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Oxygen pressure-tuned epitaxy and optoelectronic properties of laser-deposited ZnO films on sapphire

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Influence of oxygen pressure on the epitaxy, surface morphology, and optoelectronic properties has been studied in the case of ZnO thin films grown on sapphire (0001) by pulsed-laser deposition. Results of Rutherford backscattering and ion channeling in conjunction with atomic force microscopy clearly indicate that the growth mode, degree of epitaxy, and the defect density strongly depend on the oxygen background pressure during growth. It is also found that the growth mode and the defects strongly influence the electron mobility, free-electron concentration, and the luminescence properties of the ZnO films. By tuning the oxygen pressure during the initial and the final growth stages, smooth and epitaxial ZnO films with high optical quality, high electron mobility, and low background carrier concentration have been obtained. The implication of these results towards the fabrication of superlattices and controlled *n*- and *p*-type doping is discussed.
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ZnO is a direct-band-gap semiconductor with an energy gap of 3.3 eV at room temperature (RT) and being considered as a futuristic material for UV and blue light-emitting devices.[1–7] It has higher exciton binding energy (60 meV for ZnO versus 28 meV for GaN) and higher optical gain (300 cm^{-1}) than GaN (100 cm^{-1}) at room temperature.[1] Moreover, recent reports on externally pumped lasing in epitaxial ZnO thin films by Kawasaki *et al.*[2] and Bagnall *et al.*[3] have stimulated great interest in ZnO material for realizing efficient, excitonic UV blue lasers at room temperature.

Two major challenges lie ahead to realize ZnO-based current injection lasers and LEDs. One is to reduce the background carrier (free-electron) concentration in the ZnO films. The second is to achieve *p*-type conductivity. Previous attempts to achieve *p*-type doping with high hole concentration have been unsuccessful due to the compensation effect by a large background electron concentration.[8–10]

It is known that free electrons in ZnO are generated due to oxygen nonstoichiometry, possibly the formation of oxygen vacancies.[11] Thus, oxygen vacancies must be removed to effect controlled doping. In order to reduce the oxygen vacancies, we recently carried out thin-film growth by pulsed-laser deposition in a higher oxygen background pressure of 10^{-1} Torr. The resulting films showed poor crystalline quality, rough surface morphology, low electron mobility, and poor luminescence properties. High-quality epitaxial films with low-defect densities (point defects and dislocations) and smooth surfaces and interfaces must be obtained for optical devices such as lasers and LEDs; thus, it is necessary to understand the growth mechanism that controls these factors and influences both the electrical and optical properties of the ZnO thin films.

In this letter, we discuss the effects of the oxygen background pressure on the growth, epitaxy, point defect chemistry, and structural, optical, and electrical transport properties of laser-deposited epitaxial ZnO films.

A description of our pulsed-laser deposition (PLD) setup for the growth of thin films of metal oxides and wide-band-gap semiconductors can be found elsewhere.[12,13] The films were grown on sapphire (0001) at an optimized growth temperature of 750 °C.[5] Thin-film growth was carried out at various oxygen background (O_2) pressures ranging from 10^{-5} to 10^{-1} Torr. In some cases, initial stages of growth (100–500 Å) were carried out at a growth temperature of 750 °C and O_2 pressure of 10^{-4} Torr in order to grow high-quality epilayers, and then the O_2 pressure was increased to 10^{-1} Torr. The ZnO layers were characterized by x-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS)/ion channeling, atomic force microscopy (AFM) transport measurement, UV–visible spectroscopy, and photoluminescence (PL) spectroscopy.

