen anneal at 400 °C.⁵ Resistivities as low as $4 \times 10^{-4} \Omega \text{ cm}$ were obtained for B-doped ZnO prepared by chemical vapor deposition using diethylzinc and diborane,⁹ diethylzinc, ethanol, and hexafluoropropene at vapor deposition temperatures of 350–470 °C. Reactive evaporation of Zn metal¹⁶ using an argon ion

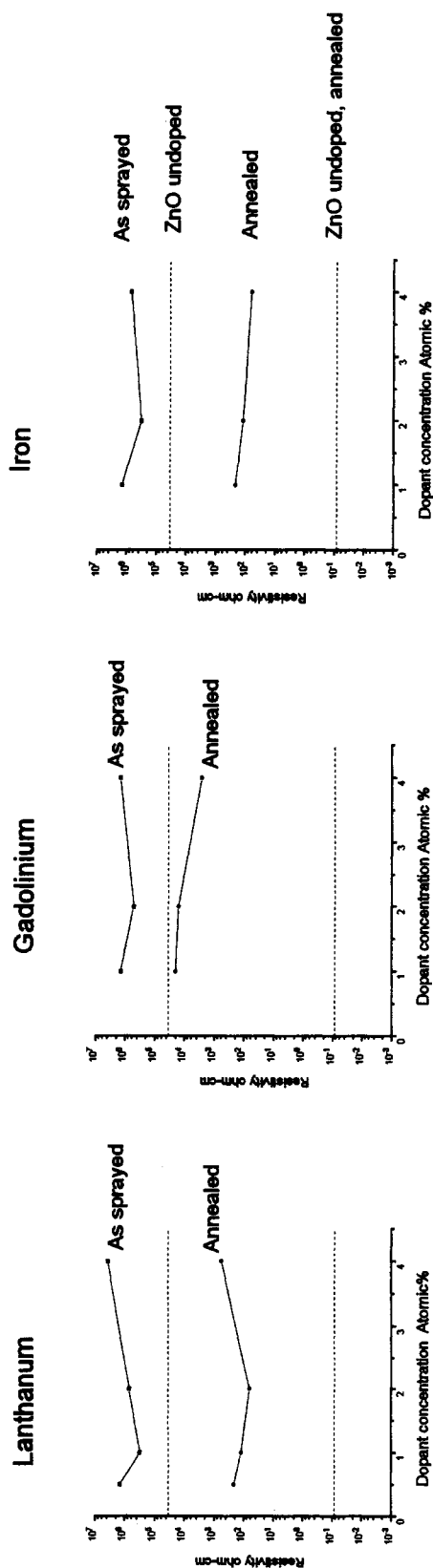


Figure 5. Resistivity of doped ZnO films, unannealed and annealed, vs dopant concentration, for La, Gd, and Fe. The dopant content is presented as a percentage of the Zn molarity in the spray pyrolysis solution. The upper and lower dashed lines represent the resistivities of undoped ZnO, unannealed and annealed in hydrogen, respectively. The anneal conditions for all films were the same as Figure 4.

Table 1. Lowest Resistivity Values Obtained for All Dopants, As Sprayed and Annealed in a Hydrogen Atmosphere at 350 °C for 5 min

dopant type	dopant thickness, μm	resistivity, $\Omega\text{ cm}$	dopant type	dopant thickness, μm	resistivity, $\Omega\text{ cm}$
none	1.0	3.83×10^4	none	1.0	8.84×10^{-2}
Al 2.0%	0.5	0.250	Al 6.0%	0.3	1.38×10^{-3}
In 1.0%	1.0	98.7	In 3.0%	0.5	6.23×10^{-3}
Ga 4.0%	0.3	1.15	Ga 2.0%	0.4	6.93×10^{-2}
Mo 4.0%	0.2	2.11×10^4	Mo 4.0%	0.2	3.19×10^{-2}
B 0.5%	0.3	770	B 1.0%	0.4	1.36×10^{-2}
Fe 1.0%	0.1	1.05×10^6	Fe 1.0%	0.1	3.51×10^1
La 1.0%	0.5	3.12×10^5	La 2.0%	0.7	6.45×10^1
Gd 2.0%	0.5	5.10×10^5	Gd 4.0%	0.8	2.65×10^3
As 2.0%	1.1	9.71×10^4	As 4.0%	0.3	6.43×10^4

