Nitrogen doping of ZnO thin films grown by plasma-assisted pulsed-laser deposition

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Abstract. ZnO epitaxial thin films were grown on r-plane sapphire substrates, in a pulsed laser deposition apparatus assisted by an electron cyclotron resonance (ECR) N₂ plasma source. The resistivities and carrier concentrations (either n- or p-type) of the thin films were measured in a Hall effect apparatus as a function of the ECR source input microwave power and the substrate temperature, respectively. P-type conduction was observed in thin films grown in conditions of enhanced activation of the nitrogen ionic species. These experimental results are in qualitative agreement with recent theoretical calculations of the activation energies of the main donor defects compensating for N acceptors in ZnO.

1. Introduction
The II-VI wide band gap semiconductor ZnO has been stimulating considerable research in recent years [1]. In particular, ZnO is considered the prime base-material for the development of short-wavelength UV optoelectronic devices. However, the controlled production of high-quality p-type ZnO still remains an obstacle towards the successful realization of such devices [2]. Theoretical investigations have shown that shallow acceptor levels in ZnO can be produced upon various doping mechanisms, such as Group-I element (Li, Na) substitution on a Zn site [3,4], large-size Group-V elements As or Sb substitution on a zinc site [5] or Group-V element substitution on the O site [6]. Nitrogen, having a comparable ionic radius to oxygen, appears to be the most likely candidate for the latter mechanism, and, whence, p-type conduction in N-doped ZnO epitaxial thin films has been reported by various groups, see Ref. [2] for a summary of these results.

Recently, Tzukasaki et al [7] used plasma-assisted laser molecular beam epitaxy (LMBE) with the lattice-matched ScAlMgO₄ (SCAM) substrate and repeated temperature modulation (RTM) to produce high-crystalline and optical quality N-doped ZnO thin films with atomically flat surfaces and hole concentrations and mobilities of around 10¹⁶ cm⁻³ and 8 cm²V⁻¹s⁻¹, respectively. The material quality of p- and n-type ZnO obtained using this RTM-LMBE technique also enabled the authors to demonstrate room temperature electroluminescence in a p-i-n junction LED. Prior to this work, plasma-assisted pulsed laser deposition had been successfully used by other workers to obtain...
p-type behaviour in N-doped [8] or N- and Ga- codoped [9] ZnO thin films. These authors studied the effects of using N₂, NO or N₂O gases in their plasma source on the amount of N-doping and the corresponding thin film properties. The compensation mechanisms for the N acceptors in ZnO grown in these plasma environments were investigated theoretically [10-12] and experimentally [13].

In this work, we have used an electron cyclotron resonance (ECR) N₂ plasma source to assist the pulsed-laser deposition (PLD) of ZnO epitaxial thin films. This plasma source is versatile and can be used either as a source of ions or as a source of neutral species. The main aim of the present study is to identify the plasma-source parameters that strongly affect the properties of the ZnO thin films and, thereby, shed light on some of the relevant N-doping atomic/molecular mechanisms. For this purpose, the electrical properties of the ZnO thin films were measured as a function of some of the primary plasma source and growth parameters such as the microwave power, the plasma gas pressure, the ion current or the substrate temperature, respectively. It was observed that p-type behaviour in the N-doped ZnO thin films was achieved only when the ECR source is used as a ion source and for substrate temperatures of at least 520 °C.

2. Experimental Details

All the experiments reported here were carried out in the same stainless steel chamber (dedicated to ZnO growth) evacuated by oil-free turbomolecular pumping to a base pressure of 2×10⁻⁸ mbar. A frequency-quadrupled Nd:YAG laser providing 120 mJ of 266 nm laser light in a 6 ns pulse was used to ablate ultra-high purity ZnO ceramic targets with a fluence on target of 1.4 Jcm⁻². The laser was always operated at the repetition rate of 4 Hz and all the samples were grown as a result of 7,200 laser shots typically producing film thicknesses between 600 nm and 800 nm. The target-to-substrate distance was kept fixed at 0.055 m in all the experiments. The substrates were 10 mm × 10 mm polished r-plane sapphire crystals. In this case, ZnO grows with its c-axis in the plane of the film with a lattice mismatch of 1.53 % along the c-axis direction [14], producing non-polar, (11-20)-oriented, thin films characterized by the absence of a columnar structure. The substrate temperature was kept fixed during growth and values between 300 °C and 630 °C were used.

