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Effects of laser wavelength and fluence on the growth of ZnO thin films by pulsed laser deposition

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Abstract

Transparent, electrically conductive and *c*-axis oriented ZnO thin films have been grown by the pulsed laser deposition (PLD) technique on silicon and Corning glass substrates employing either a KrF excimer laser ($\lambda = 248$ nm) or a frequency-doubled Nd:YAG laser ($\lambda = 532$ nm). The crystalline structure, surface morphology, optical and electrical properties of the deposited films were found to depend not only on the substrate temperature and oxygen partial pressure, but also on the irradiation conditions. The quality of the ZnO layers grown by the shorter wavelength laser was always better than that of the layers grown by the longer wavelength, under otherwise identical deposition conditions. This behaviour was qualitatively accounted for by the results of the numerical solution of a one-dimensional heat diffusion equation which indicated a strong superheating effect of the melted target material for the case of frequency-doubled Nd:YAG laser irradiations. By optimizing the deposition conditions we have grown, employing the KrF laser, very smooth *c*-axis oriented ZnO films having a full-width at half-maximum value of the (002) X-ray diffraction value less than 0.16° and optical transmittance around 85% in the visible region of the spectrum at a substrate temperature of only 300°C.

1. Introduction

Thin films of ZnO have been shown to possess high optical transmittance (energy band-gap, E_g = 3.26 eV), good electrical conductivity and, when *c*-axis oriented, large piezoelectric and piezo-optic coefficients [1]. Many techniques such as sputtering [2,3], chemical vapour deposition [4], sol–gel [5], chemical spraying [6], electron plasma sputtering [7], ion-beam assisted deposition [8] or reactive evaporation [9] have been employed for the growth of high-quality *c*-axis oriented ZnO layers at substrate temperatures as low as possible, usually below 450°C. The pulsed laser deposition (PLD) method, which has been recognised to offer the potential of producing high-quality thin films at relatively low substrate temperatures, was first used for growing ZnO films in 1983 [10,11]. More recently, new reports describing the use of the PLD method to obtain high-quality *c*-axis oriented ZnO films have been published [12–15].

We have previously shown [13,14] that higher-quality films can be grown when employing a KrF laser for ablation rather than a frequency-doubled

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Nd:YAG laser ($\lambda = 532$ nm). In this paper we present a systematic experimental investigation of the role of laser fluence and oxygen partial pressure upon film quality and determine the best conditions for ZnO growth by PLD. Under such optimised deposition conditions highly *c*-axis oriented ZnO films can be routinely grown that display a full-width at half-maximum (FWHM) value of the (002) X-ray diffraction (XRD) line less than 0.16°, electrical resistivity of around 10^{-2} $\Omega \cdot$cm and optical transmittance higher than 85% in the visible region at a substrate temperature of only 300°C. Theoretical support for the observed wavelength dependence is presented as results obtained by numerically solving the heat diffusion equation for each set of laser irradiation conditions.

2. Experimental details

ZnO targets (99.9% purity) prepared by the usual sintering techniques were ablated within our PLD set-up [13,14] either by a KrF laser or a frequency-doubled Nd:YAG laser. The incident laser fluence was adjusted within the 0.4–4.0 J/cm^2 range by varying the energy contained in each laser pulse. Since better results have been obtained when using the KrF laser, most of the films were deposited by this laser. The deposition cell was initially evacuated to pressures in the 10^{-7} Torr range and then filled with oxygen (99.999% purity) at working pressures of between 5×10^{-6} to 2×10^{-3} Torr. The films were deposited on either (100) silicon or Corning glass substrates placed on a heater situated 4 cm in front of the target. The nominal substrate temperature, from 100 up to 500°C was measured with a thermocouple attached to the heater stage.

After the deposition, the crystalline structure of the grown ZnO films was investigated by X-ray diffraction (XRD). Film composition was checked by X-ray photoelectron spectroscopy (XPS) measurements performed in a VG Escalab Mk II electron spectrometer using unmonochromatised Al Kα radiation ($h\nu = 1486.6$ eV). The thickness and refractive index value of the layers were measured by ellipsometry (at 632 nm), while the surface morphology and cross-sectional structure of fractured films were investigated using a scanning electron microscope (SEM). The optical transmittance of the films deposited on Corning glass substrates was measured in the 300–900 nm range with a double-beam spectrophotometer. Finally, the low-temperature (200–280 K) resistivity of several films was measured by the van der Pauw method.

