Study on Structural and Electronic Properties of Heavily Al-Doped Zinc Oxide Thin Films Deposited by Pulsed Laser Deposition

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Abstract:

As zinc oxide (ZnO) crystallizes into a wurtzite structure, it exhibits spontaneous polarization due to the creation of inherent zinc terminated and oxygen terminated faces. The zinc terminated face is much more chemically stable than its oxygen terminated face. This research investigates the effect of aluminum (Al)-doping and deposition rate of ZnO thin films on (11$\bar{2}$0) sapphire substrates on the polarity and the electronic properties of the film. It is reported that Al-doping with a faster deposition rate creates a zinc terminated surface. A faster deposition rate also increases carrier concentration and optical bandgap for all samples.

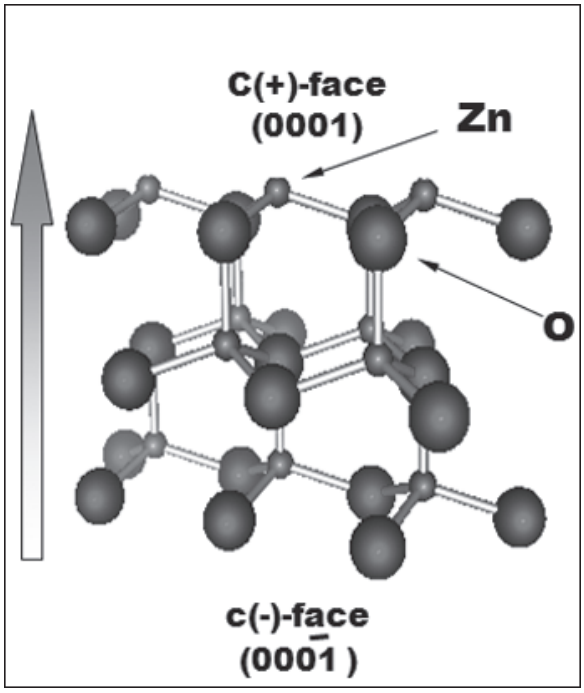

Figure 1: Crystal structure of zinc oxide.

Introduction:

Zinc oxide is a wide bandgap (3.37 eV at room temperature) semiconductor with high exciton binding energy (60 meV). Since these properties are very similar to those of gallium nitride, ZnO has been considered to be an appropriate material for light emitting diodes, which allows for bright room temperature light emission. As zinc oxide crystallizes into a hexagonal wurtzite type crystal (Figure 1), it inherently forms a (0001) zinc terminated surface or an (000$\bar{1}$) oxygen terminated surface. The zinc face is much more chemically stable and hence desirable for device applications. Under ordinary deposition methods, undoped zinc oxide has an (000$\bar{1}$) oxygen terminated surface [1]. However, it has been reported [2] that Al-doping allows for a zinc terminated surface. In this study, the effects of Al-doping and deposition rate on the electronic and structural properties of ZnO thin films will be investigated. By varying deposition rates of thin films, the surface polar orientation will be examined.

Experimental Procedure:

Four crystalline thin film samples—two 0.1 mol% Al-doped ZnO and two pure ZnO thin films—were prepared using a multi-step process. Thin films were deposited on (11$\bar{2}$0) sapphire substrates using pulsed laser deposition (PLD) at 700°C in an ultrahigh vacuum below 10^{-7} Pa. To make targets for the PLD process, ZnO and Al-doped ZnO (AZO) powders were pelletized using a hydraulic press and sintered at 1000°C for 20 hours. The (11$\bar{2}$0) sapphire substrates were cleaned in ultrasonic baths of acetone and ethylene and subsequently washed with deionized water. A pulsed laser of Nd: YAG laser (λ = 266 nm) was used at two different frequencies (10 Hz and 50 Hz) to vary deposition rate. In order to maintain equal film thickness (~ 500 nm), films were grown for 30 minutes with the 50 Hz laser and for 3 hours with the slower 10 Hz laser.

Upon film growth, electronic properties were characterized by Hall effect and transmittance measurements, while x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS) measured the films' structural properties.

