Structural and optical investigations of periodically polarity inverted ZnO heterostructures on (0001) Al_2O_3

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We report the structural and optical properties of one-dimensional grating of ZnO consisting of periodically polarity inverted structures on (0001) Al_2O_3 substrates. The inversion domain boundaries (IDBs) between the Zn- and the O-polar ZnO regions were clearly observed by transmission electronic microscopy. The investigation of spatially resolved local photoluminescence (PL) revealed strong excitonic emission at the interfacial region including the IDBs. The possible mechanism of strong PL has been discussed by the consideration of atomic configuration and carrier collection including its lifetime and diffusion process in Zn- and O-polar regions. Therefore the authors conclude that the IDBs can be active for the strong emission not a nonradiative center. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3114989]

Besides the intensive studies for framework of ZnO as optoelectronic devices including the light emitter, transparent conductor, and sensor,[1–3] recently, ZnO is considered as a potential candidate for new nonlinear optical materials since it possesses strong nonlinear susceptibilities.[4,5] In order to realize the application to nonlinear optical devices including the second harmonic generation, it is desirable to fabricate the periodically polarity inverted (PPI) structures, i.e., flipping the second order nonlinear optical susceptibility, which is essential point to accomplish the quasiphase matching conditions.[6]

ZnO crystallizes in a wurtzite structure and naturally has crystal polarity along the *c*-axis: Zn polar and O polar. Due to the importance of polarity for controlling the material properties, we previously reported the polarity controlling method of ZnO films on (0001) Al_2O_3 substrates by using the Cr-compound intermediate layers.[7] The ZnO films grown on rocksalt structured (111) CrN showed the Zn polarity, while those grown on hexagonal (0001) Al_2O_3 showed the O polarity.[7] Here, we would like to emphasize that the periodical array of polarity controlled films opens up new application fields. As an example, fabrication of PPI ZnO structures can replace the periodically poled $LiNbO_3$, $LiTaO_3$, and $KTiOPO_4$.[8,9] Although some properties on PPI structures of GaN and ZnO have been reported in the literature,[10,11] in the case of ZnO, the detailed optical properties and interfacial properties are not well understood yet.

In this letter, we report on specific optical and structural properties of PPI ZnO structures. The procedures for the fabrication of the PPI ZnO structure are described in detail. High resolution transmission electron microscopy (HRTEM) and microphotoluminescence (μ-PL) are used to investigate properties of the PPI structure, locally, which have revealed an inversion domain boundary (IDB) between the Zn- and the O-polar regions, and a stronger luminescence at the IDB regions than those of the Zn- and O-polar regions.

In order to fabricate the PPI ZnO structure on *c*-sapphire substrate, growth and patterning sequence with lithography and etching steps, as illustrated in Fig. 1, are conducted. For the preparation of template, a CrN was grown on (0001) Al_2O_3. At first, low temperature (LT) ZnO layers are grown on a Zn exposed CrN/Al_2O_3 templates by employing the standard growth procedures reported elsewhere.[12] This step shall result in the growth of Zn-polar ZnO on the CrN intermediate layer.[7] The second step for the fabrication of a PPI ZnO structure is a periodical patterning on the LT ZnO. Standard photolithography is conducted in order to make stripes

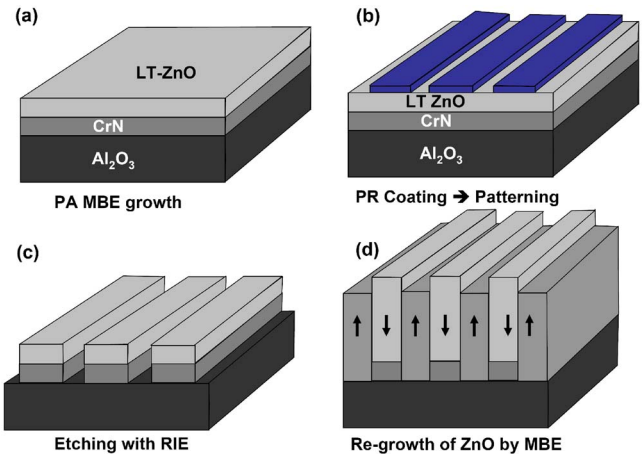

FIG. 1. (Color online) Schematic illustration of overall processes to fabricate the periodically polarity inverted ZnO structure. (a) LT ZnO growth on the Zn preexposed CrN buffer. (b) Formation of stripe patterning on the LT ZnO along the $\langle 11\bar{2}0 \rangle$ direction. (c) 1D patterned ZnO/CrN after the RIE, which results in the opening of the Al_2O_3 substrate. (d) ZnO regrowth, which results in the Zn polar on the CrN and the O-polar ZnO on the Al_2O_3.

