TRANSPARENT CONDUCTING ZINC OXIDE FILMS BY SPRAY PYROLYSIS

by

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एवं प्रवर्तितं चक्रं नानुवर्तयतीह यः ।
अघायुरिन्द्रियारामो मोघं पार्थ स जीवति ॥

"He who does not, in this world, help to turn
the wheel thus set in motion, is evil in his
nature, sensual in his delight, and he,
O Arjuna, lives in vain".

-- The Bhagvadgita
Fifth Century BC

To my brother Syed Ghayasuddin
for everything he has done for me
and
to my teacher Mohammad Mahfooz-ur-Rahman Akhtar
for directing me towards the path of intellectual pursuits.

CERTIFICATE

I am satisfied that the Thesis presented by S.S. Major is worthy of consideration for the award of the Degree of Doctor of Philosophy and is a record of the original bonafide research work carried out by him under my guidance and supervision and that the results contained in it have not been submitted in part or full to any other university or institute for award of any degree/diploma.

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ABSTRACT

In the present work, transparent conducting films of undoped and indium doped zinc oxide have been deposited by spray pyrolysis. The substrate temperature, spray rate and the In-concentration have been recognized as the important deposition parameters and their effects on the electrical and optical properties have been investigated. Films with In/Zn ratio of 0.03, deposited under optimized conditions exhibit excellent transparent conducting properties (visible transmittance ~ 82% and sheet resistance ~ 10-15 ohm/square).

Auger depth profile reveals a uniform concentration of Zn , O and In throughout the thickness. Further, the concentration of indium in the film is the same as that in the spray solution. All films are polycrystalline and exhibit the hexagonal wurtzite structure of bulk ZnO with the same lattice constants. The grain size of undoped ZnO films is ~ 80 nm while that of the doped films is ~ 40 nm. Below a thickness of 100 nm, the grain size decreases with decreasing thickness. Undoped ZnO films have a strong orientation of c-axes parallel to the substrate normal. In case of doped films with In/Zn ratio of 0.03, the c-axes of grains are preferentially tilted at an angle of $\sim 58^\circ$ with respect to the substrate normal. Doped films with thickness $\leq$ 100 nm have randomly oriented crystallites.

The resistivity of films increases on annealing in oxygen/air and decreases on annealing in vacuum. Undoped ZnO films exhibit the largest change when annealed in oxygen and vacuum, while the films with In/Zn ratio of 0.03 show marginal

changes. These results are explained in terms of chemisorption and desorption of oxygen at the grain boundaries which lead to the creation or annihilation of extrinsic trap states.

The temperature and dopant concentration dependence of the resistivity, mobility and carrier concentration of as-deposited vacuum annealed and oxygen annealed films have elucidated the conduction mechanism existing in these films. The vacuum annealed films do not have extrinsic trap states at the grain boundaries. These are degenerate semiconductors and the mobility in these films is controlled by ionized impurity scattering inside the grains and scattering due to grain boundary potential barriers. In case of films with oxygen chemisorbed at the grain boundaries, the extrinsic trap states trap free carriers from the bulk of the grains and result in the formation of depletion layer potential barriers adjacent to the grain boundary region, which leads to the lowering of mobility. Depending upon the relative magnitudes of the doping level and the trap state density, different modes of conduction process are possible. At very high doping levels, segregation of dopants at the grain boundaries leads to an increase in mobility.

The optical constants, n and k in the visible agree well with the corresponding bulk value. In case of doped films, the optical behaviour in the near IR and IR regions is dominated by free carriers, exhibiting a plasma reflection edge, beyond which the reflection in the IR increases to $\sim$ 70%. The undoped films exhibit a dielectric behaviour up to 10 μm. The free carrier effective mass and lifetime inside the grains have been estimated;

and it is concluded that the scattering mechanism inside the grains is due to ionized impurities/imperfections. The optical bandgap of the films shifts to higher energies with increasing carrier concentration. This has been explained by taking into account two competing mechanisms, namely, a bandgap widening effect due to filling of low lying states in the conduction band and a bandgap narrowing effect due to electron-electron and electron-impurity interactions.

SIS solar cells have been fabricated by spraying ZnO:In on n-Si wafers. Typical efficiencies obtained are about 4% on cells of ~ 2 cm^2 area. Preliminary characterization of the junctions has been done and an energy band diagram has been proposed.

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