Thin Film	Deposition Rate (nm/hr)	Laser Power (Watt)	Carrier Concentration (cm^{-3})	Optical Bandgap (eV)	Type
Pure ZnO	150	1	2.05E+16	3.33	N
Pure ZnO	690	5	2.86E+16	3.34	N
0.1 mol % Al doped ZnO	125	1	3.95E+19	3.42	N
0.1 mol % Al doped ZnO	625	5	7.24E+19	3.47	N

Table 1: Growth parameters and electronic and optical properties of doped and undoped zinc oxide thin films.

Results and Conclusion:

XRD results confirmed that all the films, regardless of doping or deposition rate, were c-axis oriented. Transmittance measurements showed that Al-doping increased the optical bandgap as listed in Table 1. Since Al-doping increases the carrier concentration in the conduction band, the optical bandgap energy increases. Hence, it was concluded that aluminum was successfully doped in the AZO thin films. Hall measurements confirmed that the AZO samples had a carrier concentration three orders of magnitude higher than the undoped ZnO samples as listed in Table 1. This further indicates that Al was successfully doped into the AZO thin films since Al has a higher carrier concentration than that of undoped ZnO.

Hall effect and transmittance measurements showed that the AZO films with a faster deposition rate had a higher carrier concentration and optical bandgap than the AZO films with a slower deposition rate as shown in Table 1. The solubility limit [3] of Al in ZnO at 800°C is 1×10^{-19} cm^{-3}. An Al concentration of 1×10^{-20} cm^{-3} indicates a complete non-equilibrium state. In a complete non-equilibrium state, Al dopants tend to react with the oxygen to form Al_2O_3 (sapphire) to return to a more equilibrium state. This is a probable explanation of the phenomenon active in these samples. The slower deposited thin films got more time for the Al dopants to condense into the sapphire substrate than the faster deposited AZO films. Hence the Al concentration in the faster deposited AZO film was higher than in the slower deposited AZO film. Since the optical bandgap is a function of the carrier concentration, it also increases with a faster deposition rate.

In this investigation, angle resolved XPS (AR-XPS) was employed to observe crystalline polarity. XPS is useful to determine the surface elemental composition and the surface chemical and electronic state of elements of an object. By varying take-off angles (tilt and rotation angles of the sample with respect to the electron energy analyzer direction), AR-XPS profiles were obtained. In particular, we obtained a tilt and rotation angle dependency of the relative intensity ratio between Zn 2p and O 1s peaks. Measuring both sides (oxygen-terminated and zinc-terminated surface) of a single crystalline ZnO crystal, a characteristic tilt angle was found which had high zinc to oxygen ratio for the zinc terminated surface and a very low zinc to oxygen ratio for an oxygen terminated surface. Note that etching the single crystal ZnO sample with nitric acid confirmed the results of the XPS data.

XPS measurements of the faster grown AZO sample showed a higher intensity ratio of zinc peaks to oxygen peaks near the previously determined optimum tilt angle as shown in Figure 2(a). Thus it was concluded that the faster grown AZO sample was zinc-terminated. However, no conclusive data on polarity could be observed for the slower grown AZO thin film (Figure 2(b)). This could be due to the fact that several crystals in the AZO thin film had mixed polarity with some grains being zinc terminated and others being oxygen terminated. Another possibility is that perhaps a different tilt angle is required to get more acute zinc and oxygen ratios from the XPS measurements.

Future Work:

The next steps are to conduct XPS measurements at several more tilt angles for the AZO samples. Also, growing more AZO thin film samples at various other deposition rates could also confirm the effect of deposition rate on polarity.

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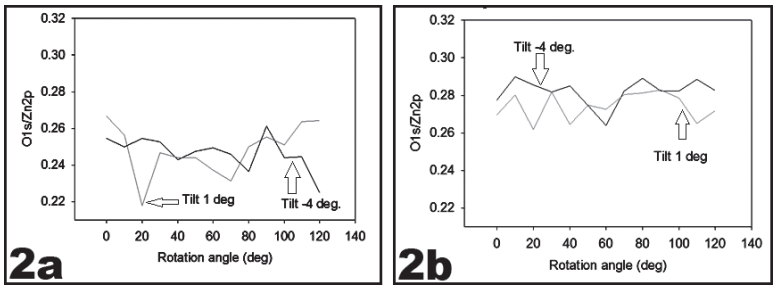

Figure 2: Relative x-ray photoelectron spectroscopy peak intensity ratio between Zn 2p and O 1s for various tilt and rotation angles of (a) the faster grown AZO film and (b) slower grown aluminum doped zinc oxide film.