

Aluminium-doped ZnO films by a modified chemical vapor deposition technique

S.Y. Pung and K.L. Choy*

*Department of Mechanical, Materials and Manufacturing Engineering,
Faculty of Engineering, University Park, University of Nottingham, Nottingham, NG7 2RD,
United Kingdom, Kwang-leong.Choy@nottingham.ac.uk

ABSTRACT

A simple, controllable and cost effective modified chemical vapor deposition (CVD) technique has been established to produce Al-doped ZnO films. In this technique, the dopant solution is located outside the reactor. Aerosol of the dopant solution is delivered into reactor during synthesis. Consequently, the amount of dopants can be controlled easily by adjusting the concentration of dopant precursor solution. The Al-doped ZnO films deposited on glass substrates consisted of polycrystal, mainly with (002) orientation. The preferred orientation of (002) Al-doped ZnO films could be further improved on the glass substrates pre-coated with highly (002) oriented ZnO buffer layer. The resistivity of the films could be varied between the order of magnitude of 10^0 and 10^2 Ω .cm by changing the concentration of dopant solution.

Keywords: ZnO, thin films, aerosol, doping, chemical vapor deposition technique

1 INTRODUCTION

ZnO has unique properties of wide-bandgap (3.37eV) and large exciton binding energy (60meV) at room temperature. These properties made ZnO a promising material for opto-electronic and electronic devices such as light emitting diode (LED) [1], solar cell [2], UV laser [3] and field-effect transistor [4]. However, it is essential to produce n-type and p-type ZnO films or NWs with controlled conductivity in order to realize these potential applications of ZnO.

Doped ZnO films have been produced by various processing techniques, for instance, pulse laser deposition (PLD) [5], chemical vapor deposition (CVD) [6], magnetron sputtering [7] and metal organic chemical vapor deposition (MOCVD) [8]. Nevertheless, the inherent limitations of these techniques such as high equipment and processing cost, lack of process flexibility to add or change dopant precursor, high synthesis temperature or difficult to control doping concentration, might be the main drawback for producing high quality and cost-effectively doped ZnO films.

A modified Vapor Deposition technique has been used to produce Al-doped ZnO films. In this technique, the dopant solution is located outside the reactor whereas the Zn powder precursor is placed in the middle of the reactor.

The arrangement by placing the dopant solution outside the reactor has become the major advantage of this technique. This unique setup provides many advantages such as a better control of the precursor supply rate and supply period, uniform doping attributes to the uniform precursor flux in the reactor, flexibility to refill precursor or change precursor composition during synthesis, low synthesis temperature as the precursor solution normally decomposes at a temperature lower than 500°C, a wider choice of precursor, and a low setting up cost [9-10].

2 EXPERIMENTAL PROCEDURE

Al-doped ZnO films were grown by a modified low pressure Chemical Vapour Deposition (CVD) technique. Two types of glass substrates, i.e. bare glass substrates and glass substrates pre-deposited by a highly c-oriented ZnO buffer layers (80 nm) were used in this study. The ZnO buffer layers were deposited by ALD technique. The detailed ALD deposition procedures and processing conditions have been discussed elsewhere [11].

The growth of Al-doped ZnO films were carried out in a horizontal tube reactor by a vapor transport process for 30 minutes. The aluminium nitrate solution at different concentration, i.e. from 0.01 to 0.75M, was kept in a volumetric flask. This volumetric flask was placed in a aerosol nebulizer, which was located outside the reactor. The aerosol generated from the aluminium nitrate solution was carried by the argon gas into the horizontal furnace. In the furnace, the aerosol precursor evaporated and decomposed into reactants vapor in the heated deposition zone, providing sources of Al and Zn for the growth of Al-doped ZnO films.

The crystalline structure of ZnO films were characterized by a X-ray Diffractometer (Bruker, Cu K_{α} radiation with wavelength of 1.5406 Å). The surface morphology of the films was examined using a scanning electron microscope (SEM, Phillips XL30 ESEM-FEG). Furthermore, the presence of Al dopants in the films was investigated by EDX. The thickness of ZnO films was determined from the cross-section SEM images. The sheet resistance of the Al-doped ZnO films was determined using Van der Pauw technique at room temperature.

3 RESULTS AND DISCUSSIONS

The crystal structures of the as-deposited films were characterized by XRD. As shown in Figure 1 (a), several ZnO diffraction peaks such as (100), (002), (101), (102), (110), and (102) were observed from the Al-doped ZnO films on glass substrates. These diffraction peaks pattern matched well with the standard diffraction pattern of wurtzite ZnO (JCP2.2CA. 01-079-2205). It is clearly seen that (002) is the most dominant crystal plane in all the Al-doped ZnO films, regardless the aluminium nitrate dopant concentration. No diffraction peaks of Zn metal were found.

