Influence of grain size on AZO ceramic synthesis

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Abstract. Aluminum doped zinc oxide (AZO) is a transparent conducting oxide (TCO) with oxygen vacancy mediated carrier density and mobility. Due to low oxygen self-diffusivity, the influence of thermal reducing treatments is strongly dependent on grain size. Electrical resistivity and Seebeck coefficient measurements suggest that mobility changes prevail to increase conductivity by reducing atmosphere anneal.

1. Introduction

Transparent conducting oxides (TCO) are semiconductors (Eg > 3 eV) with electrical resistivities in the order of milliohm.cm and optical transmittances above 80% in the visible spectrum. Their principal applications involve electrodes for liquid crystal displays (LCD), as well as various other optoelectronic devices. The use of indium oxide doped with Sn (ITO) or Zn (IZO) [1] is widespread for this purpose but cost and availability considerations have promoted the search for possible substitutes. One alternative, which has received increased attention, recently, due to low component toxicity, relative abundance and consequent low cost, as well as favorable properties is aluminum doped zinc oxide (AZO) [2]. Optoelectronic devices require TCO thin films, frequently deposited by sputtering, either from ceramic or metallic targets, in oxygen bearing reactive atmospheres. Thin film quality, in terms of electrical and optical properties depends substantially on ceramic resistivity [3] and process conditions. This work compares the electrical properties of ceramics obtained by solid-state reaction with those produced by chemical co-precipitation.

2. Experimental procedures

AZO was prepared by solid-state reaction from a mixture of oxides (Merck Analytical Grade) in stoichiometric proportions for 3.2 atomic % Al in Zn. The oxides were suspended in acetone, ground in an agate mortar, and sieved with N°270 (52 μm) ASTM gage. The powder was pelletized in 12 mm OD discs with a hydraulic press at 98 MPa and sintered for 48 h at 1400°C in a furnace with molybdenum disilicide heating elements.

Co-precipitated samples were prepared by dissolving mixtures of the commercial alloy ZAMAC-3 and 99.99% pure metallic Zn in nitric acid (65% m/m). They were subsequently treated with NH3 (28% m/m) maintaining a pH between 6 and 7, in keeping with optimal minimum solubility [4].

The sample morphology was examined by scanning electron microscopy and the wurtzite structure...
corroborated by X-ray diffraction.

Controlled atmosphere reducing anneals were undertaken with reactive oxygen fugacity buffering mixtures of CO/CO$_2$ supplied by MKS 1159 mass flow controllers in a Lindberg tubular reactor furnace fitted with a quenching rod assembly, which provided for sample cooling in the cold end of the reactor preserving the integrity of the annealing atmosphere. The codes S6-0h, S6-2h and S6-4h identify representative samples obtained by solid-state reaction annealed at 1000°C and $p_{O_2} = 10^{-16}$ atm for the indicated times, whereas Z11-0h, Z11-2h and Z11-4h are corresponding identifiers for co-precipitated samples.

Electrical measurements were made on prisms 1.2 cm x 0.25 cm x 0.2 cm carved from the sample pellets fitted with 100 nm thick sputtered aluminium electrodes, which supplied the contact for 40 gauge copper-constantan thermocouples. The D.C. electrical resistivity was measured by the Kelvin method and the Seebeck coefficient obtained by analogue subtraction during thermal relaxation [5] under gradients not exceeding 0.25°.

3. Results and discussion

Without further treatment, solid-state reaction samples exhibit lower resistivity than co-precipitated specimens (Table 1). Negative Seebeck coefficients are consistent with n-type semiconduction with a magnitude inversely proportional to carrier density but co-precipitated samples are too resistive for reliable Seebeck measurements.

**Table 1. Resistivity and Seebeck coefficient for solid state reaction (S6) and co precipitated**

| Sample | Al/Zn At. % | Resistivity [Ω-cm] | S [µV/K] |
|--------|-------------|-------------------|----------|
| S6     | 3.2         | 0.43              | -73.04   |
| Z11    | 3.2         | 78700             |          |

Since electronic conduction is sensitive to oxygen vacancy concentration [6], controlled atmosphere reducing annealings at 1000°C and $p_{O_2} = 10^{-16}$ atm, just above the zinc oxide reduction boundary were undertaken for 2 and 4 h periods. The co-precipitated specimen demonstrated extreme sensitivity to these treatments, which reduced their resistivity in five orders of magnitude within the first two hours (figure 1).

**Figure 1.** DC electrical resistivity and Seebeck coefficient of AZO samples prepared by solid state reaction (S6) and co-precipitation (Z11) as a function of annealing time at 1000°C and $p_{O_2} = 10^{-16}$ atm.
In stark contrast, solid-state reaction samples are essentially insensitive to the reducing annealing treatment. Scanning electron microscopy demonstrated that whereas solid state reaction produced an average grain size of 10 µm (figure 2a), co-precipitates are submicrometric (figure 2b) even after annealing at 1400°C for comparable times.

**Figure 2.** Scanning electron microscopy of (a) solid state reaction samples and (b) chemically co-precipitated specimens.

Preliminary solid-state reaction experiments, undertaken at 1200°C for 24 h, yielded resistivities with an order of magnitude of kΩ·cm. Higher annealing temperatures and longer sintering times contributed, not only to better homogeneity of the aluminum dopant and lower resistivity, but also to increased grain size. If the partial pressure of oxygen during the sintering process is fixed by dilution as in for instance air (log $p_{O_2} = -0.68$), increased temperature has a reducing effect because it approaches the oxide reduction boundary leading to increased oxygen vacancy concentration and consequently lower resistivity. Cooling has the opposite effect, which requires careful attention to quenching procedures. The co-precipitated texture, of reduced grain size and higher porosity, promotes higher specific surface and consequently sensitivity to the reducing treatment. This is consistent with the low intracrystalline diffusivity of oxygen in the wurtzite structure [7].

However, the influence of reducing anneals on the Seebeck coefficient, and consequently on carrier density, is limited to changes commensurate with the experimental uncertainty of the measurements. Since conductivity is proportional to the product of carrier density and mobility, the dominant cause for the drastic decrease in electrical resistivity observed within the first two hours of reducing anneal must be attributed to increased mobility. It is also significant that, whereas resistivity is sensitively dependent on high specific surface, Seebeck coefficients reflect bulk carrier density consistently with increased contribution of grain boundary conduction to the overall resistivity [8] with smaller grain size. This behavior is well established for various semiconducting oxides, widely employed as conductimetric gas sensors [9], which respond readily to changes in surface state occupation induced by a chemical stimulus, albeit at the expense of selectivity.

The effect of reducing thermal treatments or deposition conditions for zinc oxide thin films has been noted before, although direct comparison has been hampered by the absence of specific
experimental $pO_2$-T coordinates. The reactive $pO_2$ buffering systems employed in this work remove this ambiguity, as well as increase the reducing character of the atmosphere with decreasing temperature, in the critical quenching stage.

4. Conclusions

Sintering is insufficient to diminish resistivity significantly in chemically co-precipitated samples. Reducing annealing treatments to optimize the metal-oxygen stoichiometry can be employed to improve the electrical properties of sub micrometric material. In practical applications of TCO that require thin films of nanometric grain size, reducing controlled atmosphere may improve processing conditions.

5. References

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