High-Quality ZnO Thin Films Grown by Fast Pulsed Laser Deposition without a Buffer Layer

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For the first time, a fast pulsed laser deposition (FPLD) process is presented for the epitaxial growth of ZnO thin films on *c*-plane sapphire substrates. This process is driven by a 355 nm solid-state laser pulsing at 10 kHz. The ZnO thin films grown by FPLD show a width of ~ 10 arcsec in the X-ray ω -scan and distinct Pendellösung fringes in the θ - 2θ scan of the ZnO(0002) reflection. Photoluminescence spectra reveal sharp donor-bound excitons of ~ 5 meV width and free excitons up to $n = 2$. Compared to conventional (much slower) PLD, 1–20 Hz, the measurements indicate that higher quality ZnO films can be grown by FPLD. In particular, despite the large lattice mismatch, such ZnO films were grown by FPLD directly on sapphire substrates without a buffer layer. [DOI: 10.1143/JJAP.44.L995]

KEYWORDS: pulsed laser deposition, fast pulsed laser deposition, ZnO, sapphire, buffer layer, Pendellösung fringes, excitons

ZnO semiconductors with a band gap of 3.37 eV are widely used for applications such as piezoelectric transducers, varistors, phosphors, and transparent conducting films. The optical properties of ZnO are similar to those of GaN, which has been successfully applied in short-wavelength light-emitting devices.^{1,2)} However, ZnO has a larger exciton binding energy and a higher melting temperature, 60 meV and 1975°C, than GaN, 28 meV and 900°C, respectively.³⁾ Therefore, it is expected that ZnO is a more efficient and durable material for blue and even ultraviolet light emissions. In recent years, high-quality ZnO films fabricated by pulsed laser deposition (PLD),^{4–6)} molecular-beam epitaxy (MBE),^{7–9)} and sputtering^{10,11)} showed that ZnO could be a promising material for the optical devices used in the short wavelength region.

The PLD method has been used to grow oxide films, including ZnO, by many researchers.^{4–6)} The lasers for this method are usually operated at low pulse repetition rates, 1–20 Hz, yet the energy per pulse is high, ~ 100 mJ/pulse. Hence, the amount of species arriving at the substrates could be instantaneously large, causing the condensation of undesired particulates in the films and introducing various types of intrinsic defect.^{4,6)} Therefore, the film quality can be poor without carefully controlling the growth parameters. In this letter, we developed a new method of growing ZnO films: fast pulsed laser deposition (FPLD). A fast 10 kHz pulsed laser was used to irradiate the ZnO target. At the same time, atomic oxygen was introduced into a growth chamber using an RF atom source to assist the film growth. The combination of the two techniques sufficiently prevented the generation of particulates, resulting in the improvement of the quality of the epitaxial ZnO films as indicated by several structural and physical measurements.

ZnO films were grown on Al₂O₃(0001) substrates in a high-vacuum chamber maintained at 3×10^{-8} Torr by a turbo molecular pump. A diode-pumped solid-state laser (355 nm wavelength, 15 ns pulse width) running at 10 kHz was used to ablate the ZnO target, which was maintained at a distance of 50 mm from the substrate. The energy per laser pulse was fixed at 200 μ J, and the laser beam scanned over the target surface was tightly focused so that the fluence was maintained at approximately 2 J/cm². The films were grown at a rate of approximately 4 nm/min over a wide range of

substrate temperatures from 600 to 900°C. Atomic oxygen was introduced into the chamber during the growth using a RF atom source operated at 300 W, while the oxygen pressure was maintained from 1×10^{-5} to 3×10^{-4} Torr. The film quality was observed to strongly depend on the substrate temperature as well as the oxygen pressure. The characterizations of the optimized films grown at the substrate temperature of 800°C and oxygen pressure of 1×10^{-5} Torr are as follows.

The crystal structure was investigated by high-resolution X-ray diffraction (HRXRD) using a parabolic Göbel mirror and a pair of channel-cut monochromating crystals in the (+, −) setting. The total divergence of the Cu K α_1 line is less than 10 arcsec. The θ - 2θ scan of the optimized sample yields 5.2109 Å for the lattice constant *c* of the ZnO film. Compared to the bulk lattice constant, 5.2049 Å, the film was found to be relaxed. The in-plane orientation relationship, ZnO[10 $\bar{1}0$] $\parallel$ sapphire[11 $\bar{2}0$], was identified using the ω -scan, where no other domains with different orientations could be detected. Figure 1(a) shows the detailed θ - 2θ scan around the ZnO(0002) reflection, where persistent pendellösung fringes are clearly observed, indicating a uniform film with a negligible variation in lattice constant *c*. The thickness of the film obtained by fitting the period of the fringes is 128 nm. Figure 1(b) shows the ω -scan (rocking curve) of the ZnO(0002) reflection, where the narrow FWHM, ~ 10 arcsec, approaches the resolution of the X-ray machine, implying a very small tilt in the *c* planes and perfect ordering along the growth direction. A similar result has been achieved by MBE growth, however a thin buffer layer of MgO was employed.⁷⁾ Here, despite the large lattice mismatch, high-quality ZnO films were grown by FPLD directly on sapphire substrates without a buffer layer. Presumably, the growth mode in FPLD is two-dimensional layer-by-layer for ZnO to align perfectly with Al₂O₃(0001),^{7,10)} but this awaits further investigation.

