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Photoluminescence Investigation of Thick GaN Films Grown on Si Substrates by Hydride Vapor Phase Epitaxy

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The optical properties of thick GaN films grown by hydried vapor phase epitaxy (HVPE) using a low-temperature intermediate GaN buffer layer grown on a (111) Si substrate with a ZnO thin film were investigated by using photoluminescence (PL) measurement at 300 K and 77 K. The strong donor bound exciton (DBE) at 357 nm with a full width at half maximum (FWHM) of 15 meV was observed at 77 K. The value of 15 meV is extremely narrow for GaN grown on Si substrate by HVPE. An impurity-related peak was also observed at 367 nm. The origin of impurity was investigated using Auger spectroscopy.

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I. INTRODUCTION

Much research has been focused on suitable substrates for the growth of III-nitride epitaxial layers since rapid progress in the development of GaN-based materials has successfully led to the commercialization of blue/white light-emitting diodes (LEDs) and to the achievement of a blue laser diode. There have been many reports on substrates other than sapphire, such as SiC, GaAs, and Si, for the growth of GaN, AlN, InN and their compounds [1–3]. The growth of GaN on Si substrates has been one of the most interesting issues because of the advantages of large area, low cost, and good thermal and electrical conductivity [4,5]. However, the growth of high-quality epitaxial GaN on Si substrates has many difficulties because of the large lattice mismatch and difference in thermal expansion coefficients between GaN and Si [6].

There have been several reports on growth techniques, including metal organic vapor phase epitaxy (MOVPE) or molecular beam epitaxy (MBE), in order to find a successful growth process for GaN on Si substrates [7, 8]. The hydride vapor phase epitaxy (HVPE) growth method is necessary to obtain free-standing substrates even though it is difficult to grow high-quality GaN layers directly on the Si substrates [9]. One of the problems during the growth of GaN layers on Si substrates by HVPE is melt-back etching of the substrate caused by Ga droplets and chemical reactions between the substrate and the source gas (HCl) [10], so the growth of GaN layers need a buffer layer to protect the Si substrate from etching. In this reseach, we investigated the optical properties of thick GaN films grown on low-temperature intermediate GaN buffer layers on Si substrates with ZnO thin films by HVPE.

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II. EXPERIMENTS

Thick GaN crystals were grown by atmospheric pressure HVPE using an intermediate buffer GaN layer grown at low temperature (LT-GaN) on a (111) Si substrate with a ZnO thin film. The Si (111) substrates were cleaned using a 10 % HF solution for 10 s and dipped into a 34 % KOH solution for 1 min at 40 °C to remove the natural oxide layer on the Si surface. A ZnO layer, 200 nm in thickness, was deposited by sputtering. The ZnO surface was slightly etched by using a buffered oxide etch (BOE) solution for 1 s before the GaN growth. The LT-GaN layer was grown on the ZnO/Si substrate in a horizontal HVPE reactor. Metallic Ga, ammonia (NH_3), and hydrogen chloride (HCl) were used as source materials. An intermediate LT-GaN buffer layer was grown at 560 °C for 3 min. The gas flow rates of HCl and NH_3 were maintained at 1 sccm and 300 sccm, respectively, during the growth of intermediate LT-GaN buffer layer. Immediately after the formation of the intermediate LT-GaN buffer layer, a thick GaN layer was grown at 1050

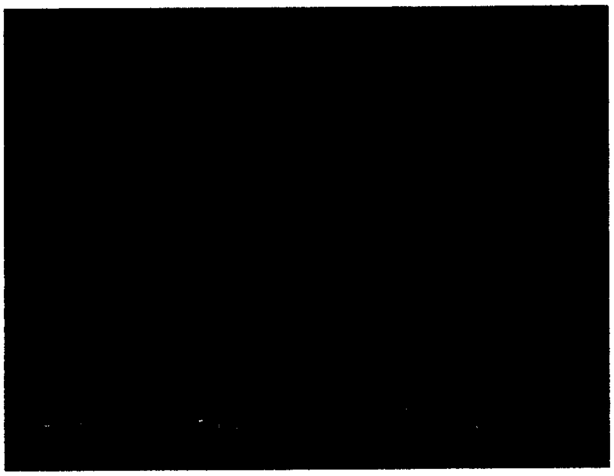

Fig. 1. Typical surface SEM image of a thick GaN film grown on a Si substrate by HVPE.

