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Development of transparent and conductive ZnO films by spray pyrolysis

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Indium-doped zinc oxide (IZO) films were deposited on Corning 7059 substrates by the spray pyrolysis technique. To achieve higher electrical conductivity both the zinc acetate concentration and indium concentration in the solution were varied. The films were characterized for their structural and electrical properties. Film stability in H_2 plasma was also checked for possible use in amorphous and microcrystalline silicon related fields. It was observed that the films can be sustained in a hydrogen plasma, and hence IZO films of high conductivity can be used for the development of amorphous and microcrystalline silicon solar cells.

1. Introduction

The development of zinc oxide films was felt necessary after the experience that both the conventional transparent conductors, namely tin oxide and indium oxide, reduce to metallic forms when exposed to hydrogen plasma [1]. Only zinc oxide films show stability in hydrogen plasma, which is of prime importance in amorphous and microcrystalline silicon related fields. The additional advantages of ZnO are the easy abundance of source material and a wide band-gap with a cut-off at 3.3 eV. Thus ZnO can be applied as a transparent conductor in thin-film solar cells.

ZnO thin films have been prepared by different methods [2–5], amongst which spray pyrolysis has its own merits such as it is economically viable, film growth rates are high and incorporation of dopants is easier. The common dopants employed are Al^{3+}, In^{3+} and Ga^{3+} [6].

In this paper we report the structural and electrical properties of sprayed ZnO films, where the stoichiometry was deviated by doping with In^{3+} as well as by increasing the molarity of the solution. The effect of hydrogen plasma exposure on structural and electrical properties of indium-doped zinc oxide (IZO) films is also reported.

2. Experimental procedure

Undoped and indium-doped zinc oxide films were deposited on Corning 7059 glass substrates using the spray pyrolysis technique. For undoped ZnO a 0.1 M solution of zinc acetate in water and methanol (1:3 volume ratio) was used, and for indium doping $InCl_3$ was added to the starting solution. The In/Zn ratio was varied from 0 to 5 at %. The other parameters controlled during deposition were as follows:

Temperature of substrate	450 °C
Air flow rate	$9\,l\,min^{-1}$
Amount of solution sprayed	50 ml

The effect of dopant level (In/Zn in at %) on the physical properties of ZnO films was studied in detail.

An attempt was made to improve the conductivity of these films further by increasing the molarity of the solution. For this purpose we deposited additional films with the molarity of the solution at 0.15 and 0.2 M. During this deposition other process parameters including the dopant level (5 at %) were kept constant.

X-ray diffraction measurements were carried out using a grazing-angle X-ray diffractometer (Rigaku rotating anode X-ray generator RU 200B). For this purpose the CuK_{α_1} ($\lambda = 0.1542$ nm) line was used. Background reduction and processing of raw collected data was done using the computer software provided by Rigaku (standard D/max-b system software). Calculation of interplanar distance, i.e. d value, and relative intensities was also performed using the same software. From the angular positions of reflections in X-ray diffractograms, lattice parameters and hence c/a ratios were calculated for thin films of IZO. Texture coefficients along [0 0 2], [1 0 1] and [1 0 0] were also calculated, using the formula given elsewhere [7].

Electrical resistivity and Hall voltages were measured using the Vander Pauw technique [8]. From these, carrier concentration and carrier mobility were calculated. For Hall voltage measurements a d.c. current of the order of 1–2 mA and a magnetic field of 0.7 T were used. The thickness of the film was measured using a conventional roughness detector with a stylus (Taylor Hobson model).

The films with the highest conductivity were then exposed to a hydrogen plasma. The conditions of exposure were selected as needed for the deposition of

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microcrystalline silicon [9, 10]. The exposure conditions are given below:

Temperature of film	350 °C
R.f. power	0.7 W cm^{-2}
Chamber pressure	0.11 torr
Hydrogen gas flow rate	75 sccm
Time of exposure	15 min

The duration of exposure was 15 min because considering the typical growth rate of microcrystalline silicon (3–6 nm min^{-1}), 15 min are sufficient to develop full coverage of microcrystalline silicon over an IZO film. Hence the hydrogen plasma will not interact during further exposure of the IZO film.

3. Results and discussion

As stated earlier, to increase the conductivity of ZnO films they are doped with group III elements, namely Al^{3+}, In^{3+} and Ga^{3+}. In our case we observed that indium doping critically affects the structural and electrical properties. The results are discussed below.

3.1. Effect of indium doping on structural properties of zinc oxide films

Fig. 1 shows the X-ray diffractograms of undoped, 2 at % and 5 at % IZO films. Undoped zinc oxide exhibits a strong *c*-axis orientation [0 0 2] perpendicular to the substrate. It is adversely affected by subsequent indium doping of the films. In fact 2 at % doped IZO films show totally random orientation, which matches closely with the powder pattern. In the case of 5 at % doped films, the grains again show preferential growth along the [1 0 0] direction. The orientations (1 0 2), (1 0 3), (1 1 0) and (2 0 1) were also observed in the X-ray diffraction pattern, but their intensities were weak and not modified significantly by indium doping.