3. Results and discussion

For the whole range of deposition conditions employed in this study, all the films were found to be *c*-axis oriented, exhibiting only the (002) and (004) XRD reflection lines. The role of oxygen partial pressure and laser fluence on film quality was mainly assessed by monitoring the position and FWHM of the (002) XRD reflection line. Since we have previously shown [14,15] that the optimum substrate temperature is between 300 and 375°C, most of the films investigated here were grown within this temperature range.

The peak position and FWHM of the (002) line recorded for films deposited at 350°C with the KrF laser using 2.1 J/cm^2 for different oxygen partial pressures and presented in Fig. 1, show that the best quality films can be obtained in the higher pressure range, i.e. around $(1\text{–}2) \times 10^{-3}$ Torr. This result, although different from that obtained when growing ZnO thin films using a frequency-doubled Nd:YAG laser [13,14], is similar to data published for indium tin oxide films prepared by PLD with an excimer

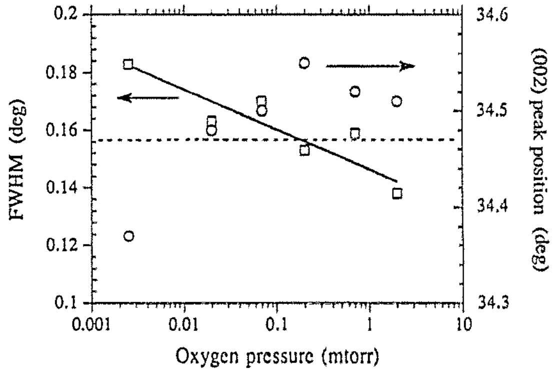

Fig. 1. Peak position and FWHM of the (002) XRD reflection lines recorded for ZnO films deposited at 350°C and 2.1 J/cm^2 for different oxygen partial pressures; the dotted line corresponds to peak position of ZnO powder.

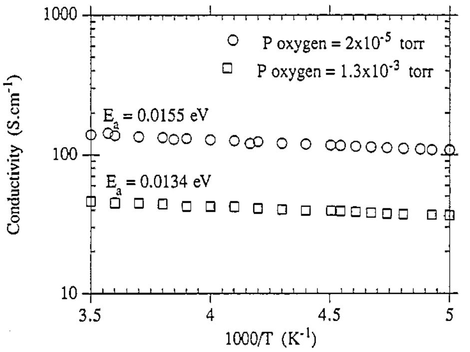

Fig. 2. Low-temperature conductivity of ZnO films deposited at 2×10^{-5} and 1.3×10^{-3} Torr oxygen partial pressure.

laser [16]. It has been suggested [16,17] that a relatively high oxygen pressure (i.e. in the mTorr range) can ensure a more uniform velocity distribution of the various constituents of the ablation plasma with a beneficial effect on the grown film quality. However, a too high oxygen pressure can drastically reduced the deposition rate and slow down the incoming atoms to energies where the surface mobility is too low to promote high-quality crystallinity.

As the conduction mechanism of the ZnO is controlled by interstitial Zn atoms or O vacancies [1,18,19], it would be expected that films deposited at various oxygen pressures will exhibit different conductivities. In Fig. 2, the low-temperature conductivity of two films deposited at 2×10^{-5} and 1.3×10^{-3} Torr is shown. As one can see, the conductivity of the sample grown at the lower oxygen pressure is a factor of 2 higher. The conductivity of both samples exhibits an Arrhenius-type dependence in this temperature range of 280–200 K, with activation energies of $E_a = 0.0155$ and 0.0134 eV. From these values a dopant energy level situated at $E_d = 2E_a = 0.031$–0.027 eV from the bottom of the conduction band can be calculated, in excellent agreement with other reported values for the Zn interstitial level in ZnO [1,18,19]. However, the absence of any structure in the shoulders of the Zn $2p_{3/2}$ and Zn $2p_{1/2}$ XPS peaks recorded for these films indicates that they do not contain, within the XPS resolution limit ($< 0.1\%$), metallic Zn. The binding energies of the O 1s and Zn $2p_{3/2}$ and Zn $2p_{1/2}$ peaks, measured with respect to that of C 1s situated at 284.6 eV, closely correspond to O and Zn in ZnO [8,20] and confirm our previous Rutherford backscattering measurements which showed that the PLD grown films, regardless of the laser employed, were essentially stoichiometric ZnO [13,14]. Narrow XRD lines and refractive index values around 1.97–2.0 were recorded for all the films grown by the KrF laser at fluences in the 1.5–2.5 J/cm^2 range, when keeping substrate temperatures around 300–350°C and oxygen partial pressures in the low 10^{-3} Torr range.

