

Transparent and highly conductive films of ZnO prepared by rf reactive magnetron sputtering

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Highly conductive films of zinc oxide have been prepared by reactive rf magnetron sputtering from an oxide target. Film conductivities ranging from $\sim 10^{-8} \Omega^{-1} \text{ cm}^{-1}$ to $5 \times 10^2 \Omega^{-1} \text{ cm}^{-1}$ can be obtained depending on the sputter conditions. Films with sheet resistivities of $85 \Omega/\square$ showed little absorption and $\sim 90\%$ transmission between $\lambda = 4000 \rightarrow 8000 \text{ \AA}$. A second low power discharge at the substrate is used to initiate growth of the highly conducting material on room-temperature substrates. Thus, during the deposition of insulating ZnO, turning on this second discharge causes the deposition to "switch" from low conductivity to high conductivity material. This is of particular interest in the fabrication of semiconductor-insulator-semiconductor solar cells where precise control over the thickness of the insulating layer is necessary and where a highly transparent and conductive window-junction layer is required.

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The increasing use of transparent, conductive films for liquid-crystal displays, IR reflective coatings, and more recently for window-junction layers in semiconductor-insulator-semiconductor solar cells, has prompted numerous studies¹⁻⁷ into the technical aspects of film deposition, particularly for less expensive coating materials.

Recently, films of indium tin oxide with high conductivity and optical transparency^{1,6} have been prepared by reactive rf magnetron sputtering. The wide choice of satisfactory substrate materials (substrates are at room temperature during deposition) and lack of any post-deposition treatment to achieve optimum characteristics are of particular importance for large-scale use of this material as a transparent, conductive coating. Zinc oxide has also been deposited using a reactive evaporation technique⁷ giving films with high electrical conductivity and optical transparency. These films represent the highest values of conductivity yet reported for zinc oxide. The low cost of this material makes it attractive for large-scale coating applications. In this letter we wish to report on the deposition of highly conductive ($5 \times 10^2 \Omega^{-1} \text{ cm}^{-1}$) films of zinc oxide with high optical transparency ($> 90\%$ $\lambda = 4000 \rightarrow 8000 \text{ \AA}$ for a 1000-\AA -thick film) by reactive rf magnetron sputtering. Like the films of indium tin oxide described above, these films can be deposited on a wide range of substrate materials, and the films required no post-preparative treatment to achieve optimum characteristics. Furthermore, the conductivity is the highest yet reported for sputtered ZnO films.

Films were deposited from a hot pressed ZnO target (Materials Research Corp.) using a vertical cathode rf magnetron sputtering system (Vac Tec Inc). Details of the system have been described elsewhere.¹ All films were deposited at a total pressure of 5 m Torr with the target self bias held constant at the chosen sputter power level, via an automatic feedback system to the rf generator. Contacts to the films for conductivity measurements were made with ultrasonically

soldered indium. A planar 4-probe geometry was employed although the results indicated that contacts to the films were in general, ohmic. The substrates used were pyrex glass.

Films deposited at various substrate temperatures (measured with a thermocouple in contact with the substrate surface) ($315 \rightarrow 550 \text{ K}$) and for various power levels (up to 300 W) gave transparent films with resistivities $> 10^8 \Omega \text{ cm}$.

