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GaN-Based Light-Emitting Diodes with Graphene Buffers for Their Application to Large-Area Flexible Devices

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SUMMARY Crystalline GaN films can be grown even on amorphous substrates with the use of graphene buffer layers by pulsed sputtering deposition (PSD). The graphene buffer layers allowed us to grow highly *c*-axis-oriented GaN films at low substrate temperatures. Full-color GaN-based LEDs can be fabricated on the GaN/graphene structures and they are operated successfully. This indicates that the present technique is promising for future large-area light-emitting displays on amorphous substrates.

key words: *GaN, graphene, glass, pulsed sputtering deposition*

1. Introduction

Group III nitride semiconductors are regarded as promising materials for optoelectronic devices, and nowadays, high-efficiency GaN-based light emitting diodes (LEDs) are commercially available [1], [2]. However, applications of GaN-based LEDs are limited to small devices because their fabrication process is associated with expensive epitaxial growth by metalorganic vapor phase epitaxy (MOVPE) on single crystalline substrates, such as sapphire. To address this issue and expand the application field of GaN-based devices, development of a low-cost epitaxial growth process, such as sputtering on large-area substrates, is highly desired.

We have recently developed a new thin-film growth technique called pulsed sputtering deposition (PSD) and found that it allows us to obtain device-quality GaN films [3]–[10]. PSD has already attracted considerable attention from industry engineers because its productivity is considerably higher than that of conventional MOVPE. In PSD, surface migration of the film precursors is enhanced. Therefore, the temperature for epitaxial growth is dramatically reduced [6], [7]. It should be noted that the conventional MOVPE growth of GaN films requires high temperatures (approximately 11000 °C), while we have reported the successful fabrication of GaN-based LEDs by PSD at a maximum process temperature of 480 °C [7]. The reduced growth temperature enables us to utilize various large-area and low-cost substrates, such as glass, which has so far not been used for GaN growth owing to its thermal and chemical vulnerability. Glass is inexpensive and state-of-the-art glass technology can offer roll-to-roll processing of flexible glass sheets [11]. Hence, fabrication of low-cost flexible GaN devices on glass may be possible with PSD.

To achieve the crystal growth of GaN films on glass, a highly oriented crystalline buffer layer should be introduced between GaN and glass as glass is an amorphous material. Graphene is one of the most promising materials for such an application owing to its highly oriented structure and the availability of large-area sheets [12]–[18]. Additionally, the layered structure of graphene enables an easy transfer onto a supporting substrate [19], [20].

In this paper, we review recent progress in PSD process for the growth of GaN films on amorphous SiO_2 and fabrication of LEDs.

2. Growth and Characterization of GaN Films

The graphene layers were prepared on Ni sheets by chemical vapor deposition, followed by transfer onto fused silica or thermally oxidized SiO_2 on Si substrates. The substrates were cleaned at 600 °C for 30 min in vacuum. Further, GaN, InGaN, and AlN films were grown by PSD. The detailed growth conditions are described elsewhere [3], [4]. The grown films were characterized by X-ray diffraction (XRD) using a Bruker D8 diffractometer and by electron backscatter diffraction (EBSD) using an INCA Crystal EBSD system (Oxford Instruments). The lattice polarities of the GaN films were studied via wet chemical etching in a 1.8-M KOH solution. The optical properties of the GaN films were characterized by photoluminescence (PL) measurements using a He–Cd laser (λ = 325 nm) as an excitation source. Figure 1 (a) shows a scanning electron microscopy (SEM) image of the GaN film directly grown on SiO_2. The surface was rough and comprised small grains having sizes of several hundred nanometers. In contrast, the GaN film with the graphene buffer layer has a smooth surface, as shown in Fig. 1 (b). The crystal orientations of the GaN films were investigated by EBSD measurements. Figure 2 shows the EBSD pole figures of $\{0002\}_{GaN}$ and $\{10\bar{1}2\}_{GaN}$ for an 20 μm × 20 μm area for the GaN films (a) without and (b) with a graphene buffer layer. The GaN film without the graphene buffer layer exhibited broad spots and broad ring-shaped patterns in the {0001} and $\{10\bar{1}2\}$ pole figures, which are attributed to the formation of polycrystalline films. In contrast, the {0001} spot for the GaN film with the graphene buffer layer was

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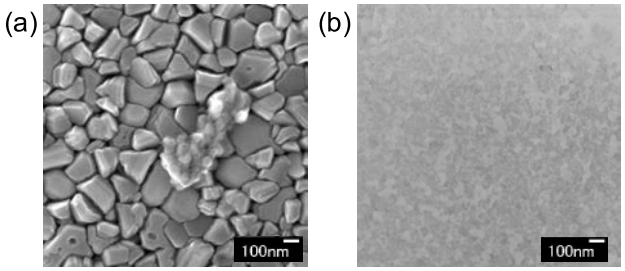

Fig. 1 Scanning electron microscopy (SEM) images of GaN films grown on amorphous SiO_2 substrates (a) without and (b) with a graphene buffer layer [3].