All of the ZnO layers grown in a wide range of O_2 pressure (10^{-5}–10^{-1} Torr) were found to be highly *c*-axis oriented. In the lower oxygen pressure regimes (10^{-5}–10^{-4} Torr), the films have a *c*-axis lattice parameter 0.25% larger than that of the bulk value. This is expected due to both oxygen deficiency and the compressive strain induced by the sapphire substrate (the lattice mismatch between sapphire and ZnO is 16.8%). However, in the higher oxygen pressure regimes (10^{-2}–10^{-1} Torr), the *c*-axis lattice constant was found to approach the bulk value. The XRD ω-rocking-curve full width at half maximum (FWHM) was 0.069° for the film grown at an O_2 pressure of

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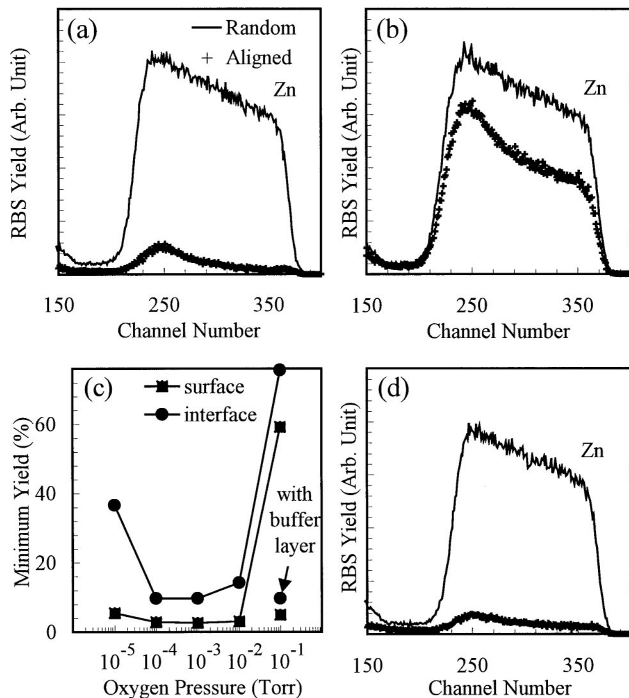

FIG. 1. Rutherford backscattering and ion channeling results for the ZnO films grown at various oxygen pressures: (a) 10^{-4} Torr, (b) 10^{-1} Torr, (c) minimum yield vs O_2 pressure for growth, and (d) 10^{-1} Torr with a nucleation layer of 100 Å grown at 10^{-4} Torr.

10^{-4} Torr, and it was weakly dependent on the O_2 pressure. The *in-plane* epitaxy, as determined by XRD ϕ scans of the ZnO $(10\bar{1}1)$ planes, however, was strongly influenced by the oxygen pressure. The FWHM of the ZnO $(10\bar{1}1)$ peak in the ϕ scan for the ZnO films grown at 10^{-4} and 10^{-1} Torr are 0.43° and 0.78°, respectively. The increase of the FWHM in the ϕ scan for the film grown at higher O_2 pressure clearly indicates a large misalignment of the ZnO grains and, hence, poor epitaxy.

The effects of O_2 pressure on the degree of epitaxy and defect density were quantitatively measured by using RBS and ion channeling techniques and the results are shown in Fig. 1. In these measurements, $\chi_{\min}$ (minimum yield), the ratio of the backscattered yield with the 1.5 MeV He^+ beam incident along [0001] (channeled) to that of a random direction, reflects the epitaxial quality (as well as defect density) of the film. Figures 1(a) and 1(b) show the aligned and random backscattering spectra for 5000-Å-thick ZnO films grown at 10^{-4} and 10^{-1}, respectively. Figure 1(c) shows the systematic dependence of $\chi_{\min}$ near the surface and the interface (ZnO/sapphire) on the O_2 pressure. It can be seen that the $\chi_{\min}$ near the surface region for the films grown in O_2 pressure regimes of 10^{-4}–10^{-3} Torr is ~2%–3% and is comparable to that of high-quality single crystals, while it is worse (50%–60%) for the film grown at an O_2 pressure of 10^{-1} Torr, indicating poor epitaxy. From Fig. 1(c), it should also be noted that the defect densities near the *interface* are strongly depended on the O_2 pressure, indicating the influence of O_2 during the initial stages of ZnO growth. The $\chi_{\min}$ near the interface is about 10%–12% for the film grown at 10^{-4} Torr and increases substantially to 50%–60% as the O_2 pressure increases to 10^{-1} Torr. The $\chi_{\min}$ of 10%–12% for the epitaxial film is a result of the unavoidably high threading dislocation density ($\sim 10^9/\mathrm{cm}^2$),[6,7] due to a large lattice mismatch between the ZnO films and the sapphire. The increase in $\chi_{\min}$ for the film grown in higher O_2 pressure clearly indicates that the film contains additional defects, such as dislocations, low-angle grain boundaries, and interstitials.

