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Layer-by-layer growth of high-optical-quality ZnO film on atomically smooth and lattice relaxed ZnO buffer layer

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The growth mode of ZnO thin films can be well regulated in a molecular layer-by-layer growth by employing a ZnO buffer layer deposited on a lattice-matched ScAlMgO₄ substrate and annealed at high temperature. The annealed buffer layer has atomically flat surface and relaxed (strain-free) crystal structure. The intensity oscillation of reflection high-energy electron diffraction persisted for more than a 100-nm film deposition under optimized conditions on such a buffer layer. Thus prepared thin films show free exciton emissions in a 5 K photoluminescence spectrum and excited-state exciton resonance structures in a reflection spectrum, both indicating very high optical quality. © 2003 American Institute of Physics. [DOI: 10.1063/1.1615834]

Demonstrations of room-temperature stimulated emission¹ and laser action^{2,3} from ZnO thin films under optical pumping triggered intensive research aiming at ultraviolet light-emitting diodes and lasers. Controlling the crystalline defects in naturally *n*-type ZnO is the critical issue to obtain *p*-type ZnO. For this purpose, we have set making the crystallinity of thin films as perfect as possible as the starting point. Employing a lattice-matched ScAlMgO₄ (0001) (SCAM) substrate, extremely small orientation fluctuations both in-plane ($<0.02^\circ$) and out-of-plane ($<0.01^\circ$) were achieved.⁴ This technique resulted in very clear exciton resonance spectra⁵ and very low ($<10^{15} \text{ cm}^{-3}$) residual electron carrier concentration.⁴ Based on such high-quality thin films, we have been able to make systematic studies on ZnO/(MgZn)O superlattices as represented by even enhanced exciton binding energy up to 105 meV (Ref. 6) and further efficient stimulated emission at shorter wavelength⁷ due to quantum size effect. However, doping of N or codoping of N with Ga into such high-quality ZnO films on SCAM substrates could not turn the polarity into *p*-type.^{8,9} Therefore, further detailed examination of crystalline quality and optical properties were carried out by positron annihilation¹⁰ and time-resolved photoluminescence (PL),¹¹ respectively, to find out that there is still enough room to improve the crystalline quality of ZnO thin films.

We thought heteroepitaxy of ZnO on SCAM substrate

would proceed as quasihomoepitaxy due to the very small lattice mismatch of 0.09%. However, initial growth mode had not been controlled well enough to observe intensity oscillation of reflection high-energy electron diffraction (RHEED). This fact prompted us to reconsider that the chemical dissimilarity between ZnO and SCAM and/or small but finite lattice mismatch might be the origin for the absence of RHEED oscillation. To solve these problems in this study, we employ ZnO buffer layer annealed at high temperature to obtain fully relaxed lattice strain and atomically smooth surface. Preliminary results on the annealing of ZnO single crystal and films grown on Al₂O₃ substrates were already reported to yield in rather smooth surface,¹² relaxed lattice, and high electron mobility.¹³ The use of SCAM substrate substantially improve the surface and lattice quality of the annealed film, because of high crystallinity due to coherent lattice connection at the interface in the film to be annealed. This idea comes from a recent letter on the interface dislocation engineering for (BaSr)TiO₃ films on SrTiO₃ substrate reported by K. Terai *et al.*¹⁴

In this letter, we demonstrate persistent molecular layer-by-layer growth of ZnO thin films on self-template ZnO buffer layer to obtain high-optical-quality films, which exhibits $n=2$ exciton resonance structure in reflection spectrum, where n denotes the quantum number. We believe the crystalline quality of undoped ZnO has been dramatically improved so as to be feasible to challenge *p*-type conduction by chemical doping with N.

The ZnO buffer layer (100 nm) was grown on cleaved surface of SCAM substrate at 650 °C in 1×10^{-6} Torr oxygen by ablating ZnO single-crystal target with KrF excimer laser pulses (248 nm, 5 Hz, 1 J/cm²). The buffer layer was annealed *ex situ* in a furnace at 1000 °C for 1 h in air. The

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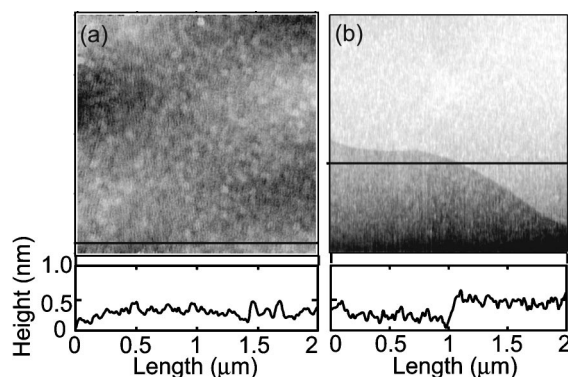


FIG. 1. AFM images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) and cross-sectional profiles for as-grown (a) and annealed (b) ZnO buffer layers. Annealed surface shows very wide atomically flat terraces (rms roughness of 0.07 nm) and 0.26-nm-high steps corresponding to the half-unit cell of ZnO, whereas as-grown film has a featureless surface, with rms roughness of 0.2 nm.