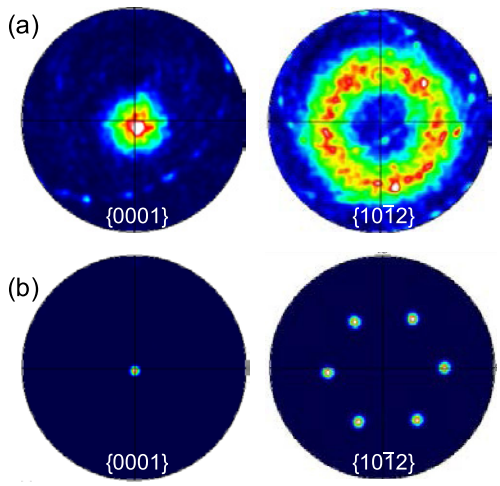

Fig. 2 {0001} and {10$\bar{1}$2} electron backscatter diffraction pole figures for GaN films on amorphous SiO_2 (a) without and (b) with a graphene buffer layer [3].

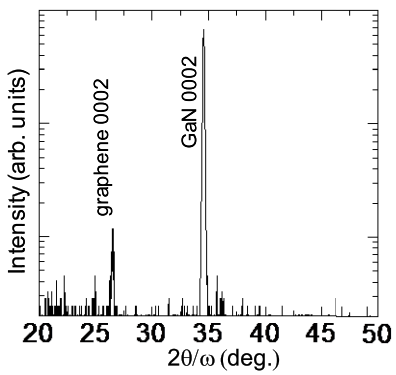

Fig. 3 Typical X-ray diffraction (XRD) plot for GaN films on graphene/SiO_2 [4].

sharp, and a clear six-fold rotational symmetry appeared in the {10$\bar{1}$2} pole figure.

This indicates that the crystalline quality of the GaN film was drastically improved by the introduction of the graphene buffer layer, which can probably be attributed to sufficient epitaxial growth of GaN on the highly oriented graphene [21]. Figure 3 shows an XRD $2\theta/\omega$ plot of the GaN film with a graphene buffer layer on fused silica. The

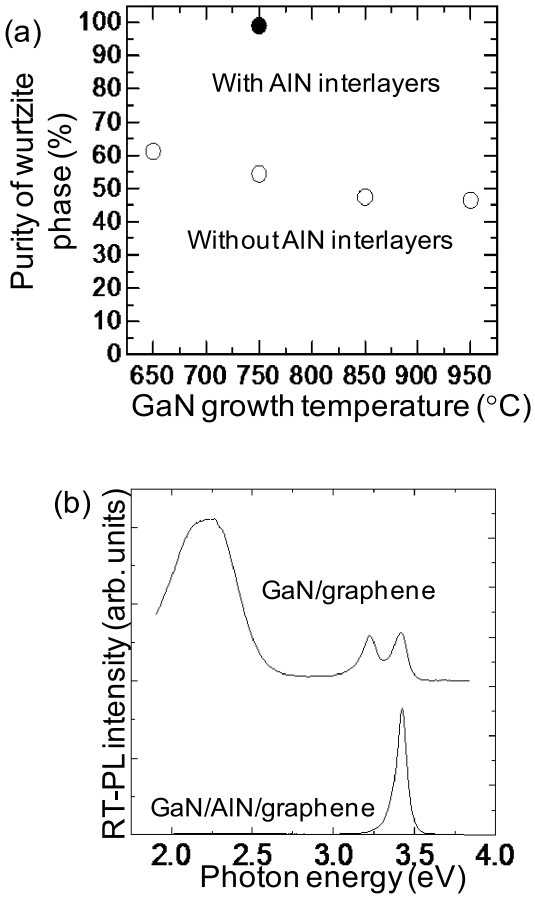

Fig. 4 (a) Proportion of Wurtzite phase in GaN films as a function of growth temperature and (b) photoluminescence spectra of GaN films grown on graphene with and without AlN interlayers [4].

diffraction peaks at around 26.5° and 34.5° originate from the diffraction from graphene {0002} and GaN {0002}, respectively.