SEM investigations revealed smooth surfaces for the KrF deposited films and a relatively high density of droplets for those deposited by the Nd:YAG laser. The structure of fractured films was also found to be different for each laser, as shown in Fig. 3.

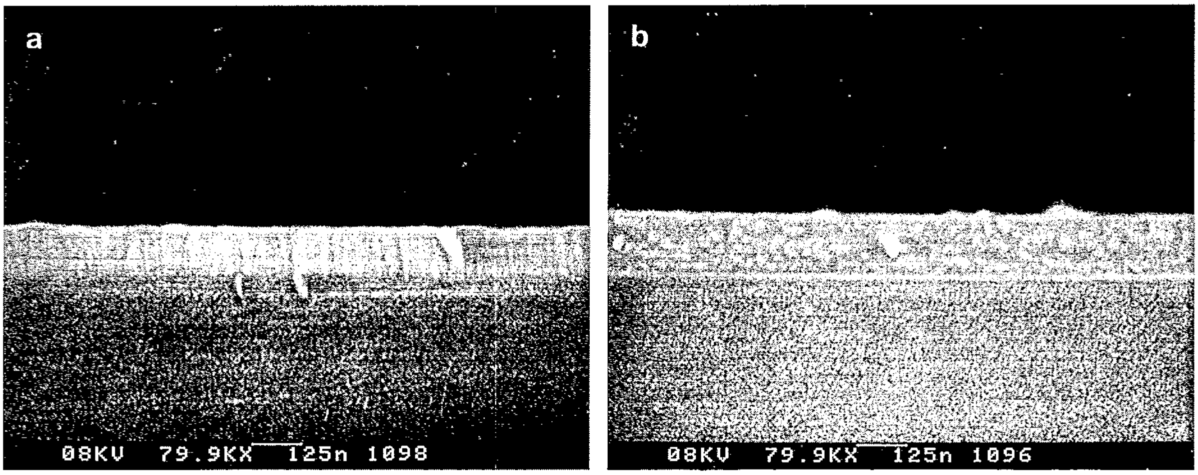

Fig. 3. SEM micrographs of the structure of fractured films deposited by (a) KrF laser and (b) Nd : YAG laser.

