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High quality aluminium doped zinc oxide target synthesis from nanoparticulate powder and characterisation of sputtered thin films

P.J.M. Isherwood [a,*], N. Neves [b], J.W. Bowers [a], P. Newbatt [b], J.M. Walls [a]

[a] Centre for Renewable Energy Systems Technology, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK
[b] Innovnano, S. A., Rua Coimbra Inovação Parque, IParque Lote 13, 3040-570 Antanhol, Coimbra, Portugal

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ABSTRACT

Nanoparticulate aluminium-doped zinc oxide powder was synthesised through detonation and subsequent rapid quenching of metallic precursors. This technique allows for precise compositional control and rapid nanoparticle production. The resulting powder was used to form sputter targets, which were used to deposit thin films by radio frequency sputtering. These films show excellent sheet resistance and transmission values for a wide range of deposition temperatures. Crystal structure analysis shows that crystals in the target have a random orientation, whereas the crystals in the films grow perpendicular to the substrate surface and propagate preferentially along the (002) axis. Higher temperature deposition reduces crystal quality with a corresponding decrease in refractive index and an increase in sheet resistance. Films deposited between room temperature and 300 °C were found to have sheet resistances equivalent to or better than indium tin oxide films for a given average transmission value.

1. Introduction

Transparent conducting oxides (TCOs) are an unusual class of material with a wide range of uses. These include electronic screens and displays including touchscreen panels through to electrochromic windows, light-emitting diodes (LEDs) and solar cells [1,2]. They are easily produced, and techniques such as chemical vapour deposition, magnetron sputtering and spray pyrolysis are regularly employed [3,4]. The major concerns surrounding the metal oxide conductors are their brittleness and lack of flexibility, their inherent trade-off between transparency and conductivity [4,5] and in a few cases cost, rarity and environmental issues associated with obtaining the raw materials [3,4]. Despite these concerns, doped metal oxides are still the dominant type of transparent conductor, largely because of their good electrical properties, ease of formation and deposition and their relatively good chemical and thermal stability [6]. At present the most commonly used TCO is tin-doped indium oxide (indium tin oxide, or ITO) [1], but due to concerns over supply and cost of indium there has recently been an increasing interest in alternatives [7]. Aluminium-doped zinc oxide (AZO) is another commonly used TCO and is a cheaper alternative to ITO [7,8].

In order to compete with ITO, alternatives must have as good or better electrical and optical properties. This means an average visible light (400–800 nm) transmission of around 80%, and sheet resistances of 20 Ω/sq or less [9]. The best quality ITO films are usually deposited at elevated temperatures, which can cause serious problems for any temperature-sensitive technology such as organic solar cells and LEDs [9]. Materials that can achieve similar transmission and sheet resistance values at lower deposition temperatures are therefore of significant interest.

The electrical and optical properties of sputtered thin films depend not only on the deposition parameters but also on the characteristics of the sputter target. In particular, grain size, density, oxygen content and homogeneity play an important role in the determination of target quality [10–14]. Innovonano S.A. has developed a patented nanoparticle-based route for the synthesis of AZO powders [15]. The following is a description and analysis of the material synthesis technique and characterisation of films sputtered from targets formed using this material.

2. Experimental details

2.1. Powder synthesis and target preparation

A pyrolysis production method was used to synthesise AZO nanostructured powder containing 0.5 wt.% Al dopant [15]. Nanoparticulate powder was synthesised by detonation of an emulsion containing metallic Zn and Al precursors in the same concentrations as the desired material composition (Fig. 1).

This method combines high pressures (>1000 MPa), high temperatures (500–3000 °C) and ultrafast quenching (10^8 °C/s to 10^9 °C/s). Powder crystal size is determined by the precise conditions used. The resulting material shows a structure composed of both individual and agglomerated nanoparticles (Fig. 2). Subsequent to formation, the powder was disaggregated in order to improve sinterability [11].

* Corresponding author. Tel.: +44 1509 635306.
E-mail address: P.J.M.Isherwood@lboro.ac.uk (P.J.M. Isherwood).

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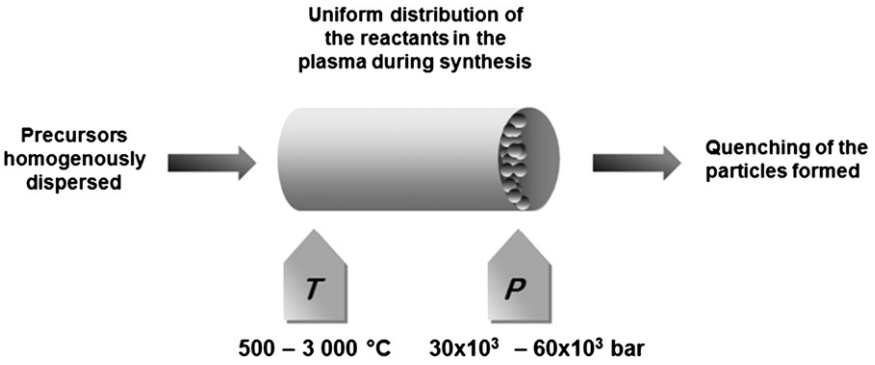

Fig. 1. Synthesis method for the formation of AZO nanostructured powder.