An ECR plasma source was also used during the PLD growth chiefly as a source of N-dopants. The magnetron/tuning unit provides a maximum of 250 W of microwave power at 2.45 GHz. This plasma source can be equipped with either a multi-grid electrostatic extractor set, in which case it behaves as a source of ions (N₂⁺) and highly-excited neutral species (e.g. N₂⁺ in the C 3Π_u electronic state at 11.5 eV), or with an alumina aperture in which case it provides lowly-excited neutral species (e.g. N₂⁺ in the B 2Π_g electronic state at 7.4 eV) and neutral N atomic species. The optical emission spectra (200 nm - 850 nm wavelength range) of the source operated in these two modes are shown in figure 1(a) and 1(b), respectively. Vibrational transitions in the 2nd positive system of N₂ (upper state C 3Π_u) and the 1st negative system of N₂⁻ (upper state B 2Σ_u⁻) dominate the spectrum of figure 1(a), whereas figure 1(b) shows enhanced relative emission intensities from N atoms and the 1st positive system of N₂ (upper state B 3Π_g). Other excited species are probably present in our experiments, for it is well known that collisional processes in ECR plasmas lead to significant populations of metastable states. The spectra of figure 1 are very similar (bar the oxygen emission lines since we use N₂) to those presented by Matsui et al [10] in the case of N₂O and NO ECR plasma sources. The source typically provided an ion beam current of 0.25 mA, as measured with a Faraday up in our chamber, when used in ion beam mode, and atom fluxes of 10¹⁵ cm⁻²s⁻¹ when used in atom beam mode. The plasma source output was directed at an angle of 30° with respect to the film surface normal at a distance of about 0.14 m. In general, we found these parameters to play an important role in influencing the thin film electrical properties. High purity nitrogen was used in the plasma source at a constant rate of 12 sccm and ultra-high purity oxygen was also introduced into the chamber through another port with a flow rate adjusted so as to maintain a constant total pressure of 7 mbar and N₂:O₂ partial pressures in the ratio 15:85. These growth conditions...
constitute a Zn-rich environment for the nascent ZnO thin films in the presence of either active or inactive nitrogen species.

The as-grown samples were characterized ex-situ without further processing. Their crystalline properties were obtained using a θ-2θ texture diffractometer and their electrical properties measured with a standard Hall effect apparatus in the 4-point probe Van der Pauw configuration.

![Figure 1. Optical emission spectrum of an ECR plasma source (175 W microwave power) used to provide nitrogen active species during the pulsed laser deposition of ZnO thin films, operated in (a) ion beam source mode or (b) atom beam source mode.](image)

3. Analysis and Discussion of results

To characterize and understand the effects of the ECR plasma, a number of ZnO “reference” thin films were grown with the plasma source turned off. At a substrate temperature of 580 °C and a total oxygen pressure of 8 mbar, the ZnO thin films were all n-type, with typical carrier concentrations of $2 \times 10^{18}$ cm$^{-3}$, resistivities of 0.2 Ωcm$^{-1}$, Hall mobilities of 20 cm$^2$V$^{-1}$s$^{-1}$ and 0.27° for the FWHM of the (0002) Bragg reflection. We found that all the thin films grown in the presence of the ECR plasma featured comparatively higher resistivities, lower mobilities and carrier concentrations and larger (0002) Bragg peak FWHM, indicating degradation of the material/crystalline quality. Hence, only methods which allow the recovery of the crystalline quality during N-plasma doping of PLD grown samples will lead to reproducible p-type behaviour in ZnO. This is the underlying principle of the RTM-LMBE growth technique of Tsukazaki et al [13].

In the range of conditions used, we found only n-type behaviour in ZnO thin films grown with the ECR plasma source operated as an atom beam source, whereas p-type behaviour was obtained with the plasma source operated in ion beam mode at microwave powers of at least 125 W, substrate temperatures above 520 °C and ion extraction kinetic energies (EKE) of at least 700 eV.

