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Low temperature growth of highly transparent c-axis oriented ZnO thin films by pulsed laser deposition

S. Amirhaghi[a], V. Craciun[a], D. Craciun[a], J. Elders[b], and I. W. Boyd[a]

[a]Electronic & Electrical Engineering, University College London, London WC1E 7JE, UK
[b]University of Twente, MESA Research Institute, Enschede, The Netherlands

The effects of the oxygen partial pressure, substrate temperature and laser wavelength on the structural and optical properties of thin films of ZnO grown on silicon and glass substrates by pulsed laser deposition have been studied. Regardless of thickness, all the grown layers are c-axis oriented and optically transparent. At substrate temperatures as low as 300°C, featureless layers with a FWHM value for the (002) XRD reflection less than 0.18° and exhibiting an optical transmission higher than 80% in the visible region were produced. For otherwise identical deposition conditions, the KrF excimer laser (at 248 nm) was always found to produce better quality thin films than the frequency-doubled Nd:YAG laser (532 nm). This is explained by the large difference between the optical absorption coefficients of ZnO at the two wavelengths employed, which play a key role in the laser-target interaction. SEM investigation of the target surface after deposition revealed very different surface morphologies for the two wavelengths employed supporting this assumption.

1. INTRODUCTION

ZnO is an optically transparent (E_g=3.2 eV) n-type semiconductor with a hexagonal wurtzite structure [1]. Its electrical properties can be easily modified by doping with In, Al, Li, Ga or Sn [2-8]. When c-axis oriented, it also exhibits large piezoelectric and piezooptic coefficients [9-11]. These qualities have attracted considerable interest in recent years with thin ZnO films being used in acoustoelectric and acoustooptic devices [12], solar cells [13], liquid crystal displays, gas sensors and window coatings [14-17]. Many of the major deposition techniques for obtaining thin films have been employed to grow ZnO, including sputtering [2, 4-6, 8, 16], chemical vapour deposition (CVD) [7, 15], and chemical spraying [3]. However, studies have shown that each technique has inherent advantages and disadvantages, and none can yet successfully meet all the requirements necessary for these applications. Additionally, for the full exploitation of the ZnO properties, there is a growing demand for high quality c-axis oriented thin films grown at high deposition rates but at low substrate temperatures.

The pulsed laser deposition (PLD) technique, first used in 1965 [18], has since been refined to produce high quality thin films at relatively lower substrate temperatures than other techniques. To the best of our knowledge, PLD was first applied to ZnO film growth in 1983 [19, 20]. More recently, further reports describing the application of the PLD method to ZnO thin films growth have been published [21-23]. In this paper we present the most complete systematic investigation reported thus far of the structure, morphology and optical properties of ZnO thin films deposited by the PLD technique. In addition to different oxygen partial pressures and substrate temperatures, we also show significant wavelength dependent effects. These results are also compared with those previously published using PLD or other techniques.

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2. EXPERIMENT

The experimental set-up employed for PLD and the preparation route of the targets have already been described in detail elsewhere [23]. Cylindrical ZnO pellets of 99.9 % purity were ablated either by a frequency-doubled Nd:YAG laser (λ=532 nm, pulse duration τ_{FWHM}=4 ns) or by a KrF excimer laser (λ=248 nm, pulse duration τ_{FWHM}=20 ns). In both cases, the laser fluence was set at 2.5-3 J/cm^2 and the repetition rate was 5 Hz. The deposition chamber was initially evacuated with the aid of a turbomolecular pump to pressures in the 10^{-7} torr range. During deposition, oxygen (99.999 % purity) partial pressures of between $2*10^{-6}$ to $2*10^{-2}$ torr were employed. The thin layers were deposited either on Corning glass 7059 or (100) Si substrates, which were chemically cleaned (acetone, alcohol, DI water) and dried in N_2 prior to film growth.

The crystalline structure of the deposited layers was investigated by X-ray diffraction (XRD) using an unchromatised Cu Kα source. The film thickness was measured with a mechanical stylus while the optical transmittance of the layers deposited on the Corning glass substrates was recorded in the 300-1000 nm range (referenced to a clean glass substrate) using a Philips spectrometer PU 8625. The values of refractive index and thickness were also measured by fixed wavelength ellipsometry (λ=633 nm).

