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Annealing Effects on GaN/ZnO/Si Structures Prepared by RF Magnetron Sputtering

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Abstract. This study shows the effect of thermal annealing on GaN/ZnO/Si structures prepared by rf magnetron sputtering. Thermal annealing tended to induce a different crystalline orientation from the c-axis orientation observed with as-deposited films. The sample annealed at 900 ^{o}C under excitation at 325 nm showed two emission bands centered at approximately 380 and 550 nm.

Introduction

Gallium nitride (GaN) is considered a promising material on account of its potential applications in optoelectronic devices [1]. Although the major part of semiconductor devices has now been realized, one of the challenging subjects of GaN growth is the lack of a suitably adapted substrate. Normally, sapphire has been used as a substrate for GaN epitaxy. However, there is a great lattice mismatch between GaN and sapphire. One of the methods used to obtain high quality GaN films is the use of a buffer layer. Zinc oxide (ZnO) layer has some potential advantages for this application, because it is structurally the closest to GaN, having a lattice mismatch of only 1.8% with GaN [2]. However, ZnO single crystal wafers are very expensive.

ZnO-coated silicon (Si) substrates might be a candidate because large size Si wafers can be used at a low cost, which may pave the way for the integration of devices containing GaN films grown on ZnO/Si substrates with the mature Si integrated circuit technology. Accordingly, GaN films have been grown on ZnO/Si using various methods such as low-pressure metal organic chemical vapor deposition (CVD) [3], plasma enhanced CVD [4], and laser ablation of a liquid Ga target [5]. In addition, a successful growth of GaN film on Si substrate with a ZnO buffer using the sputtering method has recently been reported [6]. Since the GaN film system has potential applications in optoelectronic devices that undergo VLSI circuit fabrication, it is very important to examine the effects of thermal annealing not only for scientific interest but also for practical applications. Therefore, the aim of this study was to investigate the effect of thermal annealing on the structural and luminescence properties of GaN/ZnO/Si structures.

Experiments

Sputtering was carried out at room temperature using a conventional rf magnetron sputtering system [7]. The sputtering chamber was evacuated to a pressure of 1.0×10^{-5} Torr with a turbomolecular pump prior to the introduction of the sputtering gas. Ar was used as an ambient gas. A Si wafer with an (001) orientation was selected because it is commercially available at a lower cost and has many advantages in device operations, with respect to the transport properties of charge carriers. The wafers were cleaned in acetone for 10 min, followed by HF (20:1) for 10 sec. The wafers were then rinsed in deionized water for 1 min, and loaded into the reactor. The target (ZnO or GaN)-substrate distance was maintained at approximately 80 mm.

The ZnO films as a buffer layer were grown on Si(001) substrates at an rf power of 100 W with a frequency of 13.56 MHz. The GaN films were then grown at a rf power of 50 W. After sputtering, the samples were annealed under flowing nitrogen at temperatures ranging from 700 to 900 ^{o}C for 1 h.

The thicknesses of the GaN and ZnO layers used in this study were measured to be approximately 270 and 300 nm, respectively.

The crystallographic orientation was examined by X-ray diffraction (XRD, DMAX-2500-Rigaku) in θ-2θ scan mode and by grazing incident angle (0.5°) XRD (X'pert MPD-Philips), using CuKα_1 radiation (λ = 0.154056 nm). The structural morphology of the films was observed by scanning electron microscopy (SEM, Hitachi S-4200). The photoluminescence (PL) was measured at room temperature using a He-Cd (325 nm, 55 mW) laser as the excitation light source.

Results and Discussion

Figure 1 shows typical top-view SEM images of the as-deposited, 700 ^{o}C-annealed, and 900 ^{o}C-annealed GaN/ZnO/Si structures, revealing a similar grainy morphology. Although thermal annealing slightly increases the apparent grain size, the structural changes induced by thermal annealing cannot be clearly shown by SEM analysis.

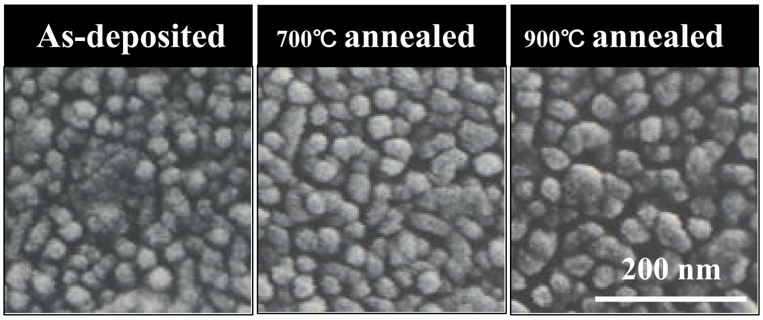

Fig. 1 Plan-view SEM images of the as-deposited, 700 ^{o}C-annealed, and 900 ^{o}C-annealed GaN/ZnO/Si structures.