beam gave ZnO with resistivities between 4×10^{-4} and $10^{-3} \Omega\text{ cm}$. Spray pyrolysis of zinc acetate or zinc chloride solutions onto a substrate heated between 350 and 490 °C gave a minimum resistivity around $10, 9 \times 10^{-4}, 22 \times 10^{-3}, 19, 11$ and $10^{-3} \Omega\text{ cm}$.²⁰ As can be seen, ZnO prepared by the present procedure had a minimum resistivity within a factor of 3 or 4 of the minimum values reported for a variety of procedures, which either involved substantially higher deposition temperatures and/or vacuum techniques.

Composition. The ratio of zinc to oxygen was measured using energy-dispersive spectroscopy (EDS) and was found to have a Zn/O ratio of 1.14. A slight excess of zinc was thus found in the films. Previous workers⁴ suggested that Zn was in excess in their films and that the higher conductivity in these films was due to oxygen vacancies. Our results are consistent with this suggestion. The increased conductivity of our films after annealing in hydrogen could be explained by removal of some of the oxygen from the films to increase the density of oxygen vacancies. Consistent with this conclusion, Zhang et al.²³ found an increase of 9 orders of magnitude in resistivity when their films were annealed in air 773 K. They attributed this increase to a loss of oxygen vacancies by the reaction of absorbed oxygen with zinc. For many of the procedures mentioned above, ZnO was usually prepared at high temperatures of the 300–500 °C range^{5,7,8,10} under oxygen-deficient conditions, thus increasing the possibility that the Zn content would exceed the oxygen content. In the present work, ZnO was prepared in air, increasing the likelihood the film would be more stoichiometric. For this reason, a hydrogen anneal was necessary to reduce the oxygen content and decrease the resistivity.

Dopant Content. The extent to which the dopants were incorporated into the film from the spray solution depended on the nature of the dopant. In an earlier study, the behavior ranged from a very low degree of incorporation to preferential incorporation but remained linearly related to the amount of dopant in the initial spray solution.²⁴ In the case of Al-doped ZnO, the film content was also linearly related to the solution composition. As assayed using ICP and AA for films prepared from solutions containing 1.0, 2.0, and 3.0 atomic %, the films contained almost exactly one-third less than the spray solution. Thus Al had a slightly

(22) Major, S.; Banerjee, A.; Chopra, K. L. *Thin Solid Films* **1983**, *108*, 333.

(23) Zhang, D. H.; Brodie, D. E. *Thin Solid Films* **1994**, *238*, 95.

(24) De Merchant, J.; Cocivera, M. *Chem. Mater.* **1995**, *7*, 786.

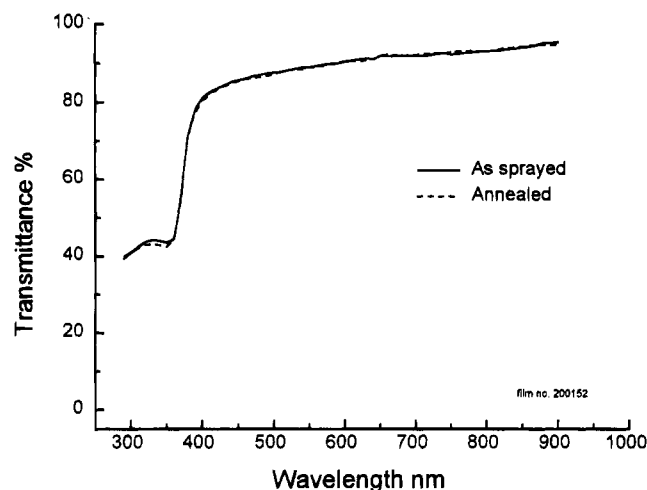


Figure 6. Effect of annealing on transmittance of a ZnO film doped with 2% Al. The anneal conditions were the same as Figure 4. The film thickness was 0.1 μm .