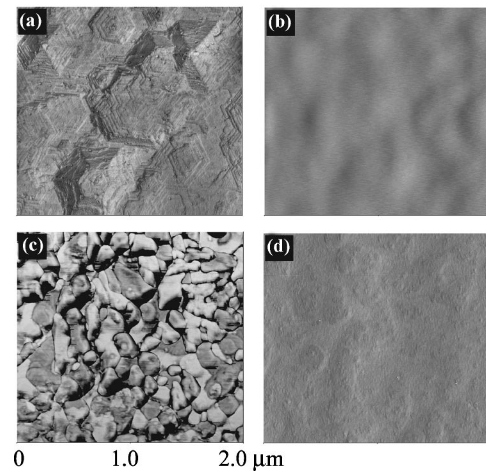

FIG. 2. AFM images of the ZnO films grown at various oxygen pressures: (a) 10^{-4} Torr, (b) 10^{-2} Torr, (c) 10^{-1} Torr, and (d) 10^{-1} Torr, with a nucleation layer of 100 Å grown at 10^{-4} Torr.

Figure 2 shows the surface morphology of the ZnO films grown at various O_2 pressures. The morphology of the films grown at 10^{-5}–10^{-4} Torr is dominated by a typical ''honeycomb'' -like structure with three-dimensional (3D) growth features as evidenced by well-faceted hexagons [Fig. 2(a)]. These features could be due to a high interfacial energy associated with the ZnO film on sapphire, a high surface mobility of the Zn adatom, and a substantial desorption of Zn. We also observed a high density of atomic steps on the facets with a step height of about 5.0 Å, which corresponds to a single unit-cell height. These high densities of steps formed in a low-oxygen pressure during the initial stages of growth can significantly influence the growth of the ZnO film subsequently deposited, and is an important issue, which is discussed later. The transition towards the growth of a smooth film was found for an O_2 pressure of 10^{-2} Torr. This change in growth mode results in a substantial reduction of rms roughness to 10–20 Å for a flat surface. A further increase of O_2 pressure to 10^{-1} Torr showed an adverse effect on the surface morphology [Fig. 2(c)], with typical features of high nucleation densities, irregular grains with different sizes, and increased surface roughness to about 400 Å.

Now we discuss the influence of oxygen pressure on the optoelectronic properties of the ZnO films. Figure 3 shows the electrical properties, namely, the Hall mobility (μ) and carrier concentration (n), for the ZnO films grown under various oxygen pressures. The highest electron mobility (72 $\mathrm{cm}^2/\mathrm{V\,s}$) was obtained for the film grown at 10^{-4}–10^{-3} Torr, but that film also showed the highest carrier concentration ($7\times10^{17}/\mathrm{cm}^3$). Further increase in O_2 pressure reduces the Hall mobility, possibly as a result of electron scattering by the defects. Figures 4(a) and 4(b) show 80 K PL spectra for the ZnO films grown at 10^{-4} and 10^{-1} Torr, respectively. In both cases, the spectra indicate distinct peaks due to the free and bound (D^0X) excitons and

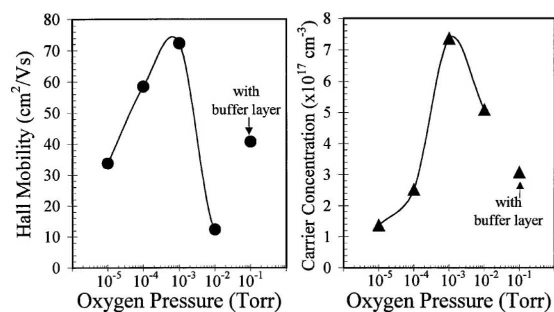

FIG. 3. Hall mobility and carrier concentration vs oxygen pressure for ZnO growth. For comparison, the data for the ZnO film grown at 10^{-1} Torr with the nucleation layer grown at 10^{-4} Torr are also provided.