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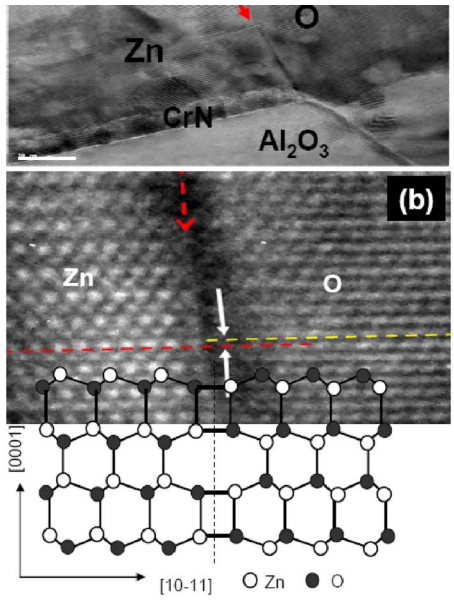

FIG. 2. (Color online) (a) High resolution TEM micrograph for the detailed structure showing the Zn-polar ZnO on the CrN layer and the O-polar ZnO on the sapphire. (b) Magnified image for the region around the IDB and schematic representation of an IDB in PPI ZnO structure.

along the ZnO $[11\bar{2}0]$ direction, as shown in Fig. 1(b). The directions of stripes are selected by consideration of flat surface and etching rate.[13] Periods of the stripe patterns were varied from 2 to 30 μm and the pattern of 2 μm was mainly used in this study. Next, reactive ion etching (RIE) was conducted, which completely etched both the LT ZnO and the CrN layers. This process made opening of sapphire substrate through the stripes, as shown in Fig. 1(c), which is essential for the O-polar ZnO growth. Finally, a high temperature ZnO layer was grown on LT ZnO with suppression of rotational domain at 750 °C, which shall grow the Zn-polar ZnO on CrN/Al_2O_3 and the O-polar ZnO on sapphire.

The spatially resolved local optical properties of Zn-polar, O-polar, and interfacial regions are investigated by μ-PL at room temperature. Optical excitation is carried out using a continuous-wave He–Cd laser light with a wavelength of 325 nm and a power 5 mW. The backward PL from the sample was collected by an objective lens, reflected by a half mirror and its image was monitored by a charge-coupled device (CCD) camera (Sony XC-EU50) having near UV sensitivity with a peak around 369 nm. The scattered light from the exciting laser light was excluded by a sharp cutoff absorption filter, the spatial and spectral resolutions were less than 1 μm and 0.1 nm, respectively.

The determination of lateral polarity flipping in fabricated structures has been conducted by piezoresponse microscopy technique. The image of piezoelectric response for the fabricated structure clearly showed the different brightness and revealed the periodical change in response voltage (phase) by applied ac voltage (not shown here), which was found out in another reference.[12]

In order to get insight of the structural and interfacial properties of PPI ZnO, cross-sectional TEM observations have been performed for the fabricated PPI structures along the ZnO $\langle 11\bar{2}0\rangle$ zone axis. In addition, HRTEM observation was performed to investigate the detailed structure, as shown in Fig. 2. In this figure, we can clearly see two ZnO regions

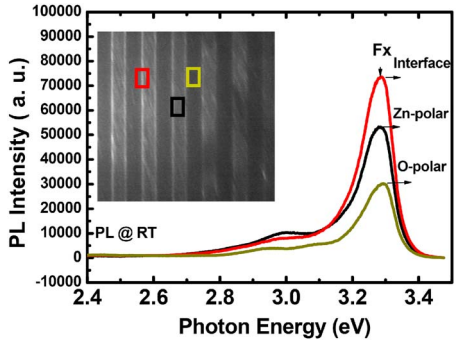

FIG. 3. (Color online) μ-PL spectra obtained from the Zn-polar, O-polar, and interfacial regions in the PPI ZnO structure. The inset shows PL image in PPI ZnO.