Atomic force microscopy (AFM) was used to study the surface morphology of the films grown by FPLD and conventional PLD. For conventional PLD, a KrF excimer laser (248 nm wavelength, 23 ns pulse width and 1 Hz repetition rate) was used, and the fluence was also maintained at 2 J/cm² on the target for comparison. The flat surface of the film grown by FPLD was confirmed by AFM measurement. The AFM image [Fig. 2(a)] of the FPLD film shows that the roughness of the surface is about 0.9 nm

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Fig. 1. (a) X-ray θ - 2θ scan of the ZnO(0002) reflection showing pronounced Pendellösung oscillations. (b) X-ray ω -scan of the ZnO(0002) reflection showing a width of only 10 arcsec.

and no grain boundary can be clearly observed. Compared to the film grown by conventional PLD, with a (0002) reflection of more than 1000 arcsec typical FWHM, the roughness is about 5 nm and the grain size is about 200 nm for the boundary observed [Fig. 2(b)].

The optical emission properties were characterized by photoluminescence (PL) spectroscopy, excited by the 325 nm emission from a 20 mW He-Cd laser. The PL signal was collected using a PMT spectrometer with a resolution of 0.1 nm. In general, the emission spectrum of ZnO can be divided into two broad categories: near band-edge (NBE) emissions (~ 3.36 eV) and deep-level (DL) emissions (~ 2.4 eV) observed in the films grown by other researchers.^{7,12} Notably, the DL emissions are almost not observed in the films grown by FPLD, indicating that the number of oxygen vacancies associated with the DL emissions can be sufficiently reduced by FPLD. Figure 3 shows the temperature dependence of the NBE emissions from 250 to 10 K. At 10 K, the dominant NBE peaks located at 3.365, 3.336, and 3.222 eV were identified as the donor-bound exciton (D^0, X),^{8,13} two-electron satellite (TES),^{8,14} and donor-acceptor pair transition (D^0, A^0),^{8,13} respectively. The most intense peak (D^0, X) has an FWHM less than 5 meV. All these peaks have phonon replicas involving multiples of an LO phonon of ~ 72 meV¹⁵ located at 3.294, 3.193, and 3.150 eV, respectively. In addition, there are four shoulders on the right side of the (D^0, X) peak, which were identified as the A-band free exciton (FXA),¹⁶ B-band free exciton (FXB),¹⁶ high-order FXA ($n=2$) and high-order FXB ($n=2$). The binding energies of the A-band and B-band free excitons are approximately 36 and 62.7 meV, respec-

Fig. 2. AFM images for films grown by (a) FPLD and (b) conventional PLD.

Fig. 3. PL NBE emissions of the ZnO film from 250 to 10 K. Fine structures of exciton states with phonon replicas and high-order free exciton states are well resolved.

tively, which were calculated using the formula: $E_b = 4/3[E_{FX}(n=2) - E_{FX}(n=1)]$, and are in agreement with those previously reported.^{9,14)} The high-order free excitons are observed to last up to 40 K. These PL properties demonstrate the high quality of the ZnO films grown by FPLD.

The Hall properties of ZnO films were studied by the standard four-point Van der Pauw technique, in which the Ohmic contact was achieved using annealed Au electrodes.^{16,17)} The typical intrinsic ZnO film prepared by PLD is of the n-type with a carrier concentration of 10^{18} cm^{-3} , a resistivity on the order of $10^{-1} \Omega \text{ cm}$, and an electron mobility of $10 \text{ cm}^2/\text{Vs}$ due to various defects.^{4,6)} ZnO films grown by FPLD achieve a high mobility up to $100 \text{ cm}^2/\text{Vs}$ at 300 K with a carrier concentration in the range from 2 to $5 \times 10^{16} \text{ cm}^{-3}$, indicating that the number of intrinsic defects of the films can be reduced by FPLD.

In conclusion, an FPLD method was developed for thin film synthesis, and ZnO films were grown on $\text{Al}_2\text{O}_3(0001)$ substrates by this new method without a buffer layer. The structural, optical, and electrical properties show the high quality of the films. We expect that the FPLD method will be successful not only for the growth of pure ZnO films, but also for the doping of ZnO films and the growth of many other crystals.

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