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Growth of group III nitride films by pulsed electron beam deposition

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We have grown group III nitride films on Al_2O_3 (0 0 0 1), 6H–SiC (0 0 0 1), and ZnO (0 0 0 $\bar{1}$) substrates by pulsed electron beam deposition (PED) for the first time and investigated their characteristics. We found that *c*-plane AlN and GaN grow epitaxially on these substrates. It has been revealed that the growth of GaN on atomically flat 6H–SiC substrates starts with the three-dimensional mode and eventually changes into the two-dimensional mode. The GaN films exhibited strong near-band-edge emission in their room temperature photoluminescence spectra. We also found that the use of PED allows us to reduce the epitaxial growth temperature for GaN down to 200 °C.

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1. Introduction

Group III nitrides such as InN, GaN, and AlN have attracted much attention in recent years because of their potential applications for optical and electronic devices [1,2]. Up to now, the epitaxial growth of group III nitride films has mainly been carried out on Al_2O_3 substrates in spite of their large lattice mismatch with respect to group III nitrides. Therefore, the epitaxial growth of group III nitrides has suffered from the formation of a high density of crystalline defects. Although there are many reports on the use of alternative substrates such as ZrB_2 and ZnO, which give small lattice mismatches with GaN [3–5], the crystalline quality of the films is still poor due to interfacial reactions between the films and the substrates at the high growth temperatures (above 700 °C) that are required by conventional growth techniques such as metalorganic chemical vapor deposition (MOCVD) or molecular beam epitaxy (MBE) [4,5].

To overcome this problem, the development of a low-temperature growth technique for group III nitrides is highly desirable. Pulsed laser deposition (PLD) is one of the most suitable techniques for low-temperature growth, since laser irradiation can provide high kinetic energies to the film precursors [6–9]. We have recently reported that the use of PLD has enabled us to grow group III nitrides epitaxially on ZnO and ZrB_2 substrates with high crystalline quality, even at room temperature [10–16]. Recently, a growth technique known as pulsed electron beam deposition (PED), which is similar to PLD and which utilizes a high-energy pulsed electron beam produced by a channel spark discharge instead of the pulsed laser beam, has been developed and successfully applied to the heteroepitaxial growth of oxide films [17,18]. It is quite natural to expect that PED could also enable us to grow group III nitride films at low temperatures, since the species ablated by the pulsed electron beam possess high kinetic energies, which can enhance atomic migration on the surface of the substrate. In addition, PED is reported as offering higher production throughput than PLD, and is therefore more suitable for use in mass production. In this paper, we report on the first epitaxial growth of AlN and GaN by PED on various substrates such as Al_2O_3 (0 0 0 1), 6H–SiC (0 0 0 1), and ZnO (0 0 0 $\bar{1}$).

2. Experimental

We have grown GaN and AlN films using ultra high vacuum (UHV) PED apparatus with a background pressure of 8.0×10^{-10} Torr. We utilized polycrystalline GaN (99.999% purity) synthesized by hydride vapor phase epitaxy technique and hot-pressed AlN (99.9% purity) as target materials for the growth. The pulsed electron beams which were produced by a PED source (Neocera, Inc.) were operated at a cathode voltage of 15 kV and a pulse repetition rate in the range from 5 to 15 Hz. During the film growth, N_2 gas was introduced at up to 20 mTorr to generate the channel spark electron beam. The ablated AlN or GaN species were ejected with high kinetic energies and deposited directly onto the substrates, which were mounted 5 cm away from the target. Typical growth rates were 0.5 and 0.2 μm/h for GaN and AlN, respectively.

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The structural properties of the samples, including their crystalline quality and orientation relationships, were characterized by reflection high-energy electron diffraction (RHEED), X-ray diffraction (XRD), and electron back-scattered diffraction (EBSD). The XRD and EBSD measurements were performed with a RIGAKU ATX-G diffractometer and an Oxford Instruments INCA Crystal EBSD system attached to a field-emission scanning electron microscope (JEOL JSM-6500F) operated at 20 kV, respectively. The surfaces of the samples were investigated by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) with a monochromatic AlKα (1486.7 eV) X-ray source. Room-temperature photoluminescence (PL) measurements were performed to investigate the optical properties of the GaN films.