atomic force microscope (AFM) images for the ZnO films before and after the annealing are shown in Figs. 1(a) and 1(b), respectively. The surface of as-deposited buffer layer has sub-nanoscale corrugation, and the rms roughness is as large as 0.2 nm. The annealed surface has 0.26-nm-high steps corresponding to one molecular layer of ZnO and atomically flat terraces (rms roughness of 0.07 nm), as shown in Fig. 1(b). Most of the trials of $10\text{-}\mu\text{m} \times 10\text{-}\mu\text{m}$ AFM inspection for the annealed film resulted in step-free and atomically smooth surface. However, careful trial gives us such an area having only one step in the image, as shown in Fig. 1(b). Since the cleaved SCAM surface is atomically flat in a macroscopic scale ($>100\ \mu\text{m}$), we can finish ZnO surface with step-free and atomically smooth surface in such a scale. Taking into account the rougher surface, absence of distinct steps, and absence of RHEED oscillation, the surface of as-deposited buffer layer before annealing is thought to be rough, judging in an atomic scale. The crystallinity of the films was characterized by a high resolution four circle x-ray diffraction (XRD) apparatus. The in-plane lattice constant of as-grown buffer layer is locked with that of SCAM substrate, as has been previously reported.⁴ However, that of annealed buffer layer shifts to a value close to intrinsic lattice constant of ZnO (0.5204 nm). The misfit dislocation density can be evaluated as ($\sim 10^6\ \text{cm}^{-2}$) from lattice constant change upon annealing.

On such a surface of annealed ZnO buffer layer, ZnO films were deposited at three different laser repetition conditions of 1, 5, and 10 Hz. For an individual run, deposition temperature was varied along an axis of the substrate by employing our originally developed “temperature gradient method,” in which a focused infrared laser beam was impinged on an end of substrate holder for heating to give a continuous spread of temperature ranging from 670 to 830 °C on a substrate.⁹ During the deposition, RHEED oscillation data were simultaneously obtained for their representative positions corresponding to substrate temperatures of 700, 750, and 800 °C with scanning RHEED.¹⁵

Figure 2 shows *in situ* RHEED intensity oscillations. The oscillation period corresponds to the growth of a 0.26-nm-thick ZnO molecular layer (half-unit cell), that was confirmed by the product of required laser pulses and deposition rate calculated from x-ray Laue fringes of the resulting films.

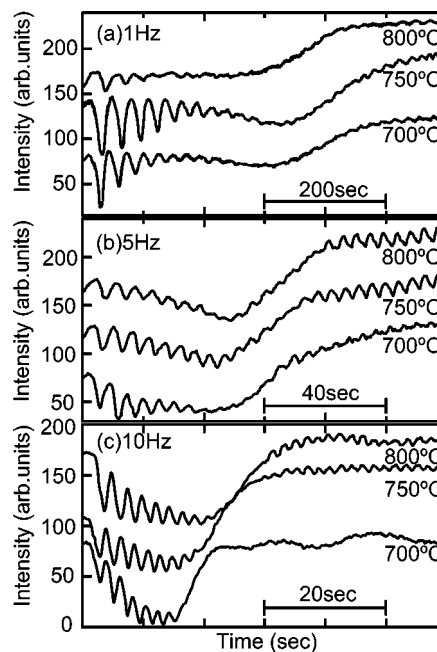


FIG. 2. RHEED intensity oscillations observed during the ZnO deposition on the annealed ZnO buffer layer. Clear oscillations with a period of 0.26-nm deposition are observed for all deposition conditions. The oscillation persists until the end of the deposition (100 nm) when the substrate temperature was 800 °C and laser repetition was 1 or 5 Hz.

The RHEED intensity was decreased at the initial stage and recovered after the deposition of about 10 molecular layers. This is presumably because the surface was contaminated by exposure to the air after annealing.¹⁶ After the recovery, the intensity oscillation for 1 or 5 Hz continued at 800 °C persistently until the growth was finished (100 nm).

AFM images of the ZnO films grown at 800 °C with observing persistent RHEED oscillation are shown in Fig. 3. At the laser repetition of 1 Hz, surface morphology was kept atomically flat. Most of the area of the image is covered with two levels of the terraces 0.26 nm apart. The surface for the film grown with a 5 Hz laser repetition also shows step and terrace structure and consists of 3–4 levels of terraces. As the repetition is increased to 10 Hz, where RHEED oscillation is smeared out around a 10-nm deposition, the surface is

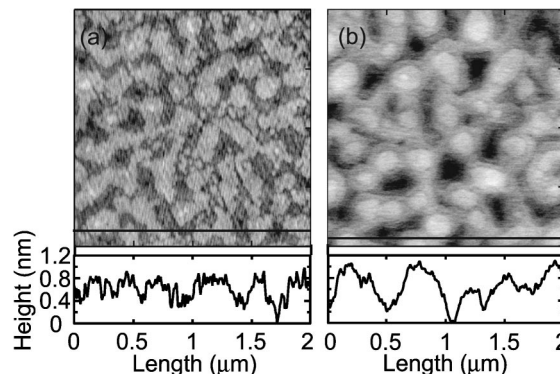


FIG. 3. AFM images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) and cross-sectional profiles for ZnO thin films (100 nm) grown at 800 °C on the ZnO buffer layer (100 nm) with the laser repetition of 1 Hz (a) and 5 Hz (b). Most of the area in (a) is covered by two levels of atomically flat terraces separated by 0.26-nm-high steps. The terrace width in image (b) is narrower, and more steps can be seen to develop four levels of terraces.