The phase purity of GaN films on graphene was investigated using EBSD phase mapping. The results show that both wurtzite and zincblende phases exist in the GaN film grown on graphene at 750 °C; however, the proportion of the wurtzite phase was as low as 55%. In Fig. 4 (a), the wurtzite phase proportion in GaN films is plotted as a function of growth temperature. Although the proportion of the wurtzite phase increased by lowering the growth temperature from 950 °C to 650 °C, it remained below 65% at 650 °C. X-ray photoelectron spectroscopy measurements detected carbon-related signals from the GaN films, which indicate the formation of an interfacial layer between GaN and graphene. Since the inclusion of the zincblende phase in the films apparently caused by interfacial reactions [22], it should be possible to suppress it by inserting a reaction blocking layer between GaN and graphene. In this study, we introduced a 50-nm-thick AlN interlayer as a reaction-blocking layer before GaN growth on graphene. EBSD phase mapping revealed that with the interlayer, the zincblende phase in the films was negligible and the proportion of wurtzite phase

was nearly 100%.

The optical properties of the GaN films were investigated via PL measurements at room temperature (RT). The GaN films grown without AlN interlayers exhibited three PL peaks at approximately 3.4, 3.2, and 2.2 eV as shown in Fig. 4 (b). The luminescence feature at 3.4 eV corresponds to the near-band-edge emission from the wurtzite GaN phase. The peak at 3.2 eV can be assigned to emission of zincblende GaN [23], [24]. The broad yellow luminescence peak at 2.2 eV is probably related to Ga vacancies or carbon impurity contamination [25]. Conversely, GaN films with AlN interlayers showed a strong near-band-edge emission from the wurtzite phase with negligible emissions from the zincblende phase or deep levels. The X-ray rocking curves of the GaN {0002} diffractions revealed that the AlN interlayers reduced the XRD full width at half maximum (FWHM) values from 144 to 37 arcmin. These structural and optical characterization results indicate that interfacial reactions can be suppressed and the crystalline quality of GaN on graphene can be improved by introducing AlN interlayers between the GaN and graphene.

Since the properties of *c*-plane GaN strongly depend on crystal polarity, understanding and controlling the polarity of the GaN films on graphene is an important issue. The lattice polarity of these films was investigated by wet chemical etching in a 1.8-M KOH solution [26]. The SEM image of the chemically etched surface of the GaN film grown on graphene with an AlN interlayer is shown in Fig. 5 (a). Etching caused roughening of the GaN surface, indicating that the GaN film was N-polar. For the fabrication of GaN-based optoelectronic devices, such as LEDs and transistors, developing a technique that inverts the polarity of the GaN films from N- to Ga-polarity is required. Recently, it was reported that Ga-polar GaN grows on N-polar GaN substrates with the introduction of surface-oxidized AlN thin films [27]. Mohn *et al.* have shown that formation of a rhombohedral AlON layer may be able to convert an N-polar surface to a metal-polar one [28]. In the present case of GaN on AlN/graphene, surface-oxidized AlN layers were formed before GaN growth by thermal oxidization in air at 200 °C. As revealed by the SEM observations shown in Fig. 5 (b), the surface morphology of GaN films grown on surface-oxidized AlN interlayers remained smooth after wet chemical etching. Such chemical robustness to KOH etching is a characteristic of Ga-polar GaN; therefore, we concluded that the GaN polarity had changed from N- to Ga-polarity. The selection of the polarity of the GaN films on graphene allows us to design high-efficiency GaN-based optoelectronic devices.

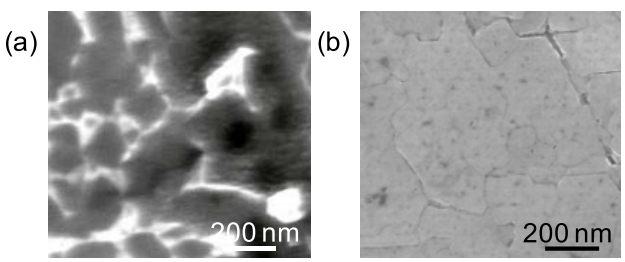

Fig. 5 SEM images of GaN films on graphene after wet etching: (a) without and (b) with surface oxidation of AlN interlayers [4].

3. Fabrication of LEDs on Amorphous Substrates

To demonstrate the feasibility of fabricating GaN-based LEDs on glass substrates, we manufactured LED structures on the AlN/graphene/amorphous SiO_2 structures (Fig. 6 (a)). For the LEDs, 1-μm-thick n-type GaN layers were grown on the AlN interlayers, followed by the formation of five periods of [InGaN/GaN] multiple quantum wells (MQWs) and Mg-doped p-type GaN layers. The thicknesses of the MQW periodic structure and p-type GaN layer were 70 nm and 600 nm, respectively. Figure 6 (b) shows the XRD curves for the sample around the GaN {0002} diffraction peak. The clear satellite peaks from the MQW structure indicates the smoothness and abruptness of the heterointerfaces in the MQWs. From the curve fitting of the experi-