Rutherford backscattering spectroscopy (RBS) measurements, performed with 2 MeV He+ ions and a scattering angle of 170°, were employed to determine the chemical composition of the films. The morphology of the grown films and of the pellets was investigated using a scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

In Fig. 1, the XRD patterns of the ZnO films deposited at 400°C on glass substrates using the Nd:YAG laser for different irradiation times from 10 seconds to 4 minutes are presented. It is worth noting that for all the XRD patterns recorded, only the 002 and a 004 reflection is present, implying a highly textured structure of the films, with the c-axis oriented perpendicular to the substrate. Such XRD patterns are a clear indication that the preferred growth of ZnO takes place at the very earliest stages of the film growth. Since such c-axis oriented films have been also obtained by using other deposition techniques when the substrate was glass or Si covered by its native oxide [2, 14-19, 22, 23], the reason for this preferred orientation is most likely chemical rather than crystallographic in nature. The central concept of this argument is that the Zn atoms as opposed to the O atoms of the ZnO are attracted preferentially and bonded to the oxygen species already present on the substrate surface. Since the 2-dimensional Zn atom population is highest in the 002 plane of the wurtzite structure, growth in this orientation results.

The linewidths (i.e. FWHM) and the diffraction angle (2Θ) of the 002 reflections recorded for the films presented in Fig.1 are shown in Fig. 2. One can see that after the first 50 nm of film has grown, the width of the line remains practically unchanged. Using the Scherrer equation [23] the grain size dimensions were estimated for the thicker films to be around 20 nm.

The effects of the substrate temperature on the crystallinity of the deposited films are shown in Fig. 3. As expected, the increase of the substrate temperature has a beneficial effect on the structure of the films, in contrast with the data presented in Ref. 22 where surprisingly no such effects were detected. However, this is less dramatic for the films deposited by the excimer laser. FWHM values of 0.43° and 0.16° were measured for the films deposited at 500°C by the Nd:YAG and excimer laser, respectively. Values of only 0.18° measured for films grown even at 300°C are amongst the best results reported so far for ZnO thin films [2-4, 14, 17] and a factor of 3 smaller than the value previously measured for thin films grown by PLD using a KrF laser [22]. The grain size corresponding to these FWHM was larger than 50 nm.

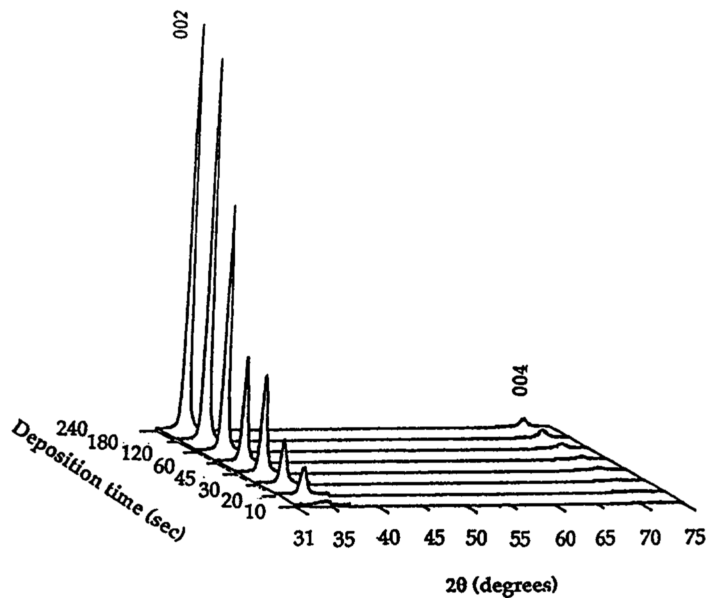


Fig. 1. XRD patterns of ZnO films deposited at 400°C for different deposition times.

A lower oxygen partial pressure (e. g. 2*10^{-5} torr versus 2*10^{-4} torr) also seems to have a beneficial, though less marked, effect on the width of the (002) peak. Almost no effect of the oxygen partial pressure on the films deposited by the KrF laser was observed.

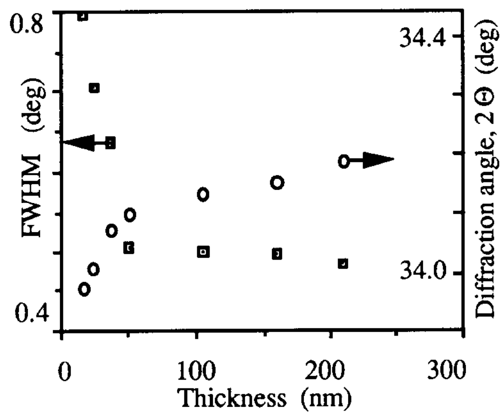


Fig. 2. Thickness-dependence of (002) X-ray diffraction peak position and FWHM for ZnO films.