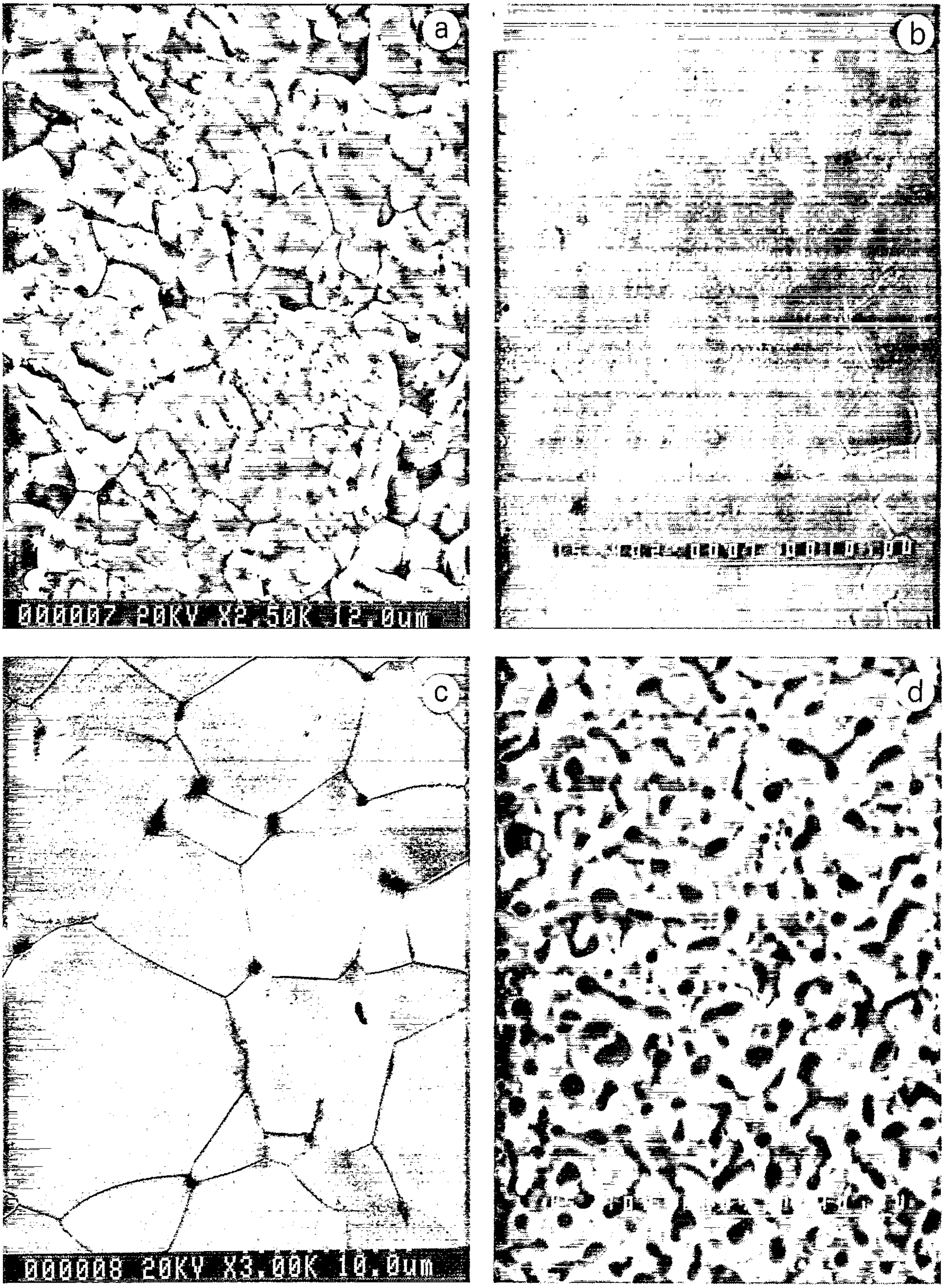

Fig. 4. SEM micrographs of the target surface after laser irradiation for different incident fluences: (a) 0.7 J/cm^2, (b) 2.1 J/cm^2, (c) 3.5 J/cm^2, KrF laser and (d) 2.1 J/cm^2, Nd:YAG laser.

While the excimer deposited films revealed a dense, columnar structure, quite similar to that of the transitional zone T of the Thornton model [21] exhibited by sputtered ZnO films [22], the Nd:YAG films presented a completely different structure, with very small and nonuniform crystallites. It is also worth noting that the films grown using the Nd:YAG laser were consistently thicker than those grown with the KrF laser even when using the same number of pulses at similar laser fluences.

SEM investigations of the target surface after laser irradiation at various incident fluences (presented in Fig. 4) and the results of temperature simulations during the irradiation treatment (presented in Fig. 5) explain this fluence dependence. The temperature profiles inside the target were estimated by numerically solving the usual one-dimensional heat diffusion equation [23–25] for each laser fluence. The thermo-physical properties of ZnO are not known at high temperatures or in the liquid phase. To address this problem, we measured the ablation rate of the target for different laser fluences and then adjusted the optical parameters of the ZnO together with the plasma shielding factor [26] to fit the experimental data. At low fluence values (those corresponding to 0.7 J/cm^2 shown in Fig. 4a) the target surface melted, but the quantity of ablated material was too low to form a dense plasma. At such low laser fluences the interaction process is more akin to the thermal evaporation than ablation.

