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Epitaxial gallium nitride thin films grown on silicon substrates utilizing gallium nitride seed-layer formed by liquid source precursor

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Abstract–Gallium nitride (GaN) epitaxial thin films were deposited on Si substrates by a modified hydride vapor phase epitaxy (MHVPE) technique utilizing the GaN seed-layer formed from liquid source precursor. Tris *N*,*N*-dimethyldithiocarbamato gallium(III) ($Ga(mDTC)_3$) powder was dissolved in chloroform ($CHCl_3$) to prepare the liquid source precursor for seed-layer formation. The developed method was found to be suitable for the epitaxial growth of GaN on Si in spite of the large mismatch in lattice constants and thermal expansion coefficients, resulting in device-quality epitaxial films with fairly smooth surface morphology. The epitaxial GaN films obtained in this study had a hexagonal structure with (0002) preferred orientation with the FWHM value of 428.6 arcsec of the (0002) GaN XRD peak. Photoluminescence spectra of GaN films exhibited a strong and sharp peak at 3.41 eV with the FWHM value of 107 meV.

Key words: Gallium Nitride, Hydride Vapor Phase Epitaxy, Seed-layer, $Ga(mDTC)_3$, Chemical Vapor Deposition

INTRODUCTION

Gallium nitride (GaN) and its alloys are currently among the most attractive semiconductor materials due to their unique properties such as direct and wide band gap (3.4 eV at room temperature), and chemical and thermal stability. GaN-based materials have been applied in LEDs (light emitting diodes) and LDs (laser diodes) with a wide spectrum range from red to UV [1,2]. GaN epitaxial films have been preferably grown on sapphire and 6H-SiC substrates by vapor phase epitaxy methods, due to their ability and low-cost [3,4]. In view of semiconductor technology, however, silicon substrate is more attractive, because silicon wafers with mature fabrication technology are available in large diameter and cheaper than other kinds of wafers. Until recently, silicon substrates have not been popular in the application of GaN epitaxy due to substantial lattice mismatch and difference in thermal expansion coefficients between GaN and Si substrates. Numerous cracks and dislocations frequently occur in GaN epitaxial layers when grown on Si substrates [5,6]. To overcome these issues, several approaches have been proposed: using a buffer layer of AlN [5] or GaAs [7]; patterning and masking the substrate; using amorphous, gliding layers such as silicon on an insulator (SOI); silicon-implanted oxide (SIMOX); and seed-layer. Most of these methods, however, employ additional process steps or complicated procedures, which are not desirable for mass production and eventually increase the manufacturing cost. The GaN seed-layer technique utilizing liquid source precursor has been recently developed and applied to the growth of GaN on sapphire substrates [8], and it was shown that the device-quality epitaxial GaN layers could be obtained. Furthermore the technique has an inherent advantage in the simplicity of the process, in that no extra process is needed except spin-coating of the precursor solution on substrates prior to the deposition.

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In this study, GaN epi-layers were grown over a GaN seed-layer formed on Si substrates in an attempt to improve the quality of GaN films on Si substrate. The GaN seed-layer was formed through the pyrolysis reaction of tris (*N*,*N*-dimethyldithiocarbamato)-gallium(III) ($Ga(mDTC)_3$) on the surface of Si substrate. The epitaxial GaN layers were deposited by a modified hydride vapor phase epitaxy (MHVPE), and the effects of the seed layer on the properties of GaN epitaxial films were investigated.

EXPERIMENTAL DETAILS

Tris (*N*,*N*-dimethyldithiocarbamato) ($Ga(mDTC)_3$), as a precursor material, was prepared by dissolving gallium nitrate ($Ga(NO_3)_3{\cdot}xH_2O$) and sodium *N*,*N*-dimethyldithiocarbamate hydrate (Na(mDTC)) in methanol. The $Ga(NO_3)_3{\cdot}xH_2O$ and Na(mDTC) solutions were then mixed; this was followed by precipitation. The precipitated material was filtered with a 5 μm micro-filter and dried at 60 °C for 4 h. As-synthesized $Ga(mDTC)_3$ powder was dissolved in chloroform to prepare the liquid source seed-layer precursor solution, which was spin-coated on (100) Si substrates. Prior to the coating step, Si substrate was dipped in diluted HF in deionized (DI) water (HF : DI water=1 : 50) and rinsed with DI water immediately. The substrates were loaded into the MHVPE reactor and went through the nitridation process in the reactor prior to the main growth to form a seed layer on Si substrates by pyrolytic transformation of the $Ga(mDTC)_3$ in a flowing NH_3 environment. After the nitridation process, the epitaxial GaN started to grow when the gaseous mixtures of trimethyl gallium (TMGa), HCl, and NH_3 were introduced to the reactor.

The MHVPE technique is a hot-wall deposition technique using TMGa, NH_3, and HCl gas phase reactants. The schematic drawing of the MHVPE reactor is illustrated in Fig. 1. A detailed description of the MHVPE technique and reactor schematic can be found elsewhere [9,10]. In the reactor, the $Ga(mDTC)_3$ precursor layer was heated and nitridated under flowing NH_3/N_2 at 850 °C for 10 min. The $Ga(mDTC)_3$ layer transforms into the GaN seed-layer by the

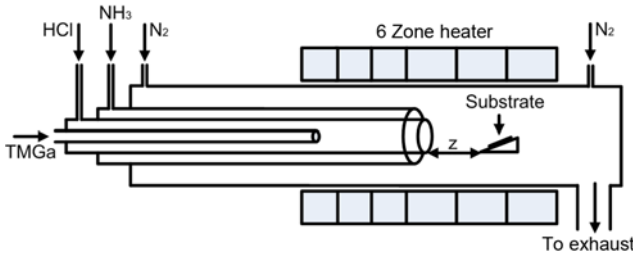

Fig. 1. Schematic diagram of the MHVPE reactor.

pyrolytic reactions shown below:

$$Ga(mDTC)_3 \xrightarrow{500\,^{\circ}C} \gamma\text{-}Ga_2S_3 \quad (1)$$

$$\gamma\text{-}Ga_2S_3 + 2NH_3 \xrightarrow{700\text{-}1000\,^{\circ}C} 2GaN + 3H_2S \quad (2)$$

The pyrolytic reactions occur during the heat-up cycle after the substrates were loaded into the reaction zone to reach the nitridation and growth temperature, and did not require additional time or extra process steps.