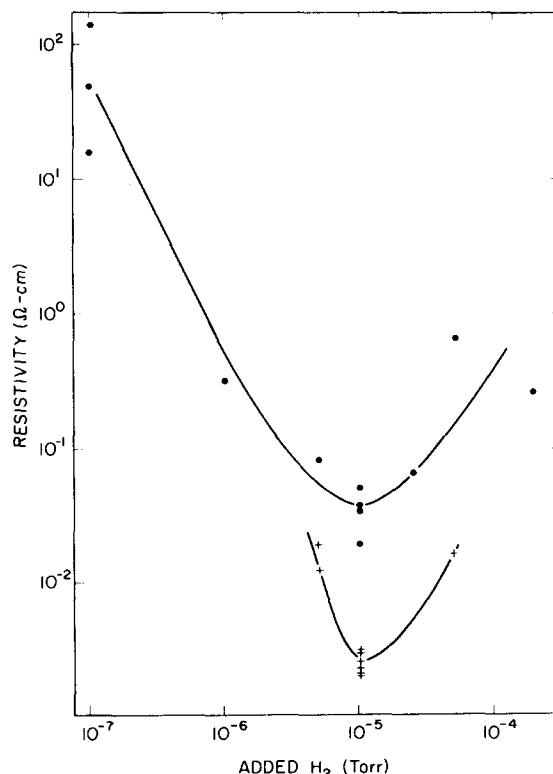


FIG. 1. Bulk resistivity vs added hydrogen; (●) $T_{\text{substrate}} = 400 \text{ K}$, deposit Power = 200 W; (+) $T_{\text{substrate}} = 315 \text{ K}$, deposit Power = 100 W, second discharge used to initiate growth (see text).

TABLE I. Carrier concentration n and mobility μ , measured for zinc oxide. Films prepared with different substrate temperatures, added hydrogen partial pressures, and rf power.

Sample	$H_2(p-p)$ Torr	Power (W)	Substrate Temp (K)	$n(\text{cm}^{-3})$	$\mu(\text{cm}^2/\text{V s})$
Z21 ^a	5×10^{-6}	100	315	4.7×10^{19}	7.0
Z18 ^a	1×10^{-5}	100	315	1.1×10^{20}	8.0
Z23 ^a	5×10^{-5}	100	315	4.0×10^{19}	3.0
Z27 ^b	1×10^{-5}	200	393	4.7×10^{19}	8.8
Z31 ^b	5×10^{-6}	200	393	5.0×10^{17}	3.8

^aSecond discharge on for first 5 min of 20-min deposition.

^bNo second discharge.

Rather than dope this material using conventional techniques (i.e., impurity doping) to achieve a higher conductivity, an attempt was made to defect dope the films during deposition, as in the case for indium tin oxide, via changes in the film stoichiometry. Hydrogen was introduced into the argon sputter gas to change the zinc/oxide ratio and the results are shown in Fig. 1 for a substrate temperature of 400 K. As shown in the figure the resistivity exhibits a minimum for an added hydrogen partial pressure of 1×10^{-5} Torr.

The rapid decrease in resistivity with increasing added hydrogen ($< 10^{-5}$ Torr) is consistent with hydrogen acting as a reactive species for the removal of oxygen and hence increasing the zinc/oxygen ratio in the deposited films. This is believed to result in the formation of either oxygen vacancies or interstitial zinc giving rise to donor levels.^{8,9} The measured carrier concentration (see Table I) shows an increasing value in this range. However, beyond 1×10^{-5} Torr added H_2 , the resistivity again increases due to a decrease in carrier concentration. Films deposited at these pressures may show increased compensation from an increase in the density of acceptor levels resulting from changes in the growth characteristics.^{8,9}

The film resistivity shows a strong dependence on substrate temperature. Increasing the substrate temperature above 400 K resulted in an increase in the resistivity of the films, whereas reducing the substrate temperature to 350 K decreased the resistivity by a factor of 2. Any further reduction resulted in a rapid increase in film resistivity (more than eight orders of magnitude).