Figure 2 shows the θ-2θ XRD patterns, with the Si(002) peak eliminated for clarity. The XRD patterns show the main peak to be approximately 2θ=34.7° corresponding to the (002) orientation. However, there is a small contribution from the (101) orientation. There were no large differences between the as-deposited GaN/ZnO/Si structure (Fig. 2b) and the ZnO/Si structure (Fig. 2a), indicating that the deposition of the GaN layer does not significantly alter the structural quality. Although the relative intensity of the (002) diffraction peak is strong compared with the neighboring (101) peak and the other almost indistinguishable peaks in the as-deposited sample, the relative intensity of the (101) diffraction peak compared with the (002) peak becomes stronger with thermal annealing.

The ZnO (002) peak is usually overlaid with the GaN(002) peak due to close lattice mismatch [5,8,9]. Therefore, grazing incident angle XRD was used to investigate the structural properties of the GaN layer remove the effects of the underlying ZnO/Si . In the grazing-angle XRD measurements, the angle of the incident beam to the substrate surface was approximately 0.5°, and the detector was rotated to scan the samples. Therefore, it is believed that the peaks originate mainly from the GaN layer, which is close to the surface. The relative intensity of the (002) diffraction peaks compared with that of the neighboring (101) and (100) peaks decreases with the thermal annealing and increasing annealing temperature from 700 to 900 ^{o}C. A comparison of Fig. 2 with Fig. 3 indicates that the induction of the (101) and (100) orientation in GaN/ZnO/Si structures as a result of thermal annealing is related to the structural changes in GaN layers.

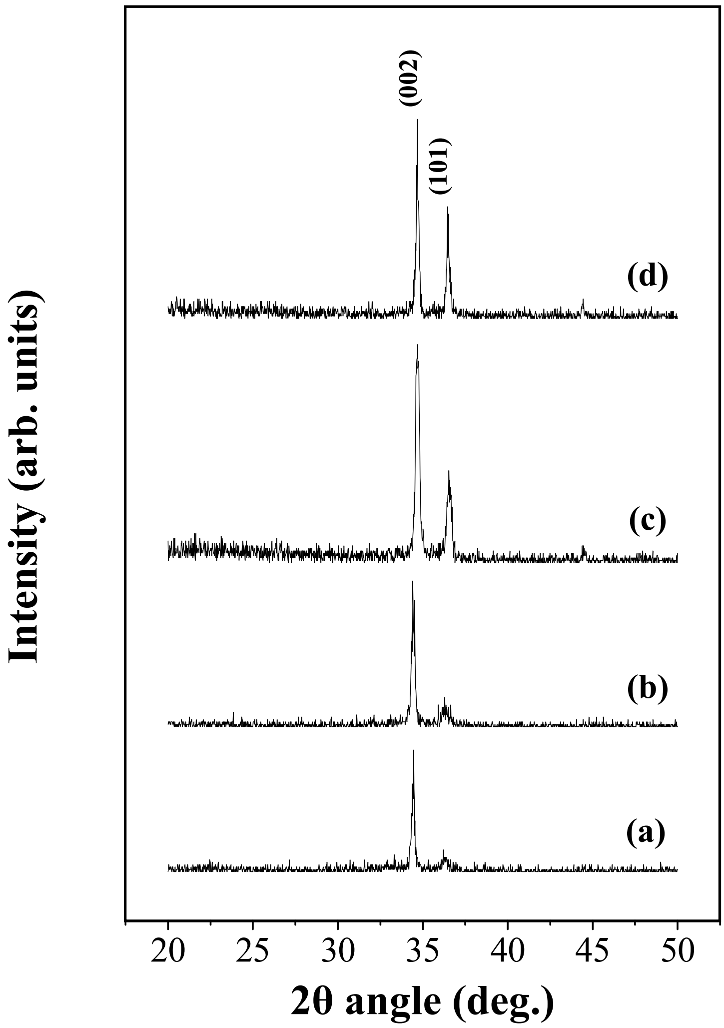

Fig. 2 XRD patterns of (a) ZnO/Si structure prior to the GaN deposition, (b) as-deposited, (c) 700 ^{o}C-annealed, and (d) 900 ^{o}C-annealed GaN/ZnO/Si structures.