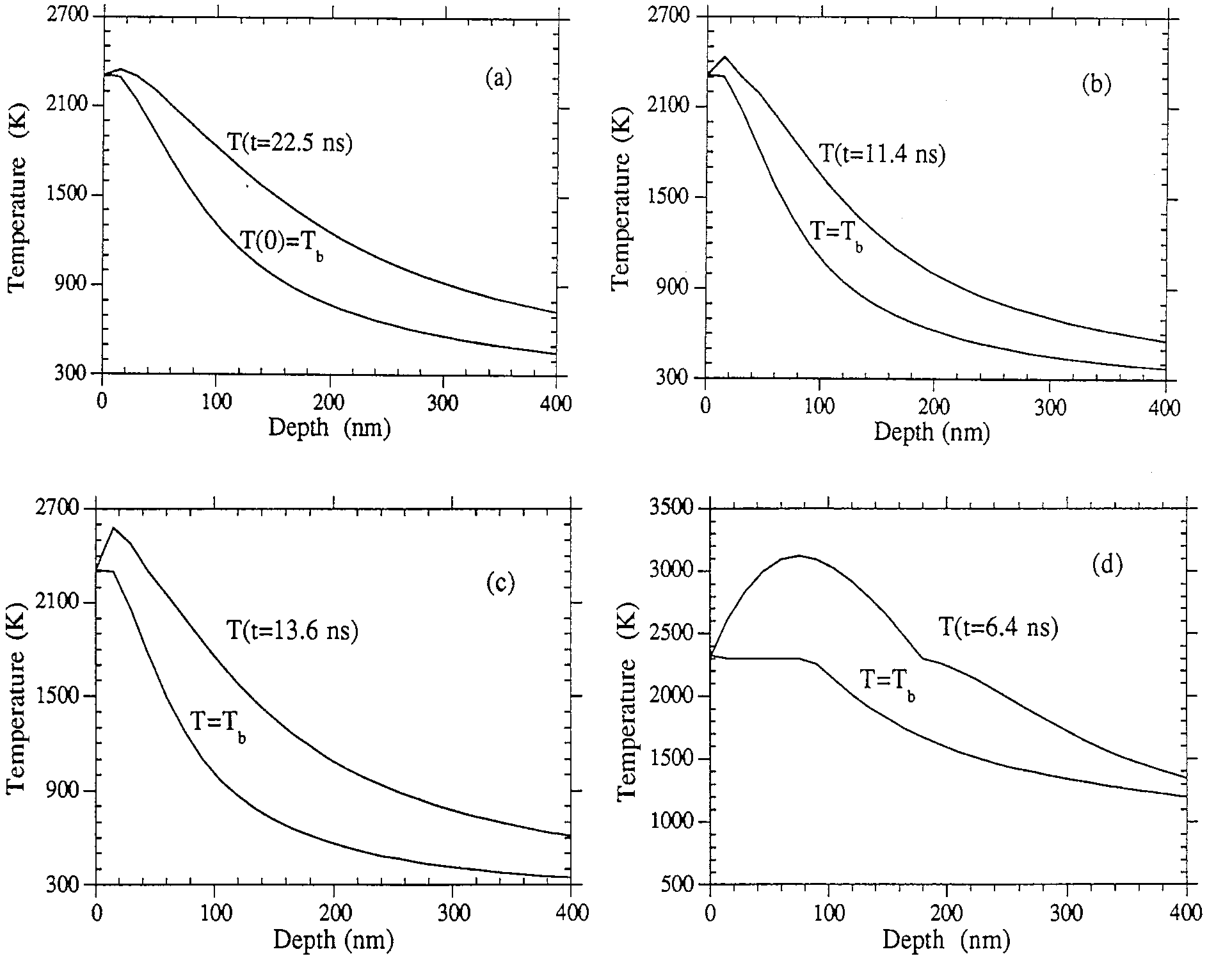

Fig. 5. Temperature profiles estimated at the moment when the surface temperature reached the boiling point and when 7 nm (only 2 nm for case (a)) of target material were ablated (laser fluences are the same as those presented in Fig. 4).

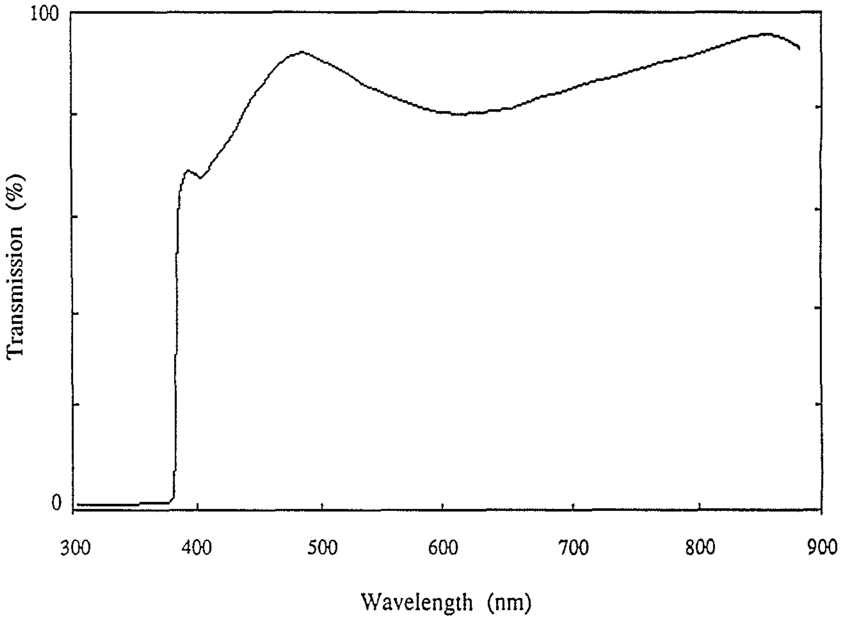

Fig. 6. Optical transmittance of PLD-grown ZnO under optimised conditions. A refractive index $n = 1.97 \pm 0.03$ and an extinction coefficient $k = 6 \times 10^{-3}$ at 600 nm have been estimated from the recorded spectra [27].