The (002) preferred orientation of the Al-doped ZnO films has been improved when the films were grown on the highly (002) oriented ZnO buffer layers as shown in Figure 1 (b). The (002) oriented buffer layer has facilitated the subsequent deposition of Al-doped ZnO films in [0001] direction. Similar to the films deposited on glass substrates, (002) crystal plane was dominant in all the Al-doped ZnO films deposited on glass substrates pre-coated with ZnO buffer layer. Highly (002) oriented Al-doped ZnO films could be used to grow vertically aligned ZnO nanowires.

The surface morphologies of ZnO films on glass substrates doped with different concentration of aluminium nitrate solution are exhibited in Figure 2. The ZnO films doped with 0.01M, 0.05M and 0.1M aluminium nitrate solution consist of polycrystals with size smaller than 4 μ m. Hexagonal disc-like crystal structures could be found on the ZnO film doped with 0.1M aluminium nitrate solution as shown in Figure 2 (c). Furthermore, as 0.5M aluminium nitrate solution was used, flower-like ZnO structures were formed on the substrate surface. The average thickness of the Al-doped ZnO films were 6 μ m.

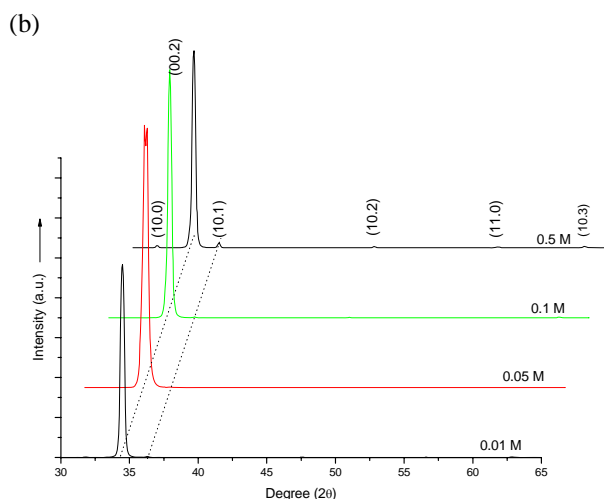
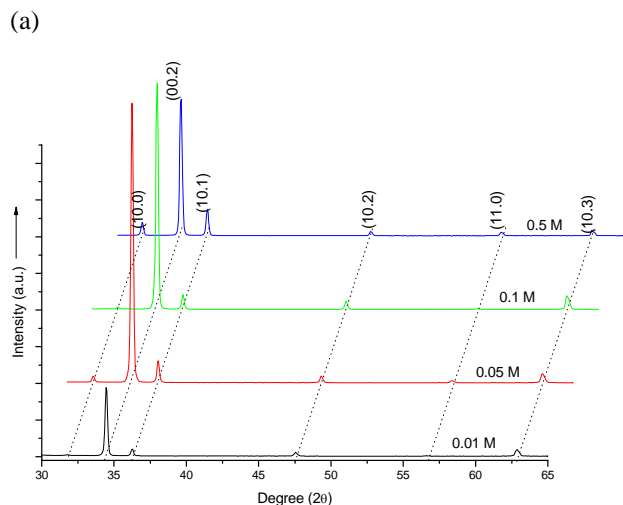


Figure 1. XRD diffraction profiles of the Al-doped ZnO films deposited on (a) glass substrates, (b) glass substrates pre-coated with highly c-oriented ZnO film.

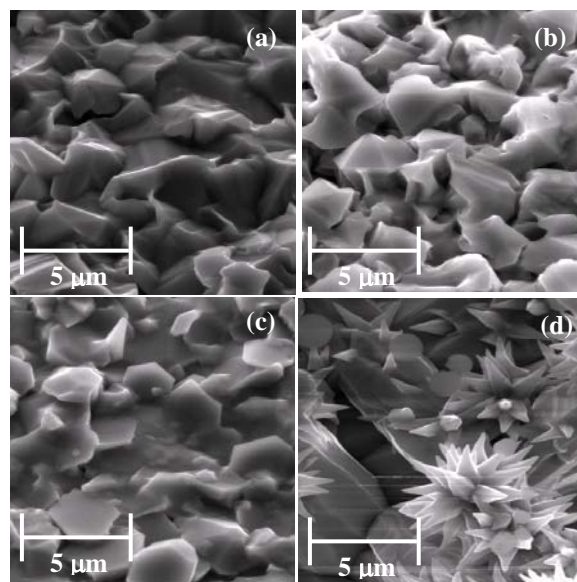


Figure 2. ZnO films deposited on glass substrate and doped with different concentration of aluminium nitrate solution (a) 0.01M, (b) 0.05M, (c) 0.1M and (d) 0.5M.

The Al dopants in the ZnO films deposited on glass substrates have been measured by EDS analysis as shown in Figure 3 (a). The atomic percentage of Al increased and achieved an average maximum of 1.02% when 0.5 M aluminium nitrate solution was used as displayed in Figure 3 (b).

