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Zinc oxide thin films: Characterization and potential applications

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ABSTRACT

Zinc oxide (ZnO) has attracted recent interest for a range of applications, including use as a transparent conductive oxide (TCO) and in gas sensor devices. This paper compares ZnO films grown using two methods designed for the production of thin films, namely sol–gel and aerosol assisted chemical vapour deposition (AACVD) for potential use in sensor and TCO applications. Materials produced by the sol–gel route were observed to be amorphous when annealed at 350 °C, but were crystalline when annealed at higher temperatures and had a relatively open grain structure when compared to the AACVD films. Electrical characterization showed that materials were highly resistive, but that their properties varied considerably when the measurements were performed in vacuum or in air. This behaviour was rapidly reversible and reproducible for room temperature measurement.

In contrast materials grown by aerosol-assisted CVD were non-porous, polycrystalline and conductive. Measured electrical properties did not vary with changing measurement atmosphere. These differences are discussed in terms of the structural characterisation of the films and some comments are made regarding the suitability of both approaches for the growth of ZnO thin film sensor materials.

1. Introduction

ZnO is a wide direct band-gap oxide semiconductor that has significant potential application in electronic, optoelectronic and information technology device platforms due to its electrical and optical properties [1–4]. ZnO is also a promising material for gas sensor applications due to its electrical sensitivity to certain gaseous species, chemical and thermo-mechanical stability, ease of doping, non-toxicity, ready availability and low cost. This material has been exploited for gas sensors in the form of single crystals, sintered pellets, nanocrystals, nanorods, thick and thin films, etc. [5–9]. However, thin films are the preferred mode of active material preparation for use in sensors due to the ease of fabrication and reduced number of processing steps required [10].

It is known that oxide formation methods and the associated thermal budget are the main factors that influence the morphology and microstructure of resulting materials. The microstructure can affect aspects of a material's properties, and can be useful for this reason. When considering gas sensing, properties are related to the material surface where the gases are adsorbed and the surface reactions occur. This reaction modifies the concentration of charge carriers in the material, giving rise to a change in its electrical resistance, which is used for detection [11]. Therefore, the microstructure and resulting surface morphology of ceramics have a significant influence on their electrical properties and corresponding sensitivity of these properties to contact with gaseous species.

Several methods have been demonstrated to produce pure ZnO films, including sputtering [12], chemical vapour deposition (CVD) [13], pulsed laser deposition [14], spray pyrolysis [15] and the sol–gel process [16–21]. Of these, AACVD and the sol–gel method were studied in detail as both methods are solution chemistry based and offer the capability to coat large surface areas. The influence of deposition method and temperature on microstructure and morphology, and their corresponding influence on gas sensing properties were examined.

2. Experimental

ZnO sol–gels were prepared as follows: anhydrous zinc acetate was first added to isopropanol at room temperature and then stirred continuously at 50 °C. Monoethanolamine (MEA) was then added to the mixture. The final concentration of the zinc acetate was 0.3 mol/L and the molar ratio of the MEA to zinc acetate was maintained at 1.0. The resulting mixture was then stirred for 1 h to form a transparent homogeneous mixture that was cooled to room temperature, syringe

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filtered using a 0.45 µm Acrodisc Versapor® filter, and aged for 24 hrs. Thin films were prepared by spin coating the aged solution onto glass wafers at rotation speeds of 3000 rpm for a duration of 30 s. Samples were dried on a hotplate at 130 °C for 10 min. Three depositions were performed and samples were then annealed from room temperature at a heating rate of 10 °C/min to 350, 400, 450, 500 and 550 °C and maintained at this temperature for 1 h before air-cooling to room temperature.

AACVD films were deposited using a modified CVD system (Electrogas Systems Ltd, UK). The system consisted of a tubular quartz reactor containing a silicon carbide coated graphite susceptor. The temperature of the susceptor was monitored using a k-type thermocouple coupled with a proportional–integral–derivative controller (PID controller), and heated with a water cooled IR lamp mounted externally beneath the reaction tube. A 0.1 mol/L solution of zinc acetate in methanol, held in a container above the metal diaphragm of a modified commercially available ultrasonic humidifier to form an aerosol, was used as the precursor. The aerosol generated was swept into the reaction zone using a nitrogen carrier gas (1.58 L/min) metered from a mass flow controller. Films were deposited onto plain glass microscope slides using a susceptor temperature of 400 and 425 °C. The total deposition time was 20 min. The AACVD deposition method lead to films containing colour fringes related to the thickness of film at that particular point. Films deposited at 400 °C contained fringes ranging from ~50 nm to 220 nm, and the 425 °C film exhibited fringes ranging from ~50 nm to 215 nm. The thickness of the films was measured via Focused Ion Beam SEM (FIB-SEM). Variation in film thickness across the substrate in cold wall CVD reactors, such as the one used here, is well documented [22].