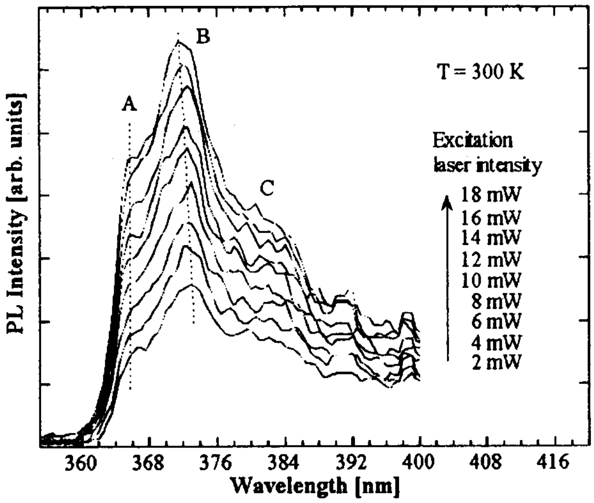

Fig. 2. PL spectra of thick GaN films for various excitation intensities at 300 K.

°C for 3 h. For the growth of the high-temperature GaN (HT-GaN) layer, the gas flow rates of HCl and NH_3 were maintained at 20 sccm and 500 sccm, respectively. The temperature of the source zone was 850 °C. The thickness of the HT-GaN layer was about 150 μm. A typical surface image of the GaN layer grown on a Si substrate taken using a scanning electron microscope (SEM) is shown in Fig. 1. The HT-GaN grown on the LT-GaN/ZnO/Si showed a mirror-like surface.

III. PL INVESTIGATIONS OF THE HT-GaN ON A Si SUBSTRATE

The photoluminescence (PL) spectra at 300 K were measured for various excitation laser intensities. The PL measurements on the GaN layers were carried out using a 100-mW He-Cd laser (325 nm) as the excitation source. The excitation intensity was varied from 2 mW to 18 mW using a neutral linear attenuator. The spot size of the laser beam on the sample was about 100 μm. The laser beam was chopped at 86 Hz. Figure 2 shows the PL spectra of the GaN layer for various excitation laser intensities at room temperature. At low excitation intensities, there are two peaks, one at 365 nm and the other at 372 nm (labeled A and B), which correspond to the band-edge emission and impurity-related emission, respectively. The weak subsidiary peak at about 385 nm (labeled C) might be related to donor-acceptor pair recombination. To understand the origin of these peaks, we investigated PL at 77 K.

Figure 3 shows a typical PL spectrum of the GaN film at 77 K. There is an intensive edge peak at 357 nm (3.47 eV, labeled A), which can be attributed to an exciton bound to a neutral donor (DBE). The FWHM of the peak is 15 meV. This value of 15 meV is extremely narrow for a GaN film grown on a Si substrate by HVPE. A second peak (labeled B) appears at 367 nm (3.39 eV) in

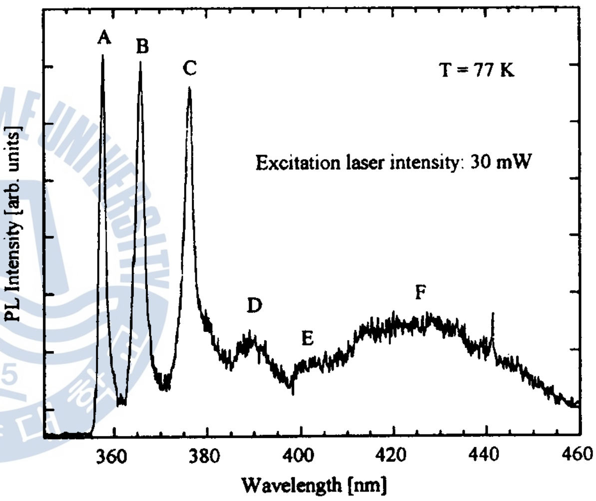

Fig. 3. Typical PL spectrum of a thick GaN at 77 K.

the PL spectrum, about 80 meV below the DBE peak, and its FWHM is 20 meV. To identify the presence of impurities in the GaN layer, we carried out Auger spectroscopy (AES) measurement with a 10-keV electron beam, and the results are shown in Fig. 4. With the results of AES measurement, we were able to speculate that the second peak might be related to oxygen from the source gases, the quartz ware, or the ZnO film [11,12]. The third peak (labeled C) at 376 nm (3.29 eV) having a FWHM of 25 meV corresponds to donor-acceptor pair recombination [13,14]. The fourth peak (labeled D) and the fifth peak (labeled E) are located at 388 nm (3.19 eV) and 399 nm (3.10 eV), respectively. We found that peak D and peak E were 98 meV and 93 meV below peak C, respectively. These peaks might be optical phonon replicas of peak C because the separation of the peak energies between peak C and peak D or between peak D and peak