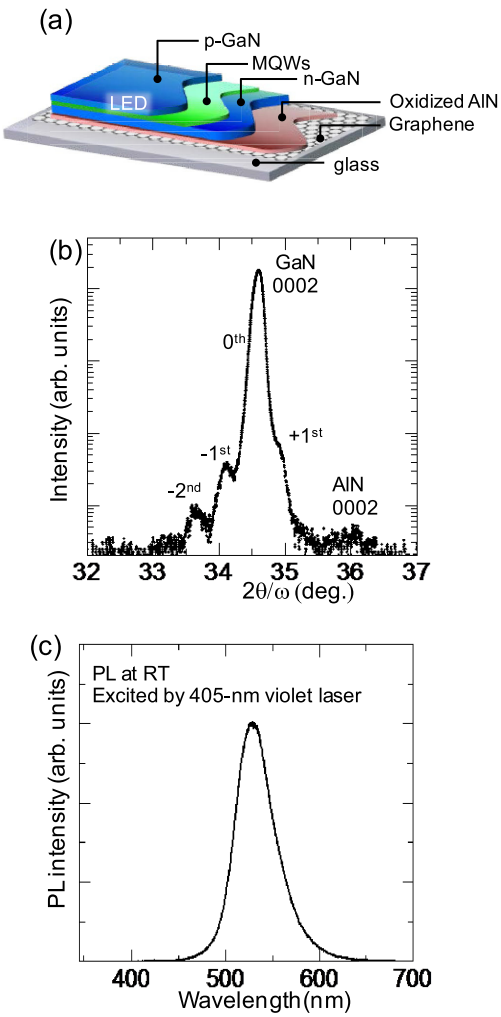

Fig. 6 (a) Schematic illustration of the LED structure on glass. (b) XRD $2\theta/\omega$ curve and (b) RT-PL spectrum for the LED structure fabricated on amorphous SiO_2 with graphene buffer layer [3].

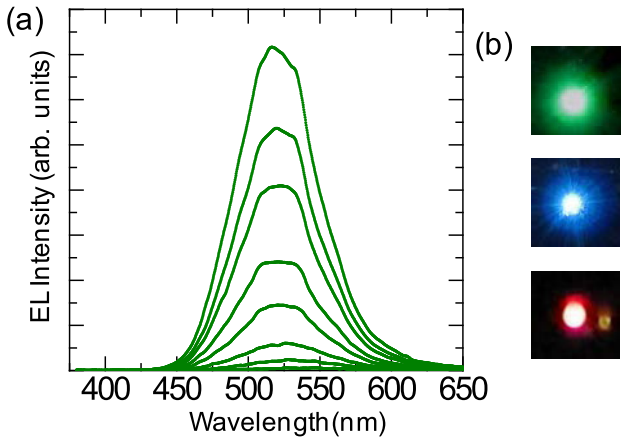

Fig. 7 Electroluminescence spectra for green LED structure fabricated on amorphous SiO_2 with a graphene buffer layer for injection currents between 2.1 and 10.8 mA. (b) Photographs taken during operation of the LEDs with various proportions of In in the InGaN MQWs [3].

mental XRD curves to the theoretical curves, it was revealed that the thicknesses of InGaN wells and GaN barriers were 3.1 nm and 8.6 nm, respectively. Figure 6 (c) shows a typical PL spectrum measured at RT with a 405 nm violet laser as an excitation source. A green PL emission feature can be clearly observed with a peak wavelength of 520 nm. We also performed PL measurements at 13 K. The ratio of the integrated PL intensity at 13 K to that at 300 K was 7.4%, which is comparable with the value for conventionally fabricated green LEDs on sapphire substrates [29]. Since this value is frequently considered to be a rough indicator of the internal quantum efficiency [30], the PL results indicate that the optical properties of the GaN films on the amorphous substrates were not significantly degraded.

Electroluminescence (EL) measurements of the LEDs were taken after the deposition of Pd/Au and In electrodes as ohmic contacts on the p- and n-type GaN surfaces, respectively. Figure 7 (a) shows the EL spectra with various injection currents between 2.1 and 10.8 mA, and thus, normal operation with reasonable emission spectra. We also fabricated the blue and red LEDs by altering the proportion of In in the InGaN MQWs, as shown in Fig. 7 (b).

4. Conclusion

In summary, PSD process for the fabrication of full-color GaN-based LEDs on amorphous substrates with graphene buffer layers was reviewed in this paper. Since sputtering is frequently used in industry, it is an established process that can be adapted for the fabrication of LEDs on large-area flexible glass substrates. We believe that the combination of these techniques paves the way toward developing large-area flexible GaN-based optoelectronic devices.

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