3. Results and discussion

Figs. 1(a) and (b) show the RHEED patterns of GaN films grown at 750 °C on Al_2O_3 (0001) and 6H–SiC (0001), respectively. One can clearly see streaky patterns for both GaN films, which indicates that the GaN layers have grown epitaxially with smooth surfaces. The RHEED pattern for the GaN film on the Al_2O_3 shows a clear 3×3 surface reconstruction, while that on the 6H–SiC shows 1×1 streaks. This phenomenon can probably be attributed to a difference in the polarity of the GaN films. It is well known that the direct growth of GaN films on Al_2O_3 (0001) and 6H–SiC (0001) results in the formation of N-face and Ga-face GaN films, respectively [19–21]. These polarities are quite consistent with the reconstructions observed in the RHEED patterns. Fig. 1(c) shows $2\theta/\omega$ XRD curves for 0.3 μm-thick GaN films grown at 750 °C on Al_2O_3 and 6H–SiC substrates. The diffraction peaks for GaN 0 0 0 2 can be clearly observed, which indicates that *c*-plane GaN films grow on these substrates. Fig. 1(d) shows a typical pole figure for the GaN {10$\bar{1}$2} diffraction measured by EBSD. Six-fold rotational symmetry can be clearly seen in this figure, which is indicative of the absence of 30° rotational domains. XRD measurements have revealed that in-plane alignments between the GaN films and the substrates are [11$\bar{2}$0]GaN//[10$\bar{1}$0] Al_2O_3 and [11$\bar{2}$0]GaN//[11$\bar{2}$0]SiC. We have also grown AlN films on Al_2O_3 and 6H–SiC substrates and have confirmed the epitaxial growth of AlN films with similar film quality from RHEED observations and XRD measurements. As shown in Fig. 1(e), the RHEED pattern of the AlN films grown by PED exhibited clear diffraction spots indicating the epitaxial growth of *c*-plane AlN films. These results indicate that GaN and AlN films can be grown epitaxially by using the PED technique.

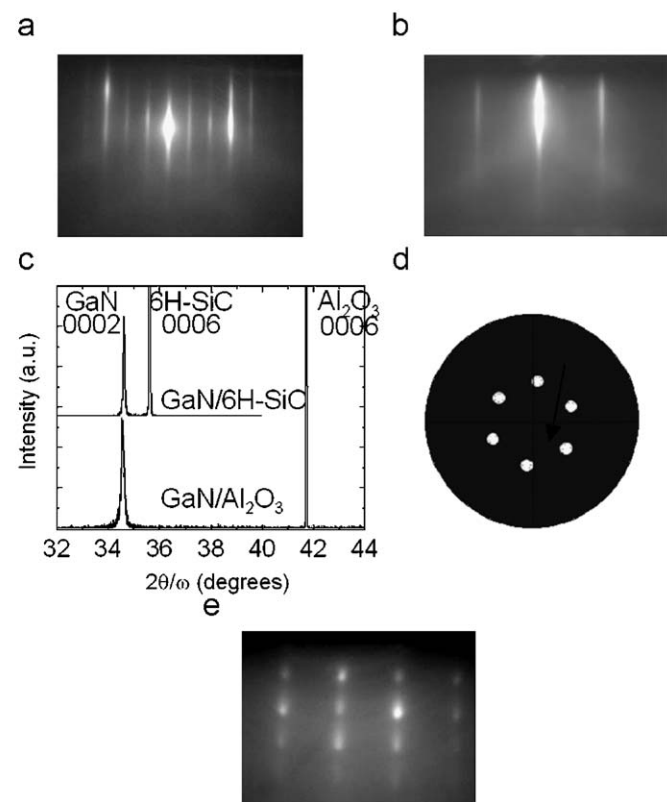

Fig. 1. RHEED patterns for GaN films grown on (a) Al_2O_3 substrates and (b) 6H–SiC substrate at 750 °C. (c) $2\theta/\omega$ XRD curves and (d) typical GaN {10$\bar{1}$2} pole figure measured by EBSD for a 0.3 μm-thick GaN film.

