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Pulsed sputtering epitaxial growth of *m*-plane InGaN lattice-matched to ZnO

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m-Plane GaN and InGaN films were grown on *m*-plane ZnO substrates at ~350 °C by pulsed sputtering deposition. It was found that the critical thickness of the *m*-plane GaN films grown on ZnO lies between 25 and 62 nm, whereas 180-nm-thick *m*-plane In_{0.12}Ga_{0.88}N can be coherently grown on ZnO substrates, which is explained well by theoretical calculations based on an energy-balance model. The coherently grown *m*-plane InGaN on ZnO exhibited narrow X-ray rocking curves compared with the *m*-plane GaN grown on ZnO. These results demonstrate the benefit of lattice-matched ZnO substrates for epitaxy of high-quality nonpolar InGaN films.

Over the last decade or so, the growth, physics, and device applications of nonpolar and semipolar nitrides have made significant progress^{1,2}. The first planar nonpolar *m*-plane GaN was grown on LiAlO₂ substrates by Waltereit *et al.*³, which motivated the researchers to grow nonpolar GaN films on other substrates such as sapphire and SiC for light-emitting diodes (LEDs)^{4,5}. Subsequently, the use of nonpolar and semipolar bulk substrates prepared by hydride vapor phase epitaxy (HVPE) increased, enabling the fabrication of bright LEDs and green laser diodes (LDs)^{6–9}. Throughout history, it was observed that high-performance devices need to be fabricated on high-quality substrates. Therefore, bulk GaN substrates are now widely used for nonpolar light-emitting devices^{10–12}; however, the use of GaN substrates presents the problem of lattice mismatch with InGaN^{13,14}. This lattice mismatch between GaN and InGaN could be detrimental, particularly for long-wavelength LEDs and LDs. To overcome the lattice mismatch problem, the use of ZnO substrates has been proposed for the growth of high-quality nonpolar InGaN^{15,16}. As shown in Fig. 1, compared with GaN, ZnO exhibits a smaller lattice mismatch along both the *a*- and *c*-axes with In_xGa_{1–x}N (*x* > 0.09). Another advantage is that high-quality ZnO substrates can be prepared using hydrothermal methods¹⁷, and ZnO substrates are larger than the state-of-the-art bulk GaN substrates. It can be noted that the use of ZnO substrates is the best way to fabricate nonpolar InGaN-based devices because nonpolar ZnO substrates are considerably cheaper than nonpolar GaN bulk substrates. It is natural to try to grow nitride films on ZnO because it is the only wurtzite material that is lattice-matched to group III nitrides.

HVPE^{18,19}, metalorganic vapor phase epitaxy²⁰, and molecular beam epitaxy²¹ of GaN and InGaN on ZnO have been reported, and a reasonable epitaxial relationship of nitride and ZnO has been confirmed²⁰. From these results, it can be expected that high-quality nonpolar nitrides could also grow on ZnO substrates. However, it is difficult to grow nitride films on chemically vulnerable ZnO substrates by chemical vapor deposition. To take full advantage of the lattice-matching nature of ZnO and grow high-quality nitride films, the chemical/interfacial reactions between nitrides and ZnO need to be completely suppressed.

A decrease in the growth temperature is important to suppress the interfacial reactions between nitrides and ZnO. Recently, a low-temperature epitaxial growth technique was developed called pulsed sputtering deposition (PSD)²². This technique enables the growth of nitride films with high control over the film thickness and allows deposition over a large area. PSD is particularly suitable for InGaN growth because its growth temperature is lower than those of MBE, MOVPE, and HVPE. In PSD growth, a pulsed supply of indium and gallium atoms with high kinetic energy enhances the migration of adatoms on the surface, leading to a dramatic reduction in the growth temperature. Using this technique, high-quality n-type²³ and p-type²⁴ GaN films were successfully grown with room temperature carrier mobilities of 1008 and 34 cm² V^{–1} s^{–1}, respectively. Moreover, LEDs were also fabricated at temperatures lower than 500 °C²⁵. These results indicate the potential of PSD for the fabrication of nitride-based devices on ZnO substrates. In this article, the structural properties of nonpolar *m*-plane GaN and InGaN films grown on ZnO substrates by PSD are reported.

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Figure 1. In-plane lattice mismatches of *m*-plane InGa_{1-x}N/ZnO and InGa_{1-x}N/GaN. Lattice constants of InGa_{1-x}N were calculated according to Vegard's law.