The preferred orientation of the crystallite can be represented by the texture coefficient TC(*hkl*) along a certain direction [*h k l*]. Fig. 2 shows the variation of texture coefficients along [0 0 2], [1 0 1] and [1 0 0] with the dopant level. It is interesting to note that TC (0 0 2) decreases continuously with an increase in the dopant level, while TC (1 0 1) and TC (1 0 0) show increase with the dopant level.

The changes in the X-ray diffractograms can be explained on the basis of *c*/*a* measurements. It is known that highly preferred-oriented zinc oxide films have internal stresses [11] which shift the angular positions of the reflection peaks in the X-ray diffractograms. The lattice constants and hence *c*/*a* were calculated using the angular positions of reflection peaks. Fig. 3 shows the variation of *c*/*a* ratio with the dopant level in IZO films. It can be seen that with an increase in the dopant level, the *c*/*a* ratio of the film decreases towards the bulk value. Actually for 2 at % doped film the *c*/*a* ratio is 1.5982, which is in very close agreement with the *c*/*a* ratio of 1.6024 calculated from powder pattern (using stoichiometric ZnO powder). After 2 at % the *c*/*a* ratio again increases but slowly, which may be due to an excess incorporation of indium which leads to preferential orientation of the grain along the [1 0 0] direction. Thus indium incorporation during the growth of an IZO film initially reduces internal stresses, so that the film possesses its natural random orientation. Excess incorporation of indium again leads to an increase in *c*/*a* and preferred growth along the (1 0 0) direction.

Reduction of internal stresses by indium incorporation in the zinc oxide film is still not understood

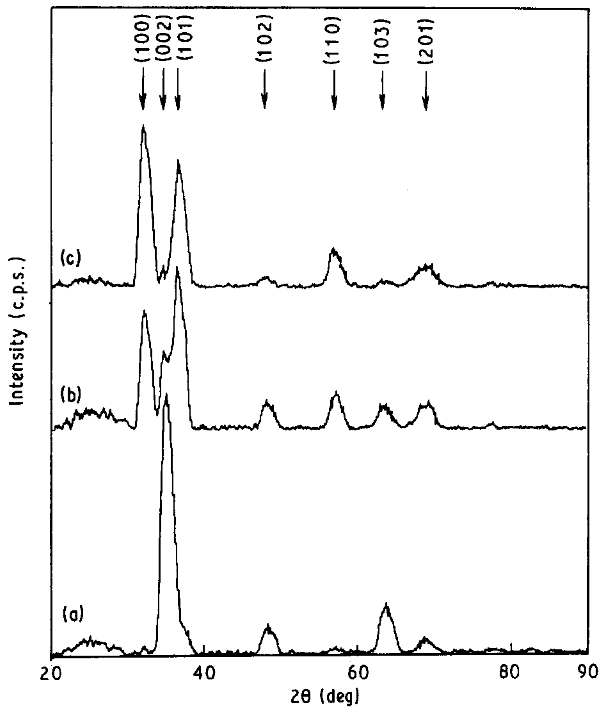

Figure 1 X-ray diffractograms of undoped and indium-doped zinc oxide films: (a) undoped, (b) 2 at % In, (c) 5 at % In.

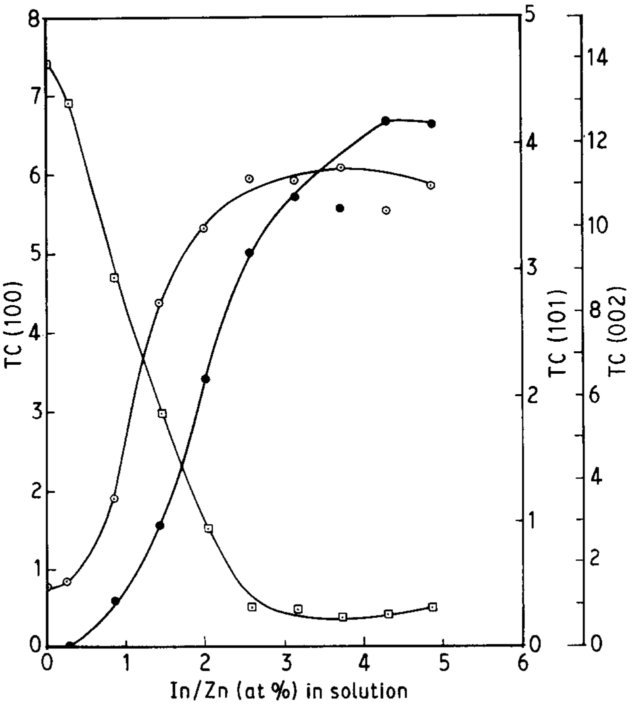

Figure 2 Variation of (⊡) TC (0 0 2), (⊙) TC(1 0 1) and (●) TC(1 0 0) with dopant level in indium-doped zinc oxide films.