Next we investigated the time evolution of GaN film growth at 750 °C in PED. We have grown GaN films on atomically flat 6H–SiC (0001) substrates with a step height of 1.5 nm, which were prepared by high temperature annealing at 1600 °C in a gaseous mixture of He (95%) and H_2 (5%) [22]. The 6H–SiC substrates immediately before the growth of the GaN films showed a sharp, streaky RHEED pattern with a $(\sqrt{3}\times\sqrt{3})R30^\circ$ reconstruction, which is commonly seen for atomically flat surfaces prepared by this technique [23,24]. After the growth of a GaN layer with a nominal thickness of 3 nm, the RHEED pattern of the 6H–SiC substrate disappeared and diffraction spots from the GaN layer appeared, as shown in Fig. 2(a). An AFM image of this surface (shown in Fig. 2(b)) has revealed that small GaN nuclei exist on the surface and that the root-mean-square (rms) value of the surface roughness is 1.6 nm. This result indicates that the growth of GaN by PED on 6H–SiC substrates starts in a three-dimensional mode, probably due to the poor surface wetting between GaN and 6H–SiC [25]. At a film thickness of 10 nm, the diffraction spots in the RHEED pattern became sharper, as shown in Fig. 2(c), which corresponds to an improvement in the crystalline quality of the GaN. As shown in the AFM image in Fig. 2(d), the diameters of the GaN nuclei increase and the rms value of the surface roughness becomes as large as 4.7 nm at this stage. Figs. 2(e) and (f) show a RHEED pattern and a surface AFM image for a 50 nm-thick GaN film, respectively. One can clearly see a sharp, streaky RHEED pattern, which indicates that the GaN film grows with a smooth surface. At this thickness, the rms value of the surface roughness has decreased to 2.1 nm. This improvement in the surface smoothness can probably be attributed to the coalescence of the GaN islands as the film thickness increases. Further increasing the thickness of the GaN film leads to two-dimensional growth of the GaN film and the rms value of the surface roughness is reduced down to 0.5 nm for a 200 nm-thick GaN film, as shown in Fig. 2(h). The FWHM value of 0002 XRC of the 200 nm-thick GaN film on SiC substrates was 147 arcsec. From this FWHM value, we can estimate the density of screw dislocations in the GaN film to be approximately $5\times10^7\,cm^{-2}$ [26]. Fig. 3 shows how the RT PL spectrum of a 200 nm-thick GaN film grown on 6H–SiC exhibited clear near-band-edge emission around 360 nm, which indicates that GaN grown by PED is optically active. The GaN films grown on Al_2O_3 also showed similar PL spectra with clear near-band-edge emission.

We have also investigated the temperature dependence of the growth of GaN by PED, and have found that it is possible to reduce the growth temperatures for epitaxial GaN films on Al_2O_3 and 6H–SiC down to approximately 400 °C. In the case of ZnO substrates, however, we have found that GaN films can be grown epitaxially at as low as 200 °C. This difference is probably due to the small lattice mismatch of 1.9% at the GaN/ZnO interface compared to those of GaN/Al_2O_3 (16%) and GaN/6H–SiC (3.4%). Fig. 4(a) shows a typical RHEED pattern for a GaN film grown at 200 °C on a ZnO substrate. One can see a clear diffraction pattern from the epitaxial GaN film in this figure. We also confirmed that