Figure 2. RHEED patterns [(a) and (b)] and AFM images ($1\ \mu\text{m} \times 1\ \mu\text{m}$) [(c) and (d)] of GaN films grown on *m*-plane ZnO substrates at 340 [(a) and (c)] and 540 °C [(b) and (d)].

Results and Discussion

First, the structural properties of the GaN films grown on *m*-plane ZnO were investigated. Figure 2 shows the reflection high-energy electron diffraction (RHEED) patterns [(a) and (b)] and atomic force microscope (AFM) images [(c) and (d)] of GaN films grown at 340 °C [(a) and (c)] and 540 °C [(b) and (d)]. A sharp streaky RHEED pattern corresponding to the growth of *m*-plane GaN was observed for the film grown at 340 °C, whereas the film grown at 540 °C exhibited a RHEED pattern with spots, indicating the growth of a mixture of zincblende and

Figure 3. Evolution of lattice constants of GaN films grown on *m*-plane ZnO substrates at 340 °C. Fully relaxed lattice constants of ZnO and GaN are also indicated. Broken lines are guide to the eye.

wurtzite GaN. The polycrystalline growth of GaN was also observed on the *m*-plane ZnO substrates when the growth was performed at high temperatures (above 500 °C) using pulsed laser deposition²⁶. The failed growth is attributed to the formation of interfacial alloys through the diffusion of Ga and N into ZnO heated above 500 °C. The formation of the interfacial layer results in nitride films with a rough surface, making it difficult to control the electrical and optical properties. AFM observations revealed that the surface of *m*-plane GaN epitaxially grown on ZnO was atomically flat [Fig. 2(c)], which is in striking contrast with the rough surface of GaN grown on ZnO at 540 °C [Fig. 2(d)].

Next, the structural characterization of a single crystalline *m*-plane GaN film on ZnO was performed using X-ray diffraction (XRD). The full widths at half maximum (FWHM) of the X-ray rocking curves (XRCs) for *m*-plane GaN (25 nm thick) grown at 340 °C were 155 and 130 arcsec with the X-ray incident angle perpendicular to [11 $\bar{2}$ 0] and [0001], respectively. In order to experimentally determine the critical thickness for the lattice relaxation of *m*-plane GaN grown on ZnO by PSD, four samples with different film thicknesses were prepared (25, 62, 110, and 160 nm) and the lattice constants of GaN films were measured using the X-ray reciprocal space map (RSM) technique. Figure 3 shows the lattice constants of GaN films with different thicknesses. While the lattice constant along the *c*-axis was almost unchanged for all film thicknesses, the lattice constant along the *a*-axis relaxed at a film thickness between 25 and 62 nm and gradually approached the lattice constant of the completely relaxed GaN. The predominant lattice relaxation along the *a*-axis can be explained by the larger lattice mismatch of the *a*-axis (1.9%) compared with that of the *c*-axis (0.4%).

The theoretical critical thicknesses of *m*-plane GaN (and InGaN) heteroepitaxially grown on ZnO were calculated by employing the energy-balance model proposed by People and Bean²⁷. In this model, the critical thickness is equal to the film thickness at which the energy density of a misfit dislocation coincides with the strain energy density stored in the film. According to Huang *et al.*²⁸, the critical thickness h_{crit} of nonpolar wurtzite crystals can be expressed as follows:

$$h_{crit} = \frac{Gb^2}{16a\pi(1-\nu)U} \ln \frac{h_{crit}}{r_c}$$

$$U = \frac{S_{33}\epsilon_{xx}^2 + S_{11}\epsilon_{zz}^2 - 2S_{13}\epsilon_{xx}\epsilon_{zz}}{2(S_{11}S_{33} - S_{13}^2)}, \quad (1)$$

where G is the shear modulus, b the magnitude of the Burgers vector of the misfit dislocation, a the lattice constant of GaN (or InGaN), ν the Poisson's ratio of GaN, r_c the core radius of the misfit dislocation, U the strain energy per unit volume, S the elastic compliance coefficient, and ϵ the strain. Figure 4 depicts the dependence of the calculated critical thickness of *m*-plane $\text{In}_{1-x}\text{Ga}_x\text{N}/\text{ZnO}$ on In composition, x . The critical thickness of GaN ($x=0$) is calculated to be 45 nm, which well explained the experimental result shown in Fig. 3. The critical thickness reaches a maximum value of 360 nm at the In composition of 11.5%. The lattice mismatches between $\text{In}_{0.115}\text{Ga}_{0.885}\text{N}$ and ZnO are -0.65% (*a*-axis) and $+0.72\%$ (*c*-axis). For an $\text{In}_{0.115}\text{Ga}_{0.885}\text{N}$ film on ZnO, both the strains are balanced, resulting in the maximum critical thickness.