At fluences between 1.5 to 2.5 J/cm^2, approximately 30 to 55 nm of target material was ablated. The target, after ablation, exhibited a very smooth surface as shown in Fig. 4b. Under these conditions, the temperature profile peaked at the target surface (see Fig. 5b). Further increase of the laser fluence resulted in the target surface exhibiting a recrystallization process (see Fig. 4c), with grain sizes significantly higher than those initially present. For fluences above 2.5 J/cm^2, the simulated temperature

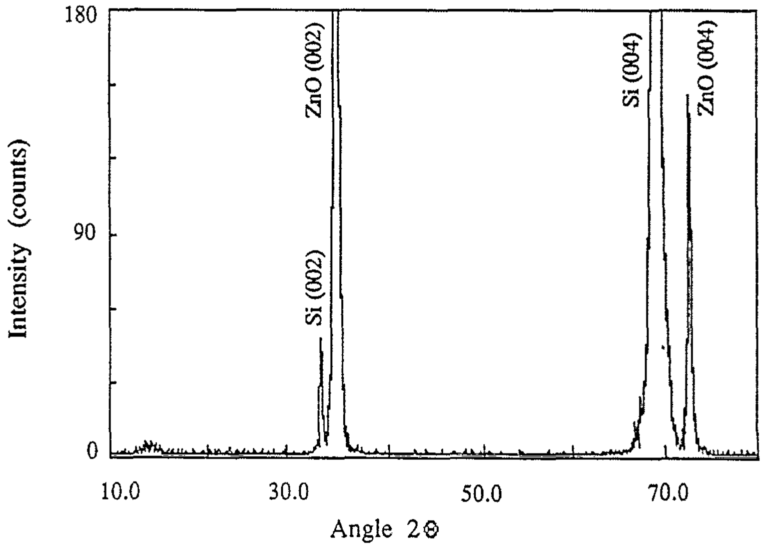

Fig. 7. XRD patterns of a ZnO oxide grown under optimised conditions.

profile inside the target showed a different behaviour, with the maximum value displaced inside the depth of the sample. Such a superheating effect can lead to microexplosions within the melted material with subsequent adverse effects on eventual film quality [23–25]. Areas corresponding to bulk microexplosions predicted by the temperature simulation can clearly be seen in Fig. 4b. This behaviour effectively limits the laser fluence one can use for high-quality growth of ZnO and explains the observed degradation of crystallinity for fluences above 3 J/cm^2. In the case of Nd : YAG laser irradiation, because of the high optical transparency of the target material at 532 nm, the superheating effect appears at much lower fluences, in fact at levels just above the ablation threshold. As one can see with reference to Fig. 4d, the target surface was heavily affected by microexplosions, preventing high-quality films from being grown with this wavelength.

These studies have shown that the best conditions for PLD of ZnO thin films correspond to substrate temperatures between 300 and 375°C, oxygen partial pressures between 1×10^{-3} and 2×10^{-3} Torr and laser fluences around 2 J/cm^2. The XRD patterns and the optical transmittance of a ZnO film grown under these optimised conditions are presented in Figs. 6 and 7. The FWHM value of the (002) XRD reflection line, corrected for the instrumental broadening is found to be only 0.15°. Together with an optical transmittance above 85% in the visible region with a sharp cut-off at 380 nm and conductivities of around 100 $S \cdot cm^{-1}$, these properties are amongst the best results reported so far for ZnO layers prepared by any method [2–12].

In conclusion, by studying the effect of deposition parameters on the film structure, optimised conditions for the growth of ZnO by PLD have been identified. Under such conditions, highly *c*-axis oriented ZnO films having a FWHM value of the (002) XRD reflection line less than 0.16° and optical transmittance above 85% in the visible region of the spectrum have been obtained at temperatures below 350°C. The surface morphology of the films was flat and the fractured surface exhibited a dense, columnar structure. The refractive index value of around 1.9 and the measured optical bandgap of 3.27 eV are characteristic of very high quality ZnO thin films. The strong superheating of the target material observed for ablation with laser photon energies less than its optical bandgap is not conducive to the growth of high-quality films.

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