Particle size distribution was measured using a CPS Disc Centrifuge (Model DC 20000, CPS Instrument Inc). A Quantachrome Nova 1000E Series equipment using helium as the carrier gas was used to determine the powder specific surface area. Crystal structure was measured using a Bruker D8 Advance X-ray diffractometer equipped with a Cu-K_α X-ray source. Scanning electron microscopy (SEM) was performed using a Zeiss Auriga CrossBeam scanning electron microscope equipped with a focused ion beam (FIB). Aperture size was 60 μm and the operating voltage was 5 kV. Transmission electron microscopy (TEM) was performed using an FEI Tecnai F20 field emission gun transmission electron microscope. TEM images were taken using a bright field detector at 200 kV. TEM samples were prepared by FIB milling using a dual beam FEI Nova 600 Nanolab SEM. A standard in-situ lift-out method was used to prepare cross-sectional samples. A platinum over-layer was deposited to define the sample surface and to homogenise the final sample thinning. Samples were thinned to 75 nm. The sputter target was prepared by hot-pressing in an argon atmosphere using an HPW 315/400-2200-1000. Sintering took place under a constant pressure of 50 MPa with a heating/cooling rate of 10 °C/min and a holding time of 60 min at 1025 °C. The final density of the target was measured using the liquid displacement technique with distilled water. An image analyser programme was used to calculate the mean grain size of the sintered sample. Target electrical properties were measured using a Biorad HL 5500 Hall Effect device at room temperature using the van der Pauw configuration.

2.2. Film deposition and characterisation

AZO was sputtered onto 50 mm by 50 mm soda-lime glass slides using the AZO ceramic target. Films were deposited using an AJA International Orion 8HV sputter coater with an AJA 600 series RF power supply. Deposition conditions were kept at 180 W power (3.95 W/cm^2) with no oxygen input, 1 mTorr pressure (0.133 Pa) and 5 SCCM (8.33×10^{-8} m^3/s) of argon, whilst the temperature and deposition time were varied. Films were deposited over 1, 2 and 3 h, and the substrate temperatures used were room temperature, 100, 150, 200, 300 and 450 °C. Each deposition temperature was used for each of the three deposition times. A second set of films was deposited from a commercially available non-nanoparticulate target for comparison. These films were deposited at 150 °C. This temperature was chosen as it was found to give the best overall performance.

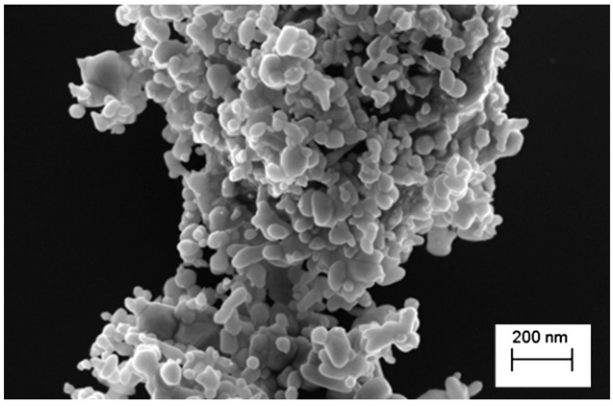

Fig. 2. SEM image of the agglomerated AZO powder. Particles are approximately 20–40 nm across.

Film optical and electrical characterisation were carried out using an Ambios XP2 stylus profilometer to measure thickness, a Varian Cary 5000 spectrophotometer for transmission spectra and an Ecopia HMS 3000 Hall effect system for mobility, resistivity and carrier concentration measurements. Film roughness measurements were taken using a Taylor-Hobson Sunstar-HD Coherence Correlation Interferometer (CCI), and refractive index and extinction coefficient measurements were taken using a Horriba iHR320 ellipsometer. A four-point probe was used to measure sheet resistance. Structural characterisation was carried out using both scanning and transmission electron microscopes. SEM was conducted using a Carl Zeiss (Leo) 1530 VP field emission gun scanning electron microscope. Aperture size was 30 μm and the operating voltage was 5 kV. TEM was conducted using an FEI Tecnai F20 field emission gun transmission electron microscope, equipped with a bright field detector and at an operating voltage of 200 kV. TEM samples were prepared by the same method as described for the sputter target characterisation. X-ray diffraction (XRD) was performed using a Brucker D2-phaser desktop X-ray diffractometer equipped with a Cu-K_α X-ray source and Lynxeye^{TM} detector. The beam slit was 1 mm wide, and the antiscatter plate was positioned 3 mm above the sample. The sample was rotated at 15 rpm. Structural characterisation was performed on selected samples only.

3. Results and discussion

3.1. Powder and sputter target characterisation

The powder particle size distribution reveals two different groups of particles. The powder is largely composed of nanoparticles (~30% wt. fraction) of about 40 nm in size (Fig. 2). Some larger particles are also present (~70% wt. fraction) which exhibit random morphology. These are composed of coalesced nanoparticles and some fragmented particles. Fig. 3 shows the XRD pattern of the powder (a) and sintered target (b).

Using the Scherrer equation [16], crystallite size was found to be 19 nm, in line with the broad diffraction curve and the high specific surface area obtained (12.55 m^2 g^{-1}). Only the wurtzite phase was identified in the powder. XRD performed on the sintered target revealed that whilst wurtzite is the primary phase, a minor secondary phase, $ZnAl_2O_4$ (ghanite) is also present. This is typically seen when Al concentrations above the solid solubility limit are used [17].