lower deposition rate than Zn. Gallium, on the other hand, as assayed by PIXE, was present in 2.4% in the films compared to 2.0% in the initial spray solution and thus had a slightly preferred deposition rate compared to Zn. Assays using differential pulse polarography of an In-doped ZnO film showed that the In to Zn ratio in the ZnO film was exactly the same as in the spray solution for a 1.0% In-doped film. Most other workers using dopants did not report the dopant concentration in their films.^{3,5,7-9} A few reported the effect of increasing either solution or gas dopant concentration on resistivity. Hu and Gordon⁹ reported a plateau of electron density as a function of dopant concentration of diborane in chemical vapor deposition, but the boron concentration in the films could not be determined using X-ray photoelectron spectroscopy. In the case of Al or In doping by spray pyrolysis using zinc acetate, the resistivity showed very little dependence on the solution dopant composition in the range 1.0–4.0 at. %.¹¹

Bandgap. Near the absorption edge, the absorption spectrum of ZnO followed a square-root dependence of the light energy, indicating a direct bandgap material. The average bandgap of undoped ZnO was 3.22 ± 0.03 eV for four different films made at substrate temperatures ranging from 150 to 250 $^{\circ}\text{C}$. According to the Burstein–Moss effect, the bandgap has a blue shift with increasing carrier concentration. In our case the resistivity, and thus carrier concentration did not change as a function of substrate temperature, so bandgap was not expected to change. A bandgap of 3.22 corresponds to a wavelength of 384 nm. Below this wavelength, there is only 7.4% of the solar constant (1353 W m^{-2}) available for absorption.²⁵ For comparison, values determined for undoped films prepared by the various techniques described above ranged from 3.24 to 3.41 eV.

Optical Transmission. Figure 6 illustrates the optical transmission measured for Al-doped ZnO films having a thickness of about 0.1 μm . In the visible range these films exhibited a transmittance over 85%. Annealing had no effect on the optical transmission spectrum as can be seen in this figure. A thicker film, 0.95 μm , had an average transmittance above 80% in

the visible range with a sharp absorption edge around 386 nm. Guillemoles et al.⁷ found that a more abrupt absorption edge indicated better crystal quality and lower defect density. Typical transmittance values of other workers were 80–90% for film thickness between 75 and 2000 nm.^{3-5,7,8,10,11,16,20,23} In a number of these studies,^{3,5,11,20,23} only transmittance measurements were employed. When reflectance was also measured, reflection in ZnO films was found to decrease the transmission by as much as 15–20%.⁷ Consequently taking these results into account, Figure 6 indicates that ZnO prepared by our process is of very high optical quality. Consistent with the results using Al dopant, doping with As and B did not cause a reduction in transmittance. The absence of any affect of the hydrogen anneal on the transmittance profiles of the film agrees with the results of other workers.^{4,5}

It should be noted that in the present research, ZnO was pyrolyzed using substrate temperatures of 150 $^{\circ}\text{C}$ using $\text{Zn}(\text{NO}_3)_2$ as precursor, while others used substantially higher temperatures ranging from 300 to 575 $^{\circ}\text{C}$ using zinc acetate,^{5,7,10} diethylzinc and dimethylzinc,⁸ and zinc chloride.¹¹ Another group used zinc nitrate but used temperatures of 1173 K to produce spherical ZnO powder rather than films of high optical quality.⁶

Morphology. The atomic force micrograph of two doped ZnO films showed a structure of hills and valleys of width approximately 1–5 μm at fwhm. Figure 7 illustrates the micrograph for one of these films. These micrographs could be used to quantify the surface roughness of the films. One film had an average peak height of 0.0991 μm , a maximum at 0.1990 μm , and a variance of 0.0386 μm with respect to the valleys in the film.

A scanning tunneling micrograph of ZnO films showed two types of structures on the same film, a microstructure superimposed on a macrostructure (Figure 8). The larger structure is one of crests and troughs of the type seen in the atomic force microscope, the smaller pattern is one of crystallites of about 30 nm in diameter. The analysis of X-ray line widths of another film prepared under similar conditions indicated that the crystallite size was approximately 50 nm. In view of this information, it appears that ZnO formed 30 nm crystallites, which were combined to make up the larger hill and valley structure apparent in the atomic force microscope. X-ray crystallographic information of other workers⁵ indicated that the size of the crystallites of their zinc oxide films was approximately 30–60 nm.