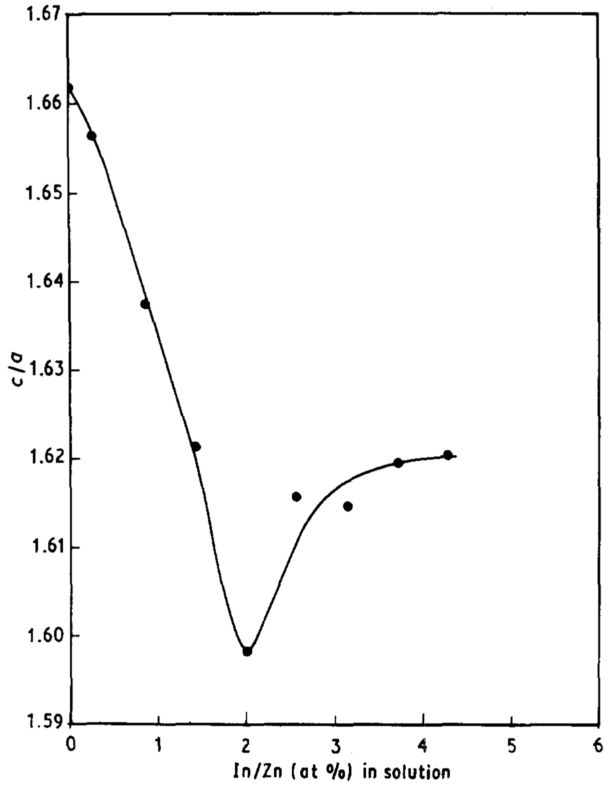

Figure 3 Variation of c/a with dopant level in indium-doped zinc oxide films.

completely and further investigations are going on. The effect of indium doping on the structural properties of sprayed zinc oxide films was also studied by Major [12]. His investigations suggest that indium doping leads to an inclination (tilt) of the c-axis at an angle of 58.3° with respect to the substrate normal.

3.2. Effect of indium doping on the electrical properties of zinc oxide films

Fig. 4 shows the variation of conductivity, σ, carrier concentration, n, and mobility, μ, with dopant level. The carrier concentration increases with dopant level and saturates at a value of about $1.4 \times 10^{20}\ \text{cm}^{-3}$. The variation in μ with dopant level shows a minimum in the range of 1–2 at %, i.e. it initially decreases with dopant level, observes a minimum and then increases sharply. This is followed by saturation at a value of about $7.0\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$.

It should be noted that zinc interstitial, oxygen vacancy and doped In^{3+} will contribute free electrons to the lattice. However, as we have kept all other parameters involved in the deposition process fixed and only the In/Zn ratio was varied we do not expect any change in the amounts of zinc interstitial or oxygen vacancy. Hence the changes in the carrier concentration with dopant level can be attributed solely to the substitutional replacement of Zn^{2+} by In^{3+}, releasing one free electron in the process.

The variation in mobility with dopant level can be correlated with the structure of the film. The initial decrease in mobility can be understood on the basis of the deterioration in the preferred growth of the film. It is known that randomly oriented grains of ZnO possess a high trap density which reduces the mobility of the charge carriers [13]. Hence for initial doping we observe a minimum in the mobility. The dependence of mobility on trap density is well established for polycrystalline silicon [14] and CdS thin films [15]. The further increase in the carrier mobility with dopant level is due to well-ordered (1 0 0) oriented ZnO grains.

The conductivity of IZO can be further increased by increasing the contribution from zinc interstitial/