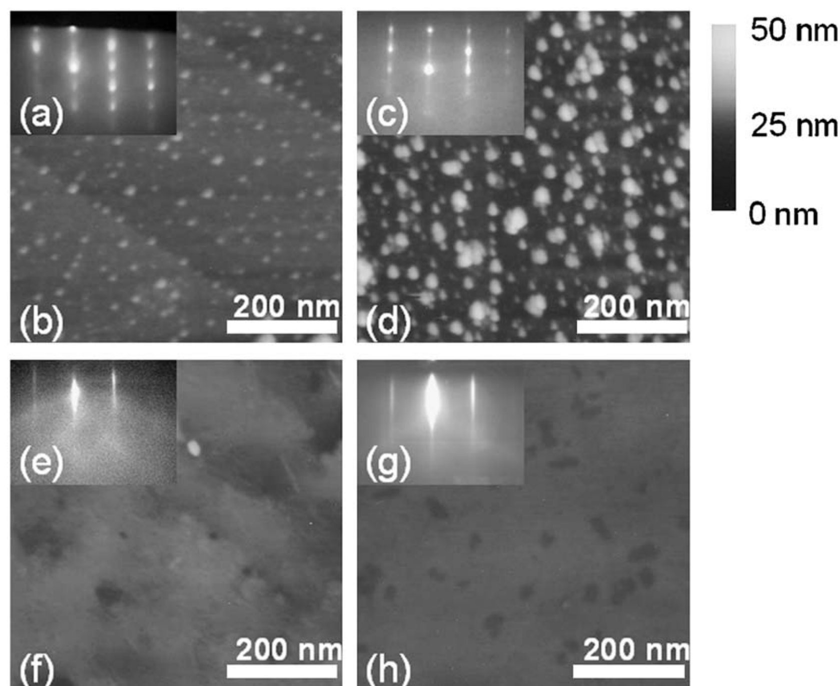

Fig. 2. Time evolution of RHEED patterns and AFM images for GaN films grown on an atomically flat 6H–SiC substrate: (a), (b) 3 nm; (c), (d) 10 nm; (e), (f) 50 nm; and (g), (h) 200 nm.

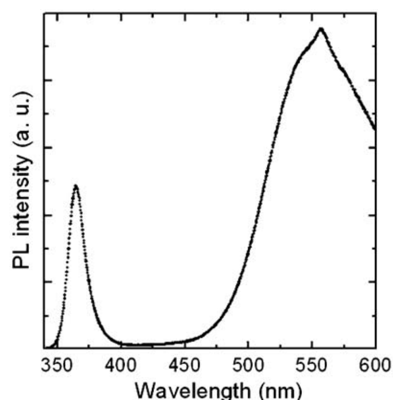

Fig. 3. RT PL spectrum for a 200 nm-thick GaN film on 6H–SiC.

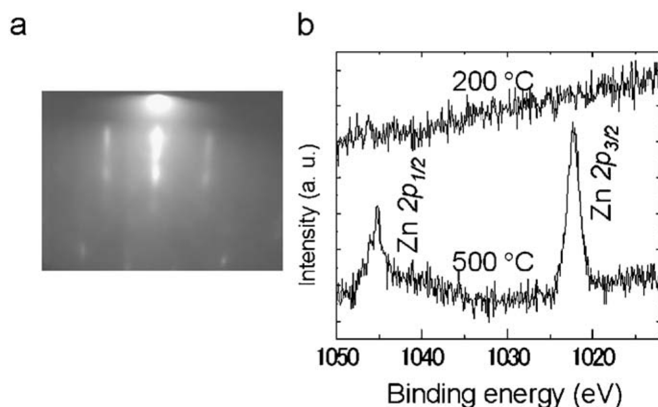

Fig. 4. (a) RHEED pattern for a GaN film grown at 200 °C on a ZnO substrate. (b) Zn2*p* XPS spectra for the GaN films grown at 500 and 200 °C.

the GaN grows epitaxially on ZnO at this temperature with an in-plane alignment of $[11\bar{2}0]$GaN//$[11\bar{2}0]$ZnO from the XRD measurements. This successful low-temperature growth can be explained by the fact that film precursors arrive at the substrate surface with high kinetic energies in PED. XPS measurements have revealed that Zn atoms exist on the surfaces of GaN films grown at high temperatures (above 500 °C) while the Zn concentrations on films grown at 200 °C are below the detection limit, as shown in Fig. 4(b). This result shows that the use of low-temperature growth enables us to suppress the intermixing reactions at the GaN/ZnO hetero-interface. These results indicate that PED is quite a promising technique for the fabrication of future optical and electronic devices that require abrupt heterointerfaces.

4. Conclusions

We have grown group III nitride films on Al_2O_3(0001), 6H–SiC(0001), and ZnO(000$\bar{1}$) by PED for the first time and investigated their characteristics. We have found that *c*-plane AlN and GaN films can be grown epitaxially on these substrates. It has been revealed that the growth mode of GaN on an atomically flat 6H–SiC substrate starts with the three-dimensional mode and eventually changes into the two-dimensional mode. The GaN films exhibited strong near-band-edge emission in room temperature photoluminescence spectrum. We have also found that the use of PED allows us to reduce the epitaxial growth temperature of GaN down to 200 °C. These results indicate that PED is quite a promising technique for fabrication of future optical and electronic devices that require abrupt heterointerfaces.

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