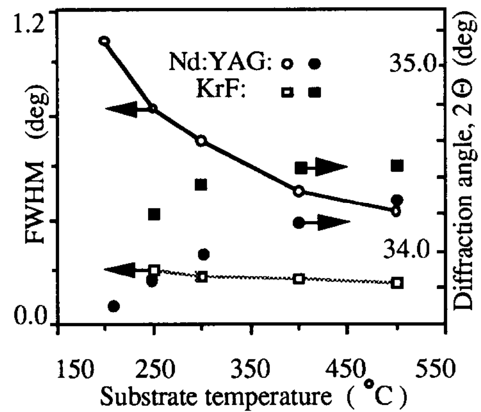


Fig. 3. The effect of substrate temperature on the crystallinity of deposited films.

The value of 2Θ measured for the grown films was always less than that for bulk material (i.e. 34.47°) more so for the Nd:YAG grown layers, implying that an in-built compressive stress developed during growth [2, 3, 14]. Nevertheless, the values for the films grown by the excimer laser were very close to the tabulated value [1], corresponding to low stress for films grown at substrate temperatures below 350°C and almost no stress at all for higher substrate temperatures.

SEM investigations of the morphology of samples grown by each laser revealed that the shorter wavelength radiation produces the smoother surface. The surface quality of excimer deposited films easily surpasses that achieved employing a cw CO_2 in the laser evaporation technique [21].

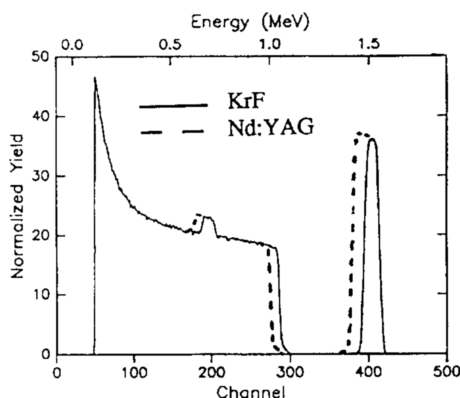


Fig. 4. RBS spectra of thin ZnO films.

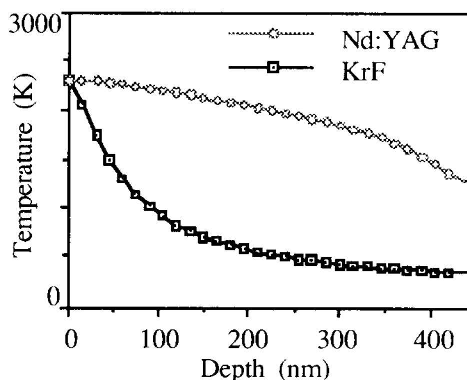


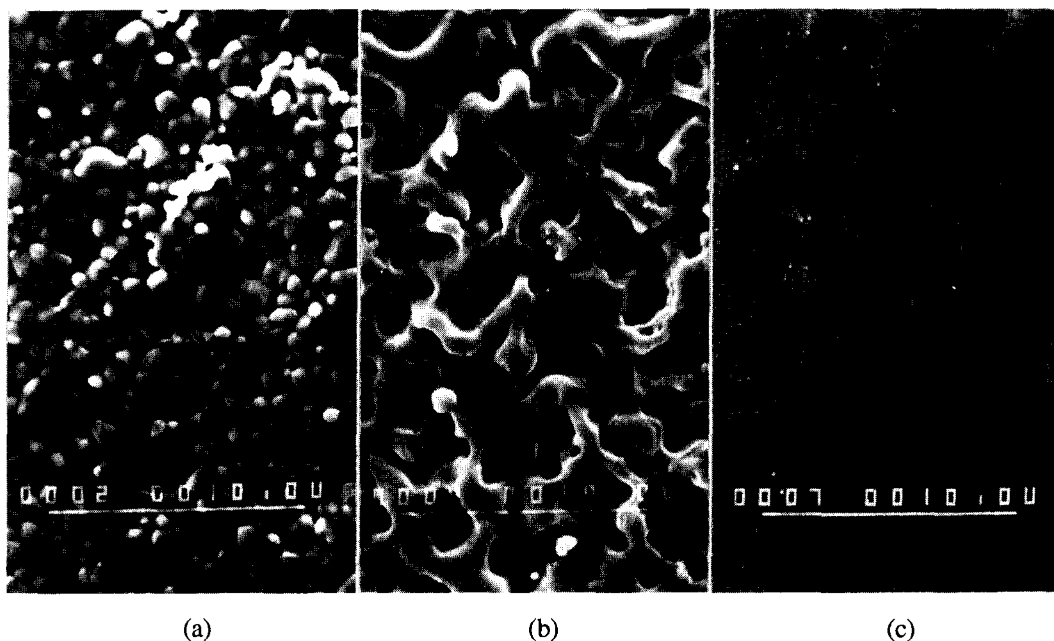
Fig. 5. Temperature-depth profile in ZnO at the onset of melting.