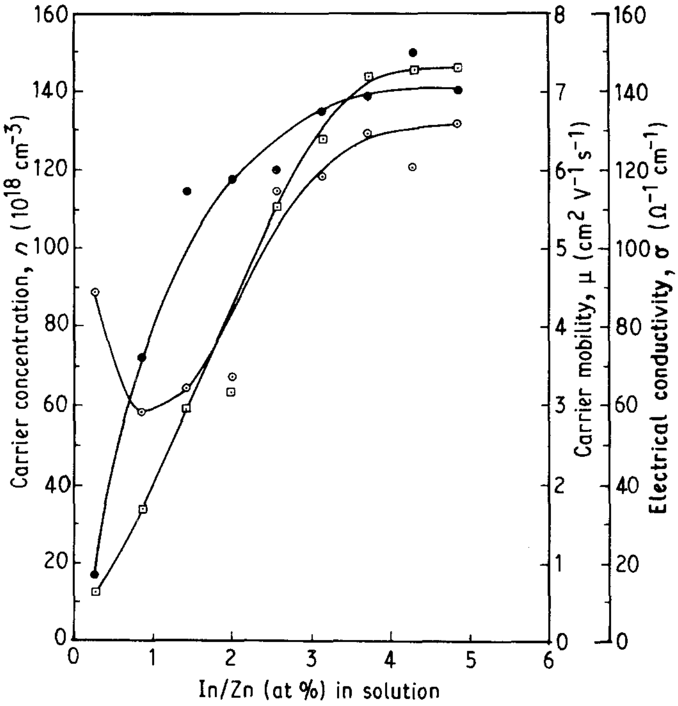

Figure 4 Variation of (⊡) electrical conductivity σ, (●) carrier concentration n, and (⊙) mobility μ with dopant level in indium-doped zinc oxide films.

TABLE I Variation in the physical properties of IZO films with molarity of the solution (In/Zn ratio constant)

Molarity of solution (M)	Thickness (nm)	Conductivity, σ (Ω^{-1} cm^{-1})	Carrier concentration, n ($\times 10^{20}$ cm^{-3})	Mobility, μ (cm^2 V^{-1} s^{-1})
0.10	450	146	1.4	6.0
0.15	600	228.5	2.04	6.9
0.20	740	426.5	3.7	7.2

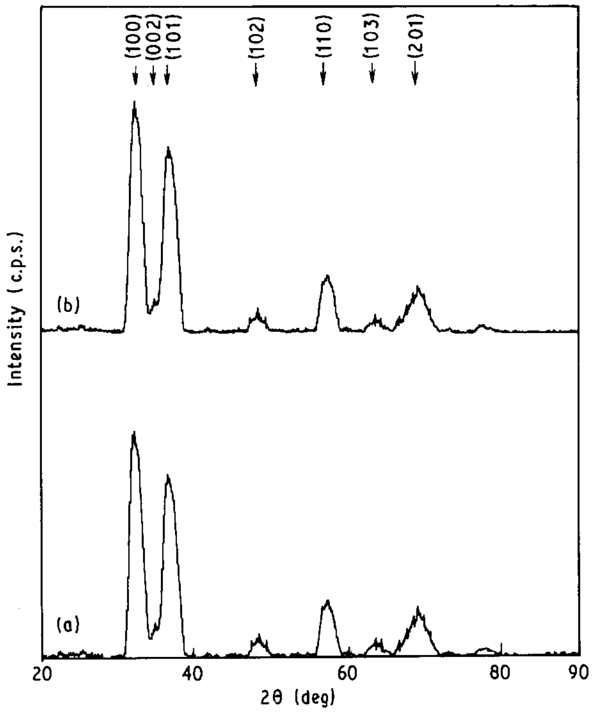

Figure 5 X-ray diffractograms of as-deposited and hydrogen plasma-exposed indium-doped zinc oxide films: (a) as deposited, (b) after 15 min H_2 plasma exposure.

oxygen vacancy. Table I shows the variations of σ, n and μ with the molarity of the solution. As the molarity of the solution is increased, the film growth rate increases. Due to the high growth rate other atmospheric impurity contamination is expected to be lower, and incorporation of zinc at interstitial sites is expected to be greater. This increases n which in effect increases the conductivity of the film. No change in the structural properties and hence mobility was observed for films deposited with the same In/Zn atomic ratio. It should be noted that the films with the highest conductivity also possess an average visible transmission above 85%.

These IZO films with high conductivity and transparency can be used as substrates for amorphous/microcrystalline silicon solar cells. During the deposition of amorphous/microcrystalline silicon film, the transparent conducting substrates are unavoidably exposed to hydrogen plasma. Excellent transparent conductors, i.e. fluorine-doped tin oxide and tin-doped indium oxide, are not sustained in hydrogen plasma and reduce to their respective metallic forms. The stability of IZO films was therefore checked in a hydrogen plasma. Fig. 5 shows the X-ray diffractograms of IZO before and after hydrogen plasma treatment. It can be seen that in both cases ZnO shows the same structure and composition. No traces of metallic zinc or indium were found in the film. The electrical properties also remained unaffected.

4. Conclusions

Indium-doped zinc oxide films were deposited by spray pyrolysis. The structural as well as electrical properties are well governed by the amount of zinc acetate and that of indium chloride in the solution. The carrier concentration is dependent on Zn^{2+} and In^{3+} incorporation, whereas the mobility is directly related to the structural properties of the films. The films are stable in hydrogen plasma. These films are found to be excellent as far as their use in amorphous/microcrystalline silicon solar cells is concerned.

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