As an example, we show in Figure 2 the room-temperature electrical properties (residual carrier concentration $n$ and resistivity $\rho$) of a number of samples grown at a substrate temperature of 520 °C and a total pressure of 8 mbar as a function of the microwave power, parametrically for EKE of 500 eV and 700 eV, respectively. We see from this graph that for 500 eV EKE, the thin films electrical properties are insensitive to the microwave power (constant n-type with $n = 10^{18}$ cm$^{-3}$ and $\rho = 8$ Ωcm) whereas at 700 eV EKE, there is a clear trend toward lower $n$ and higher $\rho$ values respectively, leading to p-type behaviour at 175 W microwave power with $n = 10^{14}$ cm$^{-3}$ and $\rho = 10^4$ Ωcm. Larger microwave powers for the plasma source and ion extraction energies produce larger
amounts of highly-activated nitrogen species present during growth (this was clearly evident from the optical spectroscopy measurements of Figure 1) and thereby an increase of the N chemical potential $\mu_N$. Figure 2 shows that when a sufficient amount of nitrogen activation/μN increase has been reached, there are enough N acceptors in the thin films to overcome the compensating effects of donors. The low hole concentrations and high resistivities measured in this case can be explained by a concomitant "strengthening" of the main compensating donor mechanisms. These results are consistent with the results of the first-principles calculations of [5, 6]. When a N2 plasma source is used, these authors predict an increased N solubility compared with a normal N2 source and a formation energy for the substitutional N acceptor N0 larger by 3.74 eV than that of the main compensating donors (substitutional N2 molecules (N2)0 and N0-(N2)0 defect complexes) in Zn-rich conditions.

Figure 2. Carrier concentration (square) and resistivity (upright triangle) of ZnO thin films grown by pulsed laser deposition and doped by nitrogen ions extracted from an electron cyclotron resonance (ECR) plasma source with 500 eV (closed symbols) or 700 eV (open symbols) kinetic energies respectively, as a function of the ECR microwave power. The letters p or n beside the symbols indicate the conduction type of the film. (The broken lines are only to guide the eye through the data points).

In Figure 3, we show the room-temperature electrical properties (residual carrier concentration $n$ and resistivity $\rho$) of a number of ZnO thin films grown with the ECR plasma source operated at 125 W microwave power, an ion EKE of 700 eV, a total pressure of 8 mbar, as a function of substrate temperature. It is seen that the films show p-type behaviour above a substrate temperature of 560 °C, (e.g for a substrate temperature of 630 °C, the carrier concentration and resistivity were $n_{\text{hole}} = 5 \times 10^{17} \text{cm}^{-3}$ and $\rho = 30 \Omega \text{cm}$, respectively). From Figure 3, we see that p-type behaviour will result from conditions of increased activation of the nitrogen and oxygen species on the surface of the growing film. In this case again, N0 acceptors dominate over the main compensating double-donors (N2)0 as a result of the increased N-solubility [7].
Figure 3. Carrier concentration (square) and resistivity (upright triangle) of ZnO thin films grown by pulsed laser deposition and doped by nitrogen ions extracted from an electron cyclotron resonance (ECR) plasma source with 700 eV kinetic energies, as a function of the substrate temperature. The letters p or n beside the symbols indicate the conduction type of the thin film. (The broken lines to guide the eye through data points).

4. Conclusions
The resistivities and carrier concentrations of ZnO thin films grown by pulsed laser deposition in the presence of active ionic or neutral nitrogen species, generated in an electron cyclotron resonance N$_2$ plasma source, were measured as a function of the source microwave power and substrate temperature. Most of the thin films were n-type, although in conditions leading to increased activation of the ionic nitrogen species, p-type behaviour was observed. These experimental observations were found to be in qualitative agreement with recent theoretical calculations of the activation energies of N acceptors and compensating donor defects in ZnO. Finally, we point out that the crystalline and optical properties of the p-type N-doped thin films obtained in the present work were significantly affected compared with the undoped films, and confirmed the presence of an increased defect concentration. These results will be published separately.

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