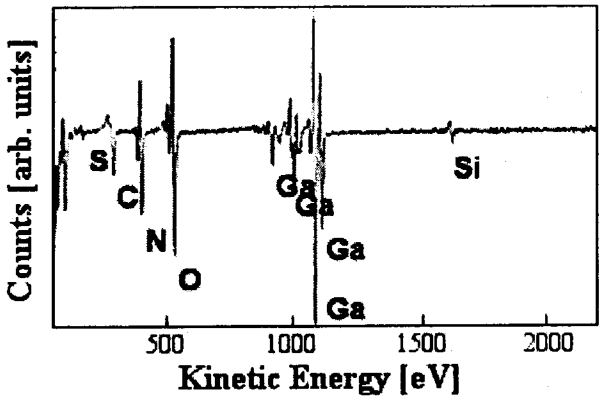

Fig. 4. AES spectrum of a thick GaN film grown on a Si substrate by HVPE.

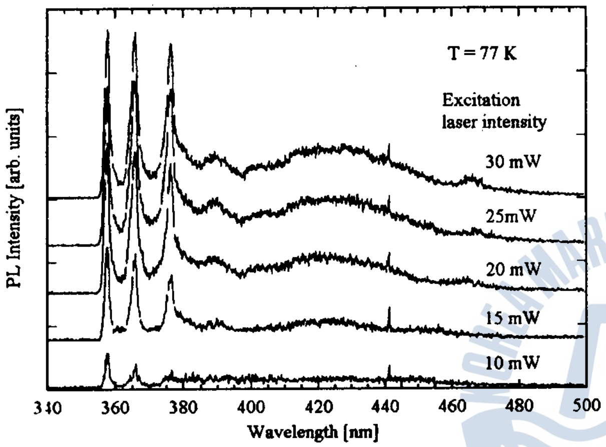

Fig. 5. PL spectra of GaN layers for various excitation intensities at 77 K.

E is similar to the optical phonon energy of 92 meV in GaN [15,16]. The origin of the broad peak (labeled F) at 425 nm (2.92 eV) has not been identified yet, but the peak might be due to a silicon-related impurity caused by the use of a Si substrate. However, we did not find the yellow band emission.

Figure 5 shows PL spectra for various excitation laser intensities at 77 K. With increasing excitation intensity, the PL peak energy of the third peak is slightly blue shifted, as shown in Fig. 6. Thus, the third peak can clearly be attributed to the recombination of donor-acceptor pairs. At a low excitation laser intensity of 5 mW, the DAP band peak is not obvious. In this case, the PL spectra represent the optical properties of the surface because the penetration depth of the excitation laser intensity is about 1 μm [17]. Thus, the DAP band emission might depend on the excitation intensity. The details of the dependence of the DAP band emission on the excitation laser intensity will be studied.

IV. CONCLUSIONS

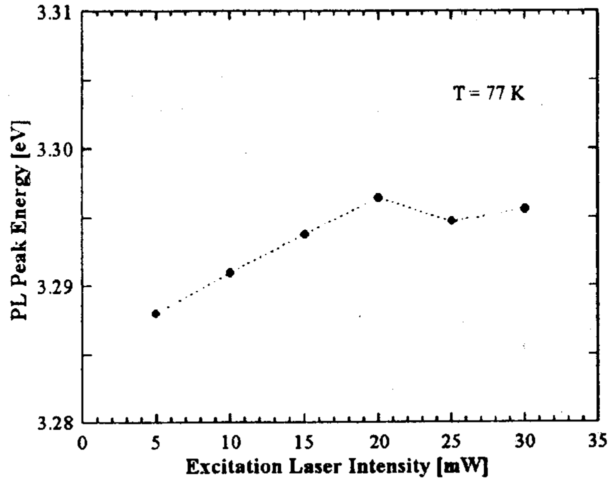

Fig. 6. PL peak energy of the DAP band emission for various excitation intensities at 77 K.

Thick GaN films grown by HVPE on (111) Si substrates with a ZnO thin film by using a low-temperature GaN buffer was investigated by using PL measurements at 300 K and 77 K. The PL spectra showed strong donor bound exciton (DBE) and impurity-related peaks. The full width at half maximum (FWHM) of the band edge emission was 15 meV, which is extremely narrow for a GaN layer grown on a Si substrate. The results of Auger spectroscopy (AES) and PL measurements showed that the impurity peaks were related to oxygen and other residual impurities caused by the source gases, the quartz ware, and the ZnO film.

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