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# The growth of Al-doped ZnO nanorods on *c*-axis sapphire by pulsed laser deposition

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ABSTRACT

Transmission and scanning electron microscopy are used to compare the growth of nanorod arrays in ZnO and Al-doped ZnO (2%Al) films grown by pulsed laser deposition. For a laser pulse energy of 10 mJ/pulse, nanorod arrays were formed at temperatures 575–625 °C for ZnO films and 650–675 °C for Al-doped ZnO films. For higher laser pulse energies, up to 30 mJ/pulse, nanorod growth in both cases moved to lower temperature regimes. By comparing nanorod growth temperature, morphology and density for ZnO and Al-doped ZnO growth, it is concluded that the differences in growth are due to lower surface diffusion rates in Al-doped films. The electrical resistivities of the Al doped ZnO films were in the range $5–7\times10^{-3}\,\Omega\cdot$cm.



## 1. Introduction

There is considerable interest in the use of ZnO films as transparent electrodes for flat-panel displays, light emitting diodes and solar cells. These films can be conveniently grown by a variety of chemical vapour deposition methods, such as pulsed laser deposition (PLD) [1–4], metal-organic chemical vapour deposition (MOCVD) [5] and sputtering [6], as well as by wet chemistry methods [7]. However, although undoped ZnO films usually show natural n-type conductivity, believed to result from the presence of O vacancies or Zn interstitials, their high resistivity generally requires that films are deposited on transparent conducting substrates, such as the commonly-used indium tin oxide (ITO). This increases cost, and, in the case of ITO, additional issues of materials availability and toxicity. Thus, there have been many studies aimed at doping these films with group 3 elements such as Ga [8,9], Al [10] and In [11] to improve their n-type conductivity. Al-doped films are of particular interest, combining low resistivity, down to about $10^{-4}\,\Omega\cdot$cm [12–17], comparable with that of ITO, with very high optical transmittance over the visible range 400–700 nm [18]. Al-doped ZnO (AZO) layers also offer good thermal stability and high resistance to damage during processing treatments [19].

There have also been many studies which have demonstrated that undoped ZnO can be grown in nanostructured forms, as nanorods [20], nanowires [21], nanobelts [22], nanotubes [23] etc., with high crystal perfection. In our own work, we have demonstrated that ZnO films grown by pulsed laser deposition (PLD) exhibit a bi-modal structure where initially continuous layers are then terminated by high densities of nanorods [24]. This promises films with high surface area, good conduction paths and potentially low carrier recombination rates, all attributes of particular interest for devices.

This paper examines the growth of nanostructured AZO films by PLD, as a means of combining good conductivity with desirable film geometry. The growth of nanostructured AZO films has been reported by a number of groups but the influence of the Al on growth has been little explored [25–29]. Here we compare the conditions for growth of AZO and ZnO (ZO) nanorod arrays by PLD. The results suggest that AZO nanorod structures generally grow at higher temperatures than ZO nanorods for a given laser fluence. By comparing the morphology and density of AZO and ZO nanorods, it is concluded that the differences in growth are due to lower surface diffusion rates in Al-doped films.

## 2. Experimental methods

ZO, AZO and AZO: ZO films were grown by PLD using a 193 nm Excimer Pulsed UV-ArF laser (Lambda-Physic COMPex 201, pulsed at 10 Hz). The target materials were 99.999% pure ZnO and a 99.999% pure ZnO (98 wt.%):$Al_2O_3$ (2 wt.%) hot pressed disk (Cerac). The target was rotated at ~1 rpm in order to prevent ablation of the same area. The growth chamber was evacuated to $\sim1\times10^{-6}$ Torr using a turbo molecular pump. The chamber was backfilled by oxygen in order to maintain a constant pressure ~10 mTorr. The substrate, (0001) sapphire, was positioned at a distance of 5 cm from the target on a halogen bulb heater. The substrate was mounted on the glass surface of the halogen bulb using silver conducting paint and subsequently allowed to dry in air for ~30 min. The substrate temperature was measured by using a digital thermocouple contacted to the front surface

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of the sample using a silver conducting paint. Prior to deposition, the substrate surface (1 cm × 1 cm square) was initially washed with acetone and then with ethanol. Larger (2 cm × 2 cm square) sapphire substrates were used for the AZO: ZO samples. For these samples, AZO films were initially deposited on the substrate surface via ablation of ZnO: $Al_2O_3$. The resulting sample was then cut into smaller samples and used for the subsequent pure ZnO deposition maintaining reference samples of AZO on sapphire. Growth parameters varied were laser pulse energy, in the range 7.5–30 mJ/pulse, (0.75–3 J/cm$^2$) substrate temperature up to 675 °C, deposition time up to 90 min, and pulse repetition rate (10 Hz & 5 Hz). The structure of the films was analysed by transmission electron microscopy (TEM) on cross-sectional samples using a Philips EM430 or a JEOL 2010 microscope, and by scanning electron microscopy (SEM) of the as-grown samples using a JEOL JSM 6330F. Finally four point probe measurements were used to measure the conductivities of the AZO films.