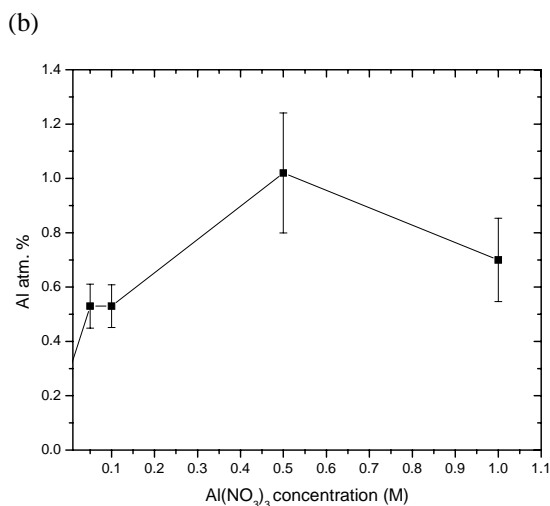
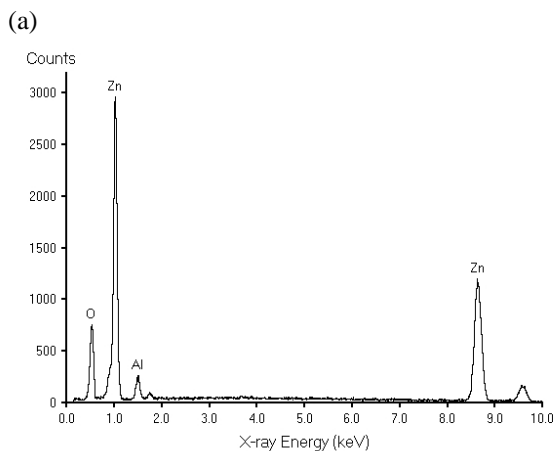


Figure 3. (a) EDS analysis of the ZnO film doped with 0.5M Al(NO₃)₃ and (b) atomic percentage of Al in ZnO films doped with different concentration of Al(NO₃)₃ solution.

This result explains well with the observations in the change of resistivity of Al-doped ZnO films as shown in Figure 4. The resistivity of the films decreases from 10² to 10⁰ Ω.cm as the concentration of aluminium nitrate solution increases from 0.01M to 0.5M. This indicates that the incorporated Al dopants have contributed charge carriers in the ZnO films, resulting lower resistivity. However, the further increase in aluminium nitrate concentration (>0.5M) did not improve the resistivity of ZnO films. As shown in Figure 5, many Al₂O₃ particles could be found on the surface of ZnO films especially when high aluminium nitrate solution (>0.5M) was used in the deposition process. The formation of these Al₂O₃ particles could be the main reason that restricting more Al dopants to be reached and incorporated into the ZnO films although the concentration of aluminium nitrate solution has been increased.

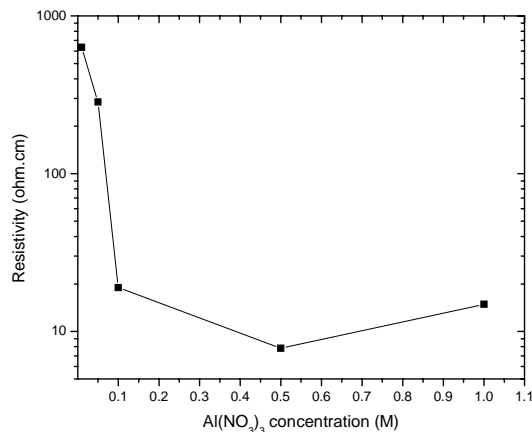


Figure 4. Resistivity of Al-doped ZnO films measured by Van der Pauw technique.

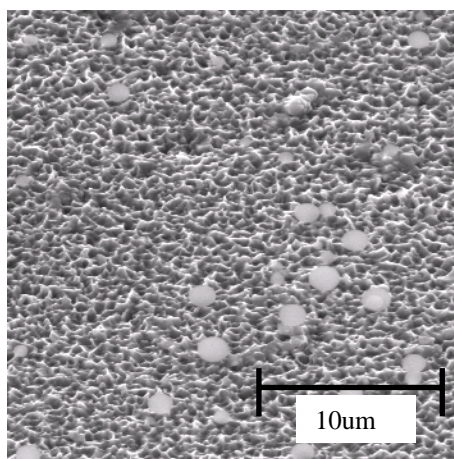


Figure 5. Al₂O₃ particles were found on the surface of ZnO film when doped with 1M Al(NO₃)₃ solution.

4 CONCLUSIONS

A modified CVD technique was established to produce Al-doped ZnO films. The Al-doped ZnO films on glass substrates were highly (002) oriented. The (002) preferred orientation of the Al-doped ZnO films could be further improved using highly (002) oriented buffer layer. The resistivity of the Al-doped ZnO films could be varied from 10⁰ to 10² by increasing the aluminium nitrate concentration solution up to 0.5M. However, further increased of aluminium nitrate concentration above 0.5M would not lower the resistivity of the Al-doped ZnO films, which could attribute to the formation of Al₂O₃ particles.

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