Typical RBS spectra of the films deposited by each laser are presented in Fig. 4. The chemical composition was found to be $Zn_{0.49}O_{0.51}$ for the Nd:YAG grown films and $Zn_{0.47}O_{0.53}$ for the excimer deposited samples, close to the ideal stoichiometry [4, 7, 8]. Thickness measurements performed with a stylus and checked by ellipsometry indicated that the growth rate was around 0.13 nm/pulse for the Nd:YAG laser grown layers and almost half this value, 0.06 nm/pulse, for the excimer grown films.

All the films grown using the excimer laser were optically very clear and transparent while those deposited by Nd:YAG laser exhibited a very pale brown hue. In particular, the excimer laser deposited films have an average transmission higher than 80% in the visible region of the spectrum [2, 3, 6-8, 13-15]. It is worth mentioning that preliminary four point-probe measurements have shown that these highly transparent layers are conductive with resistivities in the 10^{-2}-10^{-3} Ω.cm range. Both films exhibit a sharp cut-off at wavelengths shorter than 380 nm. From the linear part of the plot of the square of the logarithm of the transmittance, $(\ln T)^2$, which is proportional to the absorption coefficient (α), versus photon energy, energy band-gaps of 3.40 and 3.26 eV for the Nd:YAG and excimer deposited films respectively were extracted. These values compare favourably with the known value of 3.24 eV for single crystal ZnO [1, 7, 6]. The refractive index of excimer laser deposited films was measured to be 1.96 at 633 nm, similar to reported values for high quality ZnO layers grown by other methods [4, 6, 7]. The refractive index of the films deposited by the Nd:YAG was always higher, typical values being around 2.15 at 633 nm.

As a general observation it appears that, under otherwise identical deposition conditions, the structural and optical properties of the layers grown by the KrF laser are always better that those

obtained using the Nd:YAG laser, confirming the previous reports [22, 23]. This is a direct consequence of the much stronger optical absorption of the 248 nm radiation, $\alpha=10^6$ cm^{-1}, which is below the absorption edge, whereas the 532 nm light from the Nd:YAG laser penetrates much deeper into the bulk of the material, $\alpha=10^3$-10^4 cm^{-1}. Temperature calculations relevant to our irradiation conditions (presented in Fig. 5) showed that when the surface reached the melting temperature, the thermal gradient near the surface region was much steeper for the excimer than for the Nd:YAG heated material. According to the model of R. K. Singh et al. [25], such a small thermal gradient coupled with a low absorption coefficient can result, when the evaporation begins, in strong subsurface heating and lead to microexplosions. Unfortunately, the optical and thermo-physical constants of liquid ZnO have not yet been measured, so it is not possible to accurately check the model predictions. Nevertheless, there is certainly no evidence why subsurface microexplosions cannot occur in ZnO during Nd:YAG irradiation. Moreover, this model is supported by the SEM investigations of the target surface after irradiation.



(a) (b) (c)

Fig. 6. SEM micrographs of the pellet surface: a) as prepared, b) ablated using the Nd:YAG laser, and c) ablated using the excimer laser.

As shown in Fig. 6, the surface of the pellet ablated by the excimer laser is very smooth and featureless, even smoother than the virgin surface, indicating that the ablation process was confined only to the outermost part of the surface, whereas that of the pellet ablated by the Nd:YAG laser is very rough, with some cavity-like features being apparent.

4. CONCLUSIONS

Highly oriented ZnO thin films with good optical transmittance in the visible region have been deposited by the PLD technique. The FWHM value of the 002 reflection decreases with increasing substrate temperature and film thickness, contrary to previously published results regarding excimer deposited films. By carefully choosing the value of the laser fluence, the

FWHM value of the deposited films could be reduced by a factor of 3 with respect to previously published values. The layers grown by the excimer laser exhibit better surface morphologies, are more ordered, have a stoichiometric composition, and exhibit higher optical transmission than their Nd:YAG grown counterparts. This is a direct consequence of the shorter wavelength KrF radiation, which is strongly absorbed close to the sample surface and eliminates target damage.

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