Finally, the structural properties of the 180-nm-thick *m*-plane $\text{In}_{0.12}\text{Ga}_{0.88}\text{N}$ grown on ZnO substrates were investigated. The film was grown at a temperature as low as 350 °C to prevent interfacial reactions between InGaN and ZnO. The RHEED and AFM analyses revealed that the *m*-plane InGaN grown on ZnO possesses atomically flat surfaces similar to those at of the *m*-plane GaN on ZnO. RSMs shown in Fig. 5 revealed that the growth of 180-nm-thick *m*-plane InGaN is coherent to the ZnO substrate, which supports the calculation shown in Fig. 4. The strains in $\text{In}_{0.12}\text{Ga}_{0.88}\text{N}$ on ZnO were found to be $+0.6\%$ (*a*-axis), -0.8% (*c*-axis), and 0.0% (*m*-axis: normal to the surface). In this film, the strains along the *a*- and *c*-axes cancelled each other out, and no strains were applied along the *m*-axis. Figure 6 compares the XRCs for *m*-plane GaN and $\text{In}_{0.12}\text{Ga}_{0.88}\text{N}$ grown at 350 °C. The thickness of both films was the same (180 nm). Since the 180-nm-thick GaN film released lattice strains by introducing structural defects, the FWHM of the rocking curves was as large as 288 arcsec. On the other hand, coherently

Figure 4. Calculated critical thickness of *m*-plane $\text{In}_{1-x}\text{Ga}_x\text{N}$ on ZnO. The value reaches a maximum at the In composition of 0.115.

Figure 5. X-ray RSMs of *m*-plane $\text{In}_{0.12}\text{Ga}_{0.88}\text{N}/\text{ZnO}$ around $2\bar{3}10$ (left) and $2\bar{2}02$ (right).

grown *m*-plane InGaN exhibits a sharp rocking curve with an FWHM of 79 arcsec. These results indicate that the control of the lattice constant of InGaN by tuning the In composition is quite effective for obtaining high-quality nitride films on ZnO substrates. Electrical and optical properties of the InGaN films grown on ZnO are helpful information to assess the quality of the films. We tried to perform Hall-effect measurements of the InGaN films, but a reliable data was not obtained because of the conductive n-type ZnO substrate. In addition, for photoluminescence (PL) measurements using 325 nm excitation laser, ZnO emitted a strong UV luminescence (~ 380 nm), making it difficult to detect the PL coming from the thin InGaN film. If the InGaN film is peeled off from the substrate and transferred onto another substrate, the measurements would be successful. Unfortunately, we do not have a technique that enables the transfer of the thin InGaN film. The electrical and optical characterization of the film will be a next work.

The structural properties of *m*-plane GaN and InGaN films grown on lattice-matched ZnO substrates by PSD were investigated. It was found that *m*-plane GaN and InGaN films can be coherently grown at $\sim 350^\circ\text{C}$. Theoretical calculations have indicated that the critical thickness of *m*-plane $\text{In}_{0.12}\text{Ga}_{0.88}\text{N}$ grown on ZnO is larger than that of *m*-plane GaN grown on ZnO, in agreement with the experimental results. The XRCs of *m*-plane $\text{In}_{0.12}\text{Ga}_{0.88}\text{N}$ on ZnO were narrower than those of *m*-plane GaN on ZnO. This work is the first comprehensive study of the strains of nonpolar InGaN films on ZnO and it demonstrated the feasibility of ZnO as a substrate for

Figure 6. XRCs of $1\bar{1}00$ diffraction for m -plane GaN and InGaN grown on ZnO substrates.

growing nonpolar InGaN films. These nonpolar materials could be useful for fabricating long-wavelength (yellow and red) light-emitting devices.

Methods

GaN and InGaN films were grown by PSD. High-purity Ga and In targets were separately sputtered in a Ar-N₂ mixture gas. Before growing the film, the m -plane ZnO substrates were annealed in a ceramic ZnO box at 1025 °C²⁹ so that the surface of substrate attained atomically flat steps. The growth temperature ranged from 300 °C to 540 °C. Structural characterization of the films was performed using RHEED, AFM, and XRD.

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Author Contributions

H.F. supervised the project. A.K. performed the experiments and theoretical calculations and wrote the manuscript. A.K., J.O., and H.F. interpreted the data and commented on the manuscript.

Additional Information

Competing Interests: The authors declare that they have no competing interests.

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