After the nitridation process, the main epitaxial GaN growth was started using a gaseous mixture of TMGa, HCl, NH_3, and N_2 at 850 °C for 30 min. As a part of the study, all the process conditions relating to formation of the seed-layer and epi-layer were systematically optimized. The typical process conditions of GaN seed-layers and epi-layers are shown in Table 1. The GaN films on (100) Si substrates were grown under optimized conditions before characterization. The temperatures of the 6-zone heater were set in order to obtain a suitable temperature profile for the 2-dimensional layer-to-layer epitaxial growth mode. The temperature profile in the MHVPE reactor is shown in Fig. 2. It is noteworthy that the substrates were located in the heater-zone 5 of the reactor, at 850 °C with a flat temperature zone of ±8 °C.

Table 1. Optimized conditions for the growth of GaN films on (100) Si substrates

Conditions	Value
Nitridation temperature [°C]	850
Nitridation time [min]	10
Seed-layer solution concentration [M]	0.047
Deposition temperature [°C]	850
Deposition time [min]	30
HCl/TMGa source ratio	1
V/III source ratio	81
TMGa bath temperature [°C]	5

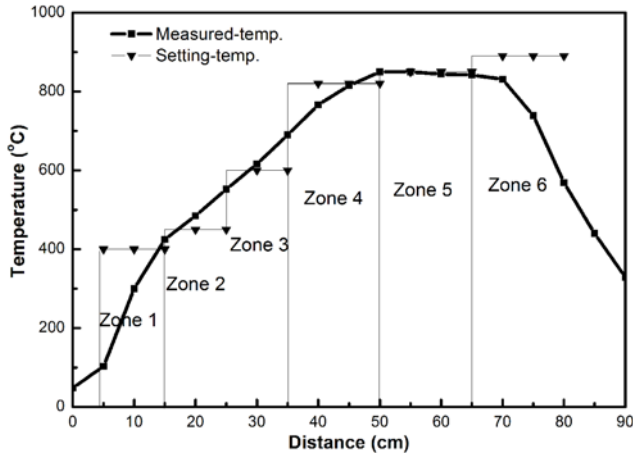

Fig. 2. Temperature profile in the MHVPE reactor.

The surface morphology of GaN layers was measured by scanning electron microscopy (SEM; Hitachi, S-4100), while the structural properties were investigated by X-ray diffractometry (XRD; PANalytical, X'Pert PRO) using Cu-Kα radiation. The chemical properties of the GaN films were investigated by X-ray photoelectron spectroscopy (XPS) using Al-Kα radiation, and the optical properties were investigated by photoluminescence (PL) spectroscopy using a He-Cd laser, with an excitation wavelength of 325 nm.

RESULTS AND DISCUSSION

The properties of GaN epi-layers grown by the MHVPE technique are strongly dependent on the position of the sample (z-position) with respect to the reactant gas outlet. The z-position is defined as the distance from the outlet of the $GaCl_x$ tube (where HCl gas reacts with TMGa vapor to form $GaCl_x$) to the position of the substrate. When the z-position is too short, incomplete mixing of reactants occurs, while with too long z-position, dilution of reactants occurs by mixing with surrounding N_2 gas, resulting in the reduction of the growth rate. Surface morphology and optoelectronic properties are also affected by the z-position, which were caused by complex flow dynamics and mass transfer phenomena in the reactor related to homogeneous and heterogeneous reaction kinetics. In this work, the z-position value was increased from 15 to 30 cm to find the optimum location for obtaining high-quality GaN epi-layers. Fig. 3 shows the XRD patterns of the GaN films grown at different z-positions. The patterns show that all the GaN films grown at various z-positions have hexagonal structures. However, the crystalline quality of those films was different, and the GaN film with best crystallinity was obtained when the z-position was 20 cm.

The chemical composition of the GaN epi-layer was determined by XPS, of which the spectra are shown in Fig. 4. In the XPS spectra

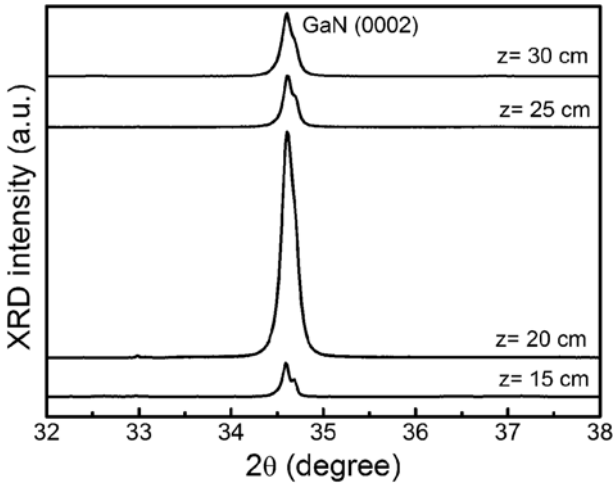

Fig. 3. XRD patterns of the GaN film on the (100) Si substrate with different positions.