## 3. Results

In general, the growth of undoped and doped ZnO films depended most sensitively on the laser pulse energy and substrate temperature. Figs. 1 and 2 compare ZO, AZO: ZO and AZO films grown at a series of temperatures for laser pulse energy of 10 mJ/pulse. Fig. 1 shows samples which had well formed nanorod arrays, while Fig. 2 shows less well-ordered structures. For the ZO & AZO:ZO films, there was a narrow window around 575–625 °C in which high densities of nanorods were grown (Fig. 1A–C). Lower growth temperatures gave a ribbon-like structure (Fig. 2A) while higher temperatures gave some nanorod growth, but with less well-ordered nanorod arrays (Fig. 2B). For AZO similar morphologies were encountered, but with higher temperatures needed for nanorod growth, in the range 650–675 °C as illustrated in Fig. 1D (temperatures higher than 675 °C were not investigated in detail). The SEM images in Fig. 1 also revealed that the densities of nanorods in ZO films (Fig. 1A and B) were lower than those in AZO films (Fig. 1D). For example, the ZO sample in Fig. 1 had ~170 ± 10 nanorods/μm$^2$, whereas the AZO sample had ~240 ± 20 nanorods/μm$^2$. In contrast, ZO films grown on AZO precursor layers showed significantly higher densities of nanorods; for example the AZO:ZO sample in Fig. 1C where both layers were grown at 600 °C had ~320 ± 10 nanorods/μm$^2$.

Fig. 3 compares TEM cross-sectional images of AZO: ZO and AZO films grown at 600 °C and 650 °C. This shows that the morphologies of the nanorods are quite different for these two cases, with the AZO nanorods being significantly more tapered than the ZO nanorods in the AZO: ZO film. Measurements of the cone semi-angle θ from the TEM cross-sections (the angle between the projection of the side facet and [0001]) gave θ = 15° for AZO nanorods and θ < 5° for AZO: ZO nanorods.

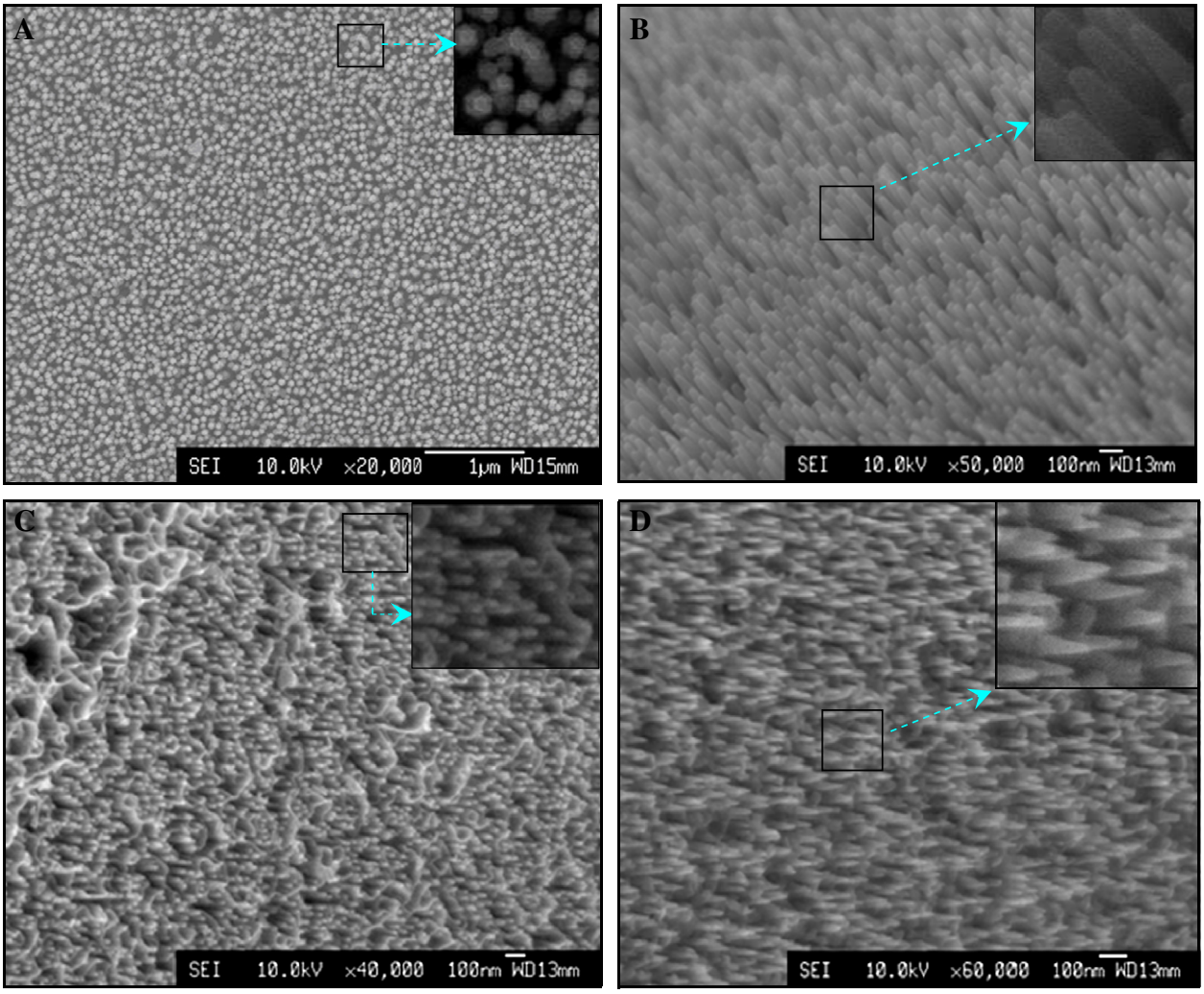


**Fig. 1.** SEM images of samples grown at a laser energy of 10 mJ/pulse: (A) ZO nanorods grown at 600 °C, viewed along the normal to the substrate surface, (B) ZO nanorods grown at 600 °C, tilted by 35° from the horizontal. (C) AZO: ZO nanorods grown at 600 °C, tilted by 35° from the horizontal. (D) AZO nanorods grown at 650 °C, tilted by 35° from the horizontal.