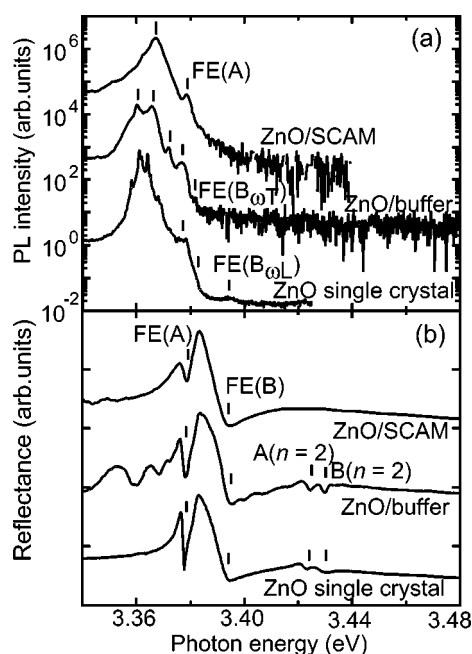


FIG. 4. PL (a) and optical reflection (b) spectra measured at 5 K for a ZnO thin film directly deposited on SCAM substrate (Ref. 10), the ZnO thin film deposited on the ZnO buffer layer at 800 °C with the laser repetition of 5 Hz, and one of the best quality bulk single crystals made by Eagle Picher Technologies, LLC. (Ref. 17). Free exciton emission lines are observed at 3.377 eV (FE_A) and 3.382 eV ($FE_{B\omega_T}$) for the ZnO thin film grown on the buffer layer. The FE_A (3.379 eV) line for the ZnO thin film grown on SCAM was shifted by the compressive strain induced by the in-plane lattice mismatch. The $n=2$ exciton structure is observed in the optical reflection spectrum for the ZnO thin film grown on the buffer layer.

consisted of about five levels of terraces, but step and terrace structure can be still seen (not shown).

Optical properties were examined by PL and optical reflection spectroscopies at 5 K. Figure 4(a) shows PL spectra taken under the excitation with a 325.0-nm line of a He-Cd laser for the following ZnO samples: (from upper to lower) an epilayer directly grown on SCAM substrate,¹⁰ that grown on the buffer layer, and one of the best quality bulk single crystals made by Eagle-Picher Technologies, LLC. (Ref. 17). The ZnO film grown on the buffer layer at 800 °C and 5 Hz shows dominant luminescence lines at 3.360, 3.365, and 3.372 eV, the origin of which are assigned: neutral donor bound-excitons (D_0X). There are also a free A-exciton (FE_A) line at 3.377 eV and a shoulder due to the transverse B-exciton (B_{ω_T}) emission at 3.382 eV. These features are very similar to those of bulk single crystal. The ZnO film directly grown on SCAM shows D_0X line at 3.367 eV and FE_A line at 3.379 eV. Both energy positions are slightly shifted by compressive strain due to coherent growth. The shift agrees with the estimation by Makino *et al.*¹⁸ accounting for the reciprocal space mapping of x-ray diffraction results. Figure 4(b) shows the reflection spectra for respective samples. The emission line positions for FE_A agree with the structures observed in reflection spectra. By inserting the ZnO buffer layer, ground-state anomaly becomes to oscillate very sharply and the high-reflectivity range of B-exciton becomes wide. The latter can be understood as a sign of the smaller damping and the thinner surface dead layer.¹⁹ The

Bohr radius of $n=1$ exciton is 18 Å and that of $n=2$ is 72 Å. The clear observation of $n=2$ resonance in ZnO film deposited on the buffer layer manifests itself in that the coherent length extends more in ZnO crystal. Since such excited-state ($n=2$) excitons have much smaller oscillator strength and are easily exposed to the influence of various scattering events, their clear observation definitely supplies one more piece of evidence of reduced inhomogeneity or reduced defect.

In conclusion, we have dramatically improved the crystallinity and optical properties of ZnO films by employing *ex situ* annealed ZnO buffer layer on SCAM substrate. The surface of the annealed buffer layer is atomically smooth, enabling persistent layer-by-layer growth of ZnO film as demonstrated by RHEED intensity oscillation. The PL and optical reflection spectra of the ZnO film on buffer layer are very similar to those for one of the best bulk single crystals. This technique should provide us with a good arena to re-examine the possibility of *p*-type doping by chemical substitution with acceptors.

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