ZnO/CdS Films. One application of ZnO conductive films is to provide a large-bandgap window material for CdS in solar cells. To test the applicability of the present preparation procedure for this purpose, the best approach would be to determine the CdS composition after ZnO was spray deposited on top of the CdS film. However, because of depth penetration limitations EDS could not be used to determine the composition of the CdS film beneath the ZnO film. For this reason, indirect evidence was obtained as follows. A film of CdS was prepared by a chemical bath deposition technique using thiourea and cut into two pieces. Since the deposition of ZnO by a spray pyrolysis technique requires the application of heat, one piece was heated to 150 $^{\circ}\text{C}$ for 90 min in air. The composition of both the heated and unheated films was analyzed by EDS to determine the

(25) Backus, C. F. *Solar Cells*; IEEE Press: Piscataway, NJ, 1976; p 2.

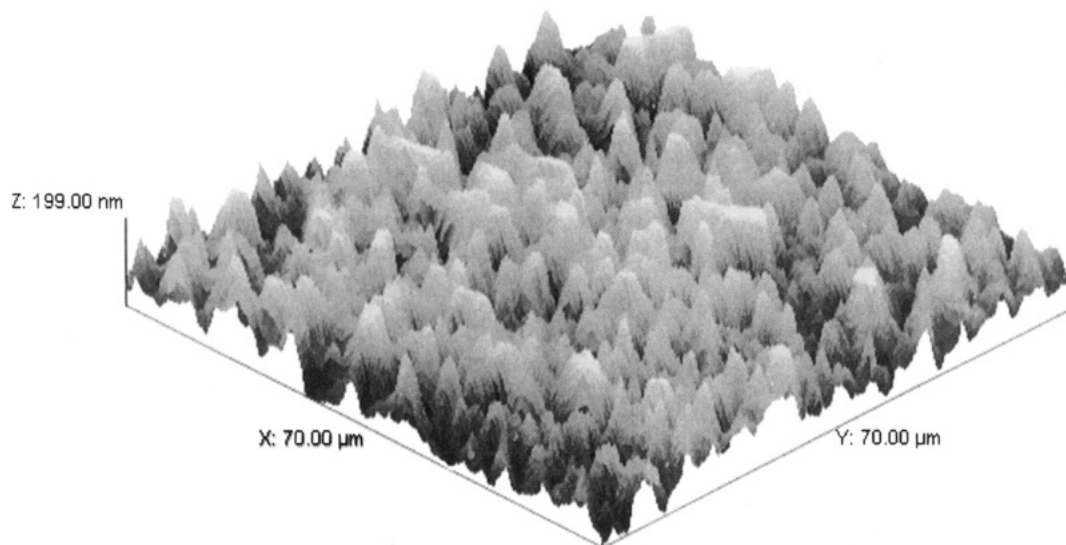


Figure 7. Atomic force micrograph of a ZnO film. The surface structure shows hills and valleys with an approximate peak width of 1–5 μm .

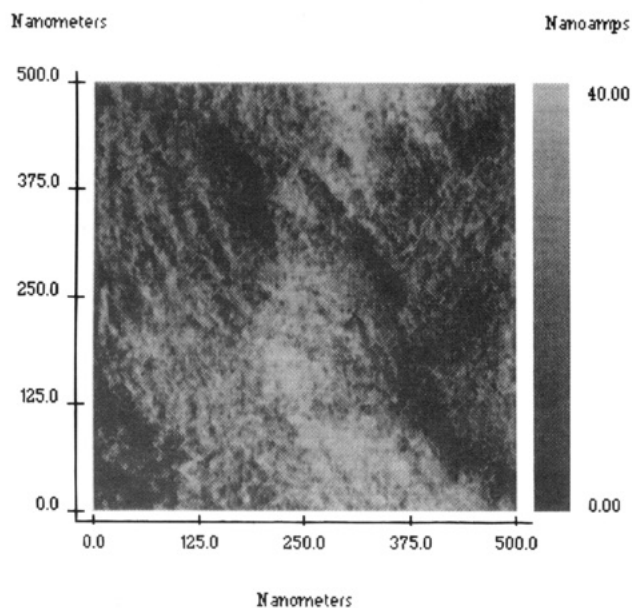


Figure 8. Scanning tunneling micrograph of a ZnO film. The film shows two structures superimposed; the smaller crystallites are about 30 nm in diameter. See the text for a more detailed description of the morphology of the films.

extent to which CdS was converted to CdO by this heat treatment. This analysis yielded S/Cd ratios of 0.99 and 0.95 for the unheated and heated CdS films, respectively, indicating that very little of the CdS was converted to CdO by the heat treatment. In addition using the Van der Pauw method, the resistivities of the two CdS films were found to be within one-half order of magnitude, whereas CdO was 7 orders more conductive than CdS. These results indicate that the CdS layer was not destroyed by the heating step.