The low values of substrate temperatures giving rise to such behavior would suggest nucleation effects rather than any major change in film stoichiometry from re-evaporation or from changes in film crystallinity, since x-ray analysis of the films (powder diffraction of the scraped films) indicated a polycrystalline structure for all values of substrate temperature. This was also apparent from scanning electron micrographs of the deposited films. The relatively large scatter in values of the resistivity (see Fig. 1) for films prepared under nominally the same conditions would also be consistent with nucleation effects. In order to investigate this further, and the role of hydrogen on the sputter conditions, a second plasma discharge was introduced at the substrate. The experimental arrangement is shown in Fig. 2. The power in this discharge is very low (< 1 W). Films prepared with this second discharge operating in conjunction with the normal

sputter process gave films with improved resistivity (see Fig. 1), i.e., the resistivity decreased by approximately one order of magnitude to $\sim 2 \times 10^{-3} \Omega \text{ cm}$. This is the lowest value yet reported for sputtered films of ZnO. Hall-effect measurements indicate an increase in the effective carrier concentration of these films to $1.2 \times 10^{20} \text{ cm}^{-3}$ from $4 \times 10^{19} \text{ cm}^{-3}$ and a doubling of the carrier mobility from $\sim 8 \text{ cm}^2/\text{V s}$ to $\sim 16 \text{ cm}^2/\text{V s}$ at 1×10^{-5} Torr added H_2 . Several important features should be noted.

(1) The hydrogen partial pressure at which the minimum value of resistivity occurs, remains unchanged at 1×10^{-5} Torr.

(2) The low values of resistivity are obtained whether the second discharge remains on throughout the entire sputtering time or is only present during the initial growth period (the first 5 minutes of a 30-min deposit, for example).

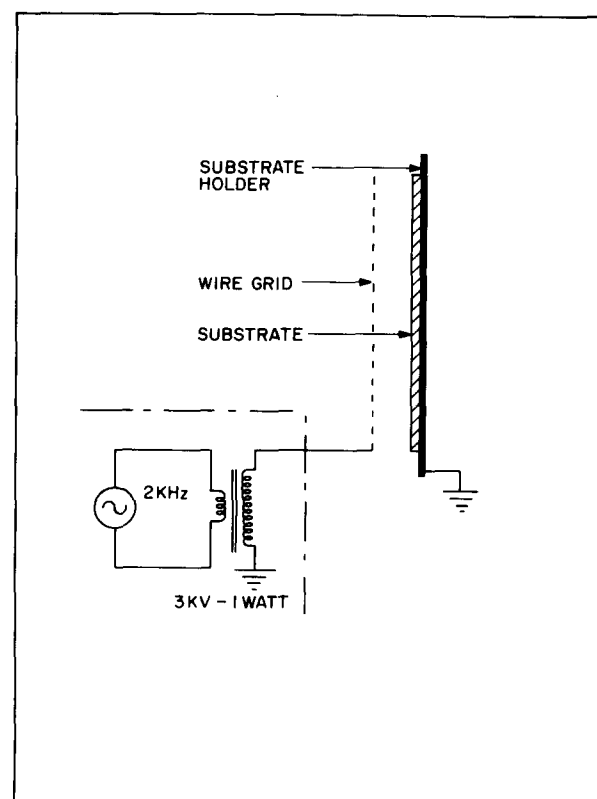


FIG. 2. Schematic representation of experimental setup to achieve secondary discharge at the substrate.