The full width at half-maximum (FWHM) of XRD diffraction peaks from Fig. 3 were calculated using the Scherrer formula in order to investigate the structural changes in the layers near the top surface. Figure 4 shows FWHM of the (002), (100), and (101) diffraction peaks of the as-deposited, 700 ^{o}C-annealed, and 900 ^{o}C-annealed GaN/ZnO/Si structures. Although the FWHM of the (002) diffraction peak is almost the same regardless of whether annealing had been performed and the thermal annealing temperature, the FWHMs of the (100) and (101) diffraction peaks decreased with thermal annealing and increasing annealing temperature in the range 700-900 ^{o}C. Since the FWHM of the diffraction peak is inversely proportional to the grain size of the film, XRD analysis indicates that while the crystallite size of the (002)-oriented grain is invariant, the crystallite sizes of the (100)- and (101)-oriented grains increase slightly with thermal annealing and with increasing annealing temperature. The slight increase in crystallite size by thermal annealing agrees with the SEM observations (Fig. 1).

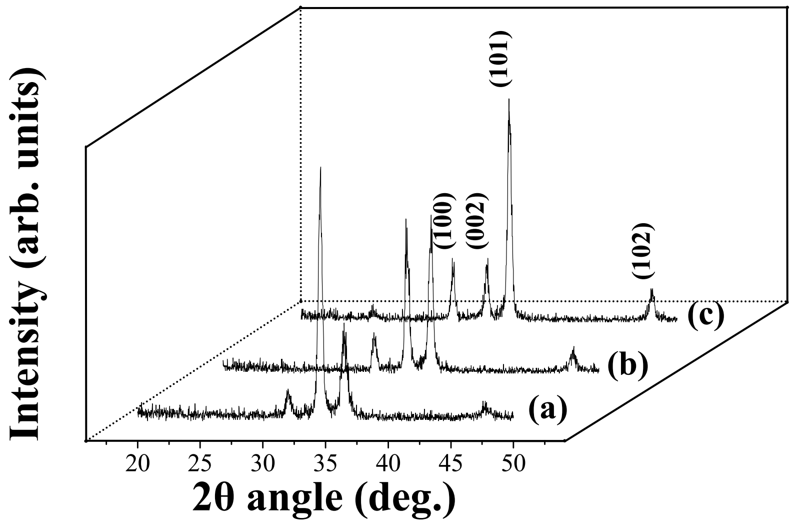

Fig. 3 Grazing angle (0.5°) XRD patterns of (a) as-deposited, (b) 700 °C-annealed, and (c) 900 °C-annealed GaN/ZnO/Si structures.

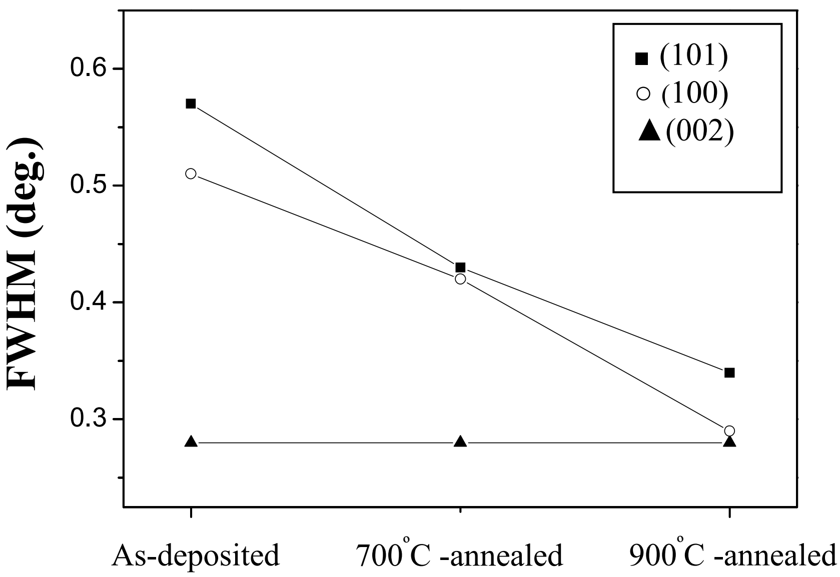

Fig. 4 Full width at half-maximum (FWHM) of the (002), (100), and (101) diffraction peaks of the as-deposited, 700 °C-annealed, and 900 °C-annealed GaN/ZnO/Si structures.