The crystalline orientation, structure and degree of crystallinity of the ZnO single and multilayer thin films were measured using a Philips (PW3719) X'pert materials research X-Ray diffractometer (XRD) with a Cu Kα radiation ($\lambda = 0.154060$ nm), and a scanning range of 2θ set between 20° and 60°. The surface morphology of the films was determined by AFM Micrographs, recorded using a Veeco D3100 system, operating in the tapping mode with a 10 nm diameter silicon tip (Asylum AC160TS) over an area of 1 µm^2. Resistivity measurements were carried out with a Keithley 617 electrometer evaporating two coplanar Al contacts with a width of 4 mm and a separation of 1 mm, in vacuum, at atmospheric pressure and ambient temperatures. In the case of the AACVD prepared films the resistivity of the thickest fringe (220 and 215 nm for 400 and 425 °C respectively) was measured as these fringes covered the greatest area on the substrate available to evaporate the Al contacts.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns from ZnO thin films prepared by the sol–gel method, as described above. Films annealed at 350 °C did not exhibit any diffraction peaks and were therefore deemed amorphous. The broad feature between 20 and 40° 2θ is due to the amorphous film and the amorphous glass substrate used. Films annealed at 400 °C exhibited three low intensity diffraction features at 31.8, 34.5 and 36.4° 2θ which correspond to the (100), (002) and (101) planes in the hexagonal wurtzite structure [19]. Annealing at 450 and 500 °C resulted in preferred orientation of crystallisation in the (002) plane. However, annealing at 550 °C resulted in diffraction features assigned to the (100), (002) and (101) planes of similar intensity. Similar behaviour has been observed by other authors [2,3]. Again, the broad feature between 20 and 40° 2θ present in samples annealed at 400, 450, 500 and 550 °C is due to the amorphous glass substrate.

Films prepared by AACVD were observed to be polycrystalline in nature, as shown in Fig. 2, with the three characteristic diffraction peaks of hexagonal wurtzite ZnO displayed at 36.4° (2θ) (101), 47.5° (2θ) (102) and 56.4° (2θ) (110). The (101) peak is dominant for both films grown via AACVD at 400 and 425 °C respectively. A similar characteristic has been reported by Waugh et al. [22] with films deposited by AACVD from a solution of zinc acetate in methanol onto glass substrates. Waugh et al. noted that as the temperature of the substrate was increased from 400 °C, where the principal peak was (101), to 450 °C the films began to exhibit a tendency toward a (002) orientation, with this plane becoming dominant and remaining so as the deposition temperature increased to 650 °C. Their films also exhibited the (102) plane at temperatures above 450 °C, with the (110) plane only observed in the film deposited at 550 °C. The AACVD films prepared in this study were deposited below 450 °C, and within a relatively narrow temperature window (25 °C), resulting in the diffraction patterns looking similar. A broad amorphous peak between 20 and 40° can also be seen in both diffraction patterns in Fig. 2. This is again characteristic of the glass substrate on which the films were deposited, and has been observed previously by other groups working in the area of metal oxide CVD coatings on glass substrates [23,24]. Tapping mode AFM micrographs were obtained for samples prepared at a range of temperatures. In the case of samples prepared by the sol–gel route (Fig. 3), spherical shaped particles were observed with mean size of 60 nm.

Samples prepared by aerosol-assisted CVD were observed to have a spherical grain structure, consistent with an island growth regime and a mean grain diameter of 35 nm. A representative AFM image is shown in Fig. 4.

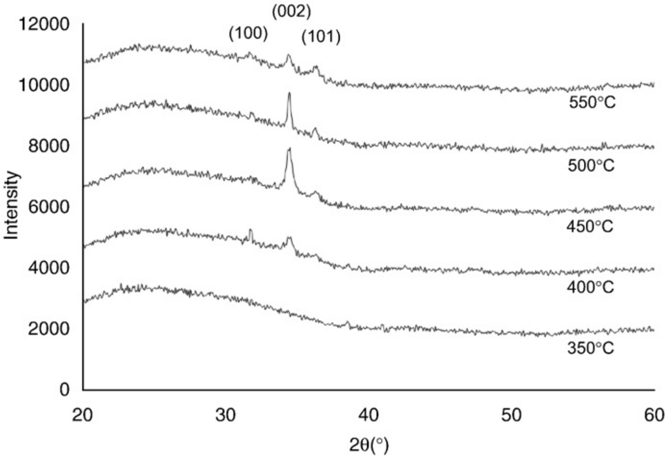

Fig. 1. XRD patterns of ZnO sol–gel films annealed at 350, 400, 450, 500 and 550 °C. (Vertical offsets have been introduced for clarity of viewing).

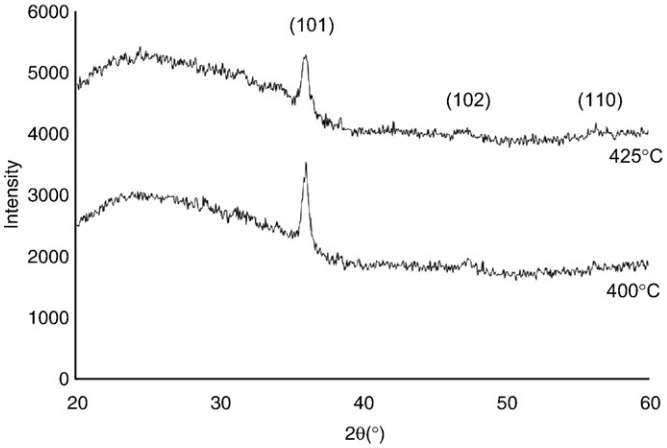

Fig. 2. XRD patterns of ZnO films grown by aerosol-assisted CVD at 400 and 425 °C. (Vertical offsets have been introduced for clarity of viewing).