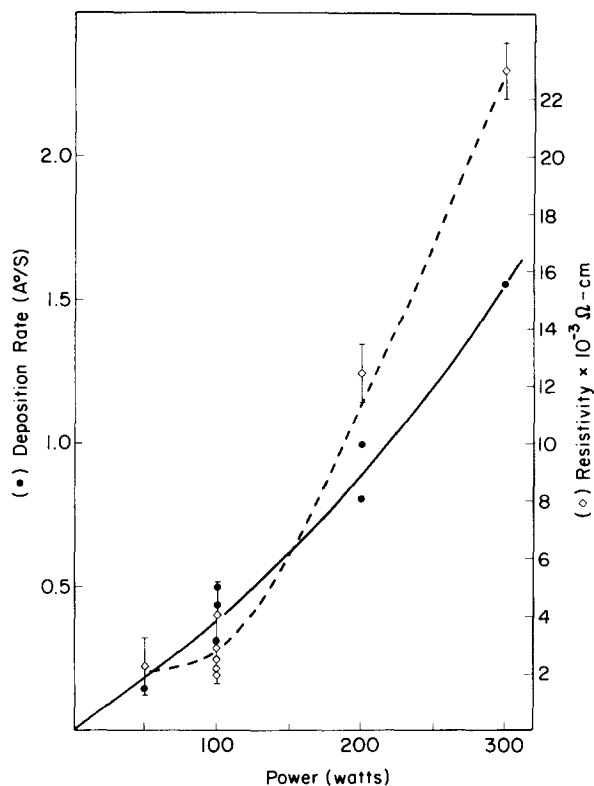


FIG. 3. Deposition rate (●) and film resistivity (dashed line) (◇) for various deposition power levels. All films prepared with second discharge initiating film growth.

(3) The low value of resistivity is obtained on room-temperature substrates, whereas without the second discharge highly insulating films are obtained.

(4) Removing the hydrogen from the discharge at any time during the sputter process results in insulating films regardless of the state of the second discharge.

(5) Unlike the reactive gas sputtering of indium tin oxide,^{1,6} no target change is observed in this study and the deposited films show resistivities independent of film thickness for thicknesses ≥ 600 Å. Below 600 Å an increase in resistivity is observed related to surface effects.

From these results one can conclude that the role of hydrogen is to change the stoichiometry of the sputtered species, either by (a) reactions on the surface of the target, (b) reactions within the main sputter discharge, or (c) reactions at the substrate, but acting independently of this second discharge [see (1) above]. However the growth of the films, which governs the defect density giving rise to free carriers, is only dependent on effects at the substrate. This is clearly shown from (2) and (3) above.

The second discharge would appear to enhance the number or types of nucleation centers on the substrate, thus defining the defect density (zinc interstitials, oxygen vacancies, etc.) of the growing film. It does not appear to be related to a simple "cleaning" of the substrate since an insulating layer of zinc oxide grown at room temperature, 1×10^{-5} Torr H_2 and second discharge off, can be coated with a high-

ly conductive layer of zinc oxide during the same deposition cycle simply by momentarily turning on the second discharge. Furthermore, the reproducibility of the electrical properties of the films is increased. This would be expected on the basis of increased control over the type of nucleation centers produced.

Finally preliminary investigations of the effects of sputtering power have been made. Generally the lower the sputtering power, the lower the resistivity of the films is regardless of whether a second discharge is used or not. This dependence on power is shown in Fig. 3 together with the sputtering rate versus power. Below 100 W the variation in resistivity is small. These effects are observed independent of the hydrogen pressure and the minimum in resistivity remains at $\sim 1 \times 10^{-5}$ Torr H_2 for power levels up to 300 W (the maximum power level investigated). Clearly, the reaction of the ionized hydrogen with the sputtered zinc oxide cannot take place within the discharge or a shift in this minimum would be observed as the power level—and thus the rate of deposition—is changed (i.e., more hydrogen would be required if the volume of sputtered material per unit time were increased). Similarly reactions at the target are also unlikely since no changes in film resistivity versus thickness (which is proportional to sputter time) is observed. It thus appears that reactions at the substrate surface—dependent on surface area and hence independent of the quantity of material sputtered per unit time—are most important in determining film properties, a concept further substantiated by the effects of the second discharge on growth behavior. The exact nature of these reactions however remains to be shown.

These experimental results all illustrate the underlying complexity involved in the growth of zinc oxide films by reactive sputtering. By choosing the requisite sputter conditions, films with resistivities from 10^{-3} Ω cm to 10^8 Ω cm can be prepared. A second discharge used to initiate growth of low resistivity films, can be used to switch the resistivity of films during growth from highly insulating to highly conducting, a feature of particular interest in the fabrication of SIS solar cells. It should be possible to form the insulating layer (~ 30 Å) and highly conducting transparent window-junction layer in a single, highly controlled deposition cycle.

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