The PL of these GaN/ZnO/Si structures was measured at room temperature. While a weak PL intensity was obtained from the as-deposited and 700 °C-annealed sample (curves a and b in Fig. 5), the 900 °C-annealed samples showed a relatively strong (at least one order of magnitude higher) luminescence (curve c in Fig. 5). A broad deep level emission band centered at around 550 nm (2.26 eV) may originate from defects in the GaN films such as vacancies [10] or defects in the ZnO films such as oxygen vacancies [11,12]. Therefore, annealing at 900 °C appears to intensify the deep level emission by generation of vacancies in ZnO and GaN films.

The strong band-edge emission peaking at approximately 380 nm (3.27 eV) may be from GaN and ZnO. The band-edge emission in GaN is known to originate from donor-acceptor pair recombination (D^0A^0) and the associated phonon replicas [10,13]. The increase in intensity of the D^0A^0 luminescence was attributed to the increase in the number of vacancy related donors [10]. The band-edge peak in ZnO is related to the radiative recombination of excitons [14]. Therefore, it is expected that the enhancement of the band-edge peak intensity by thermal annealing at 900 °C is due to increased concentration of vacancies in GaN and due to reduction in the number of non-radiative recombination centers in ZnO. However, the mechanism by which thermal annealing affects the non-radiative recombination centers in ZnO films is unclear and requires further investigation. Interesting result is that this 900 °C-annealed GaN layer is less completely oriented than the as-deposited one. Further study on the reason for the generation of a different crystalline orientation and the correlation between the crystal orientation and the optical properties is needed.

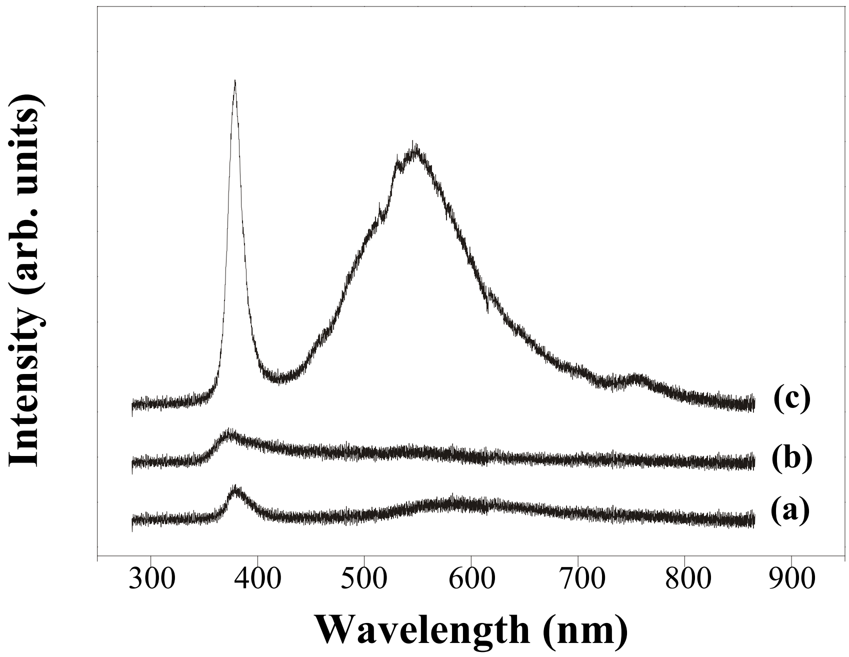

Fig. 5 Room temperature PL spectra of (a) as-deposited, (b) 700 °C-annealed, and (c) 900 °C-annealed GaN/ZnO/Si structures.

Summary

This study investigated the effects of thermal annealing on the structural and optical characteristics of GaN/ZnO/Si structures. SEM indicated that the top-view grain size increases slightly as a result of thermal annealing. XRD revealed that the relative intensity of the (002) peak compared with differently oriented peaks decreases as a result of thermal annealing. The PL spectra of the structure showed two major emissions centered at around 380 and 550 nm with thermal annealing at 900 °C.

We have discussed the possible emission mechanism.

Acknowledgements

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