grown on the CrN and on the sapphire. Here, it should be mentioned that we could observe the IDB starting from the edge of CrN buffers at the position in which the polarity of ZnO films was changed. The vertical IDBs are observed in the lateral polarity controlled GaN by using the atomic-resolution high-voltage electron microscopy.[14] The vertical IDB is marked by red arrow in Fig. 2(a), which indicates that the IDB is $\{10\bar{1}0\}$ plane parallel to stripe direction. These results agreed well with the fact that the vertical IDBs are always on the $(10\bar{1}0)$ plane whatever the stripe orientations were in the PPI GaN structures.[14] In terms of formation energy, the formation of IDB are expected that the general stacking mismatch changed via a translation along the [0001] direction into a structure having no wrong bonds which are unstable due to the Ga–Ga and N–N bonds.[15] The magnified high resolution lattice micrograph of the IDB region was shown in Fig. 2(b). Yellow and red lines were drawn, in which one is drawn based on the hexagonal closed packed (hcp) lattice units from the left side of the IDB and the other one is drawn based on the hcp lattice units from the right side of the IDB, in order to clearly visualize the shift in hcp lattice by $c/2(2.6035$ Å) along the [0001] direction as indicated by white arrow in Fig. 2(b). This shift is the typical feature of the IDB in GaN.[15] Such shift in lattice was predicted in order to form the energetically stable IDB.[15] Following the expected atomic bonding configuration at IDB in PPI structures the possible IDB between Zn and O polar was illustrated in the inset of Fig. 2(b) as indicated by dot line. Although theoretical evaluations are needed to more clarify the atomic arrangement at the interface, this observations and suggestions are first reported in the PPI ZnO structures.

The detailed special optical properties of PPI ZnO were investigated by μ-PL. Figure 3 shows room temperature μ-PL spectra for the three regions for Zn-polar, O-polar regions, and the interfacial region between the Zn- and the O-polar ZnO. The dominant excitonic PL peak was shown at 3.29 eV which was assigned as free exciton (FX) peak. In addition, the PL image of PPI ZnO is shown in the inset of figure. The different squared marks indicate the measured point of each region. The PL intensity from the interfacial region is much stronger than those from the Zn- and O-polar regions.

In the case of PPI GaN, the origin of strong PL at interface between Ga and N polar region is suggested by the theoretical model. Northrup *et al.*[15] reported that the formation of IDBs in wurtzite GaN is energetically favorable to

minimize the number of wrong bonds by first-principles calculations of domain-wall energies. Furthermore, Fiorentini[16] proposed a model for the explanation of the efficient PL from IDBs in PPI GaN by using the *ab initio* density-functional calculation. In terms of the local self-consistent electronic potential, effective collection of both electrons and holes in the vicinity of the IDB enhanced the recombination probability and excitonic interactions. It was predicted that IDBs in GaN would not induce electronic states in the band gap, implying that the IDBs should not have harmful effects on the PL efficiency. Our findings can support these predictions and further indicate that the formation of IDBs of PPI ZnO structures is energetically stable and has optically active traps that can work for bright emission.

The lifetime and diffusion process of exciton can be discussed to explain the other mechanism of strong PL at the step between Zn and O polar. We have previously reported the different lifetime depending on polarity of ZnO films and PPI structures. The excitonic lifetime of Zn polar ZnO grown on CrN buffer layer shows much longer than that of O-polar regions.[11] FX diffusion length under 77 K were reported at around ~ 2 μm and the diffusion length increases with temperature in many systems.[17] Therefore, the generated FX in Zn and O polar will diffuse toward the step between both polars. Due to the longer lifetime of Zn-polar region comparing to the O-polar region, Zn-polar ZnO regions can contribute to enhance the collective and interaction probabilities at the IDBs. Therefore, the Zn-polar regions will mainly effect on the emission at the IDBs.

In the case of PPI ZnO, there is different growth rate between Zn- and O-polar ZnO, which makes the grating with step height of about 150 nm. Although the different step height depends on the growth conditions of PPI ZnO structures, the reported value of growth rate of Zn-polar ZnO films shows the 1.3–1.5 times higher than those of O-polar films.[7,12] From the consideration of step height and geometry, the generated exciton can be easily emitted from the side $(10\bar{1}0)$ plane of step compared to the surface plane of ZnO due to the internal total reflection effect between ZnO surface and air resulting from the difference of refractive index. This escaping probability can be considered as a possible mechanism for the strong emission at the step region.

In optical properties of PPI GaN, the dominant peak from IDB is 30–40 meV lower in energy than emission from the bulk.[16,18] In our PPI ZnO samples, the dominant peak of interface well corresponds with the bulk material. Therefore, we think that the strong emission of PPI ZnO is related to the FX, which has some differences from the PPIGaN.

In summary, we demonstrated and characterized the 1-dimensional ZnO grating formed by PPI structures. The IDB with $(10\bar{1}0)$ plane was observed at the interfacial region among the different polar ZnO regions and expected atomic structure was suggested. The stronger PL intensity from the interfacial region with the IDB was observed than those from the Zn- and O-polar ZnO regions, which indicate that no active IDBs as a nonradiative center. The possible mechanisms of strong PL were discussed with the consideration of different lifetime and diffusion process of exciton. The formation of periodical grating by using the PPI structures of ZnO will be one of prime importance for the development of nanooptoelectronic devices.

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