Next, ZnO (doped with 2% Al) was sprayed onto half of a CdS film, and the other half was kept for reference. The resistivity was measured for ZnO, ZnO/CdS, and CdS films that had been annealed in hydrogen. Both the hydrogen-annealed ZnO and ZnO/CdS films were very conductive with values around $6.86 \times 10^{-2} \Omega \text{ cm}$. On the other hand, the conductivity of as deposited and annealed CdS remained in the $10^4 \Omega \text{ cm}$ range, indicat-

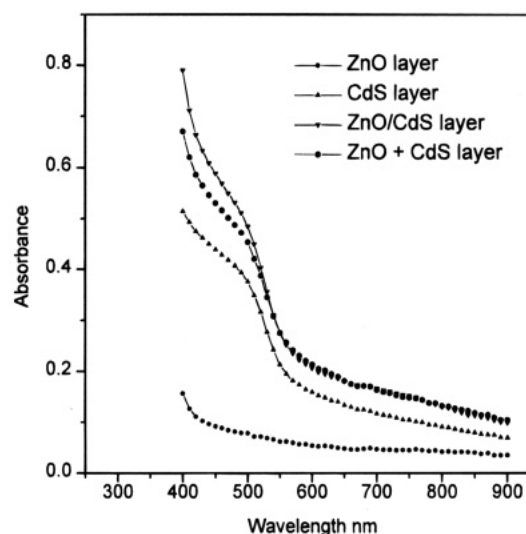


Figure 9. Absorbance spectra of (a) a ZnO film, (b) a CdS film, (c) a ZnO film deposited on top of a CdS film, and (d) a mathematical addition of the ZnO and CdS film absorbance spectrum. See text for more detail.

ing that the reduced resistivity of the CdS/ZnO film was due to a ZnO-conductive layer.

The optical properties were determined for the four films described above, i.e., as-deposited CdS, CdS heated to 150 $^{\circ}\text{C}$ for 90 min in air, CdS coated with a ZnO film, and ZnO alone. The optical bandgap of the unheated CdS was measured to be 2.40 eV, compared to the literature value of 2.42 eV. After heating, the heated CdS film did change color from bright yellow to a light brownish color. Although the elemental analysis detected only a slight change in composition, the bandgap did change from 2.40 to 2.26 eV. The bandgap of CdO is 2.5 eV, so it is not clear why the bandgap decreased.

The transmittance spectra of the ZnO, CdS, and ZnO/CdS films were measured and shown in Figure 9. The ZnO transmission spectrum can be added mathematically to the CdS spectrum and compared to that obtained experimentally for ZnO/CdS. The spectra matched almost exactly up to 500 nm wavelength. The small difference that resulted at lower wavelength may have been due to the slight reversion of CdS to CdO or

formation of ZnS or simply that some of the CdS films evaporated and produced a more transparent spectrum due to its reduced thickness. Thickness could not be measured accurately below $0.1\ \mu\text{m}$. The results indicate that deposition of ZnO on top of CdS by our procedure did not alter markedly the optical or electrical properties either film.

Conclusion

Deposition of ZnO by the present spray pyrolysis procedure effectively provided low-resistivity films under fairly mild conditions. Some of the best results were obtained when ZnO was doped with aluminum, indium, and gallium. Boron and molybdenum were not successful in lowering the resistivity of ZnO films, unless a hydrogen anneal step was used. Annealing in hydrogen effected large reductions in the resistivity of most films including the undoped films. Compared to the undoped films, films doped with Fe, Gd, La, and As had larger

resistivities when unannealed or annealed in hydrogen. A conductive ZnO layer was successfully applied to CdS films, with minimal deterioration of the CdS layer, thus providing a conductive, transparent layer.

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