features due to the donor–acceptor pair transitions at 3.32 eV with phonon replicas at 3.25 and 3.18 eV (see the inset of Fig. 4). The free- and bound-exciton peaks have FWHMs of 27 and 7 meV, respectively. The optical quality of the ZnO epilayer grown at 10^{-4} Torr is such that the excitonic luminescence intensity produced is two orders of magnitude higher than that of the textured film grown at 10^{-1} Torr. This indicates that a high concentration of defects in ZnO film affects the radiative processes. In addition, no green band (often attributed to structural defects in the ZnO) near 500 nm is observed for the high-quality epilayers grown at 10^{-4} Torr, while it is clearly present for the textured film. We did not see any broadening in the exciton peaks, probably due to the very small radius (~17 Å) of excitons in the ZnO.

From the abovementioned results, we have clearly established that the growth of high-quality epitaxial ZnO films with smooth surface morphology and desirable electrical and optical properties have different sets of optimum oxygen pressure regimes. To circumvent these problems, a two-step growth process has been developed for the fabrication of high-quality ZnO films. In this process, the nucleation layer is grown at low-oxygen pressure (10^{-4} Torr), which produces a high-quality crystallographic template for subsequent growth of ZnO at a high-oxygen pressure (10^{-1} Torr). This two-step process produces ZnO films with superior epitaxy, resulting in ion channeling characteristics [Fig. 1(d)] similar to those in films grown in 10^{-4} Torr oxygen pressure. The surface morphology [Fig. 2(d)] and electrical properties are also improved as compared to those in films grown in 10^{-1} Torr. High-optical luminescence quality without a green band [Fig. 4(c)] is also achieved in these films. These results are important in the context of fabrication of high-quality ZnO-based heterostructures, superlattices, and quantum wells for which smoother films with good electrical and optical properties are required. Additionally, growth of ZnO films under high-oxygen pressure is desirable for *p*-type doping studies in order to avoid compensation due to oxygen vacancies.

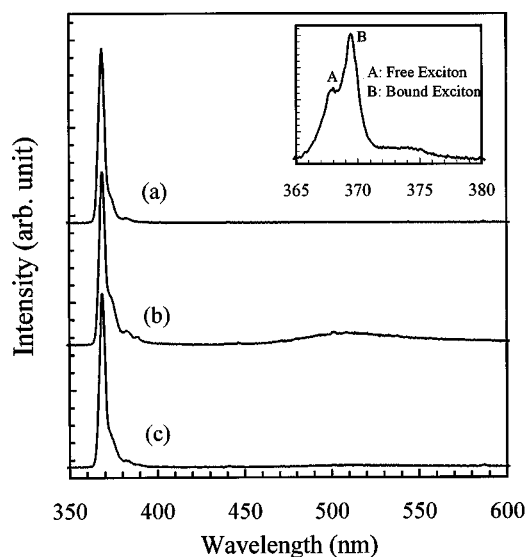

FIG. 4. 80 K PL spectra for the ZnO films grown at various oxygen pressures: (a) 10^{-4} Torr, (b) 10^{-1} Torr, and (c) 10^{-1} Torr with the nucleation layer grown at 10^{-4} Torr. The inset shows a high-resolution spectrum indicating free and bound excitons.

In conclusion, we have shown that oxygen pressure strongly influences the growth and nucleation characteristics, defect densities, and electronic and luminescence properties of the ZnO films. A low-oxygen background pressure (10^{-4}–10^{-3} Torr) in the initial stages of growth is critical for control of the epitaxy, while moderate-oxygen pressure (10^{-2} Torr) is required in the later stages to minimize the surface desorption process in order to achieve smooth films. The point defects caused by reduced surface mobility of the Zn adatoms, multiple nucleation, and dislocations, influence the electrical and optical properties of the films grown at high-oxygen pressure. By tuning the oxygen pressure during the initial and final stages of growth, it is thus possible to control desirable surface, interface, and optoelectronic properties of the films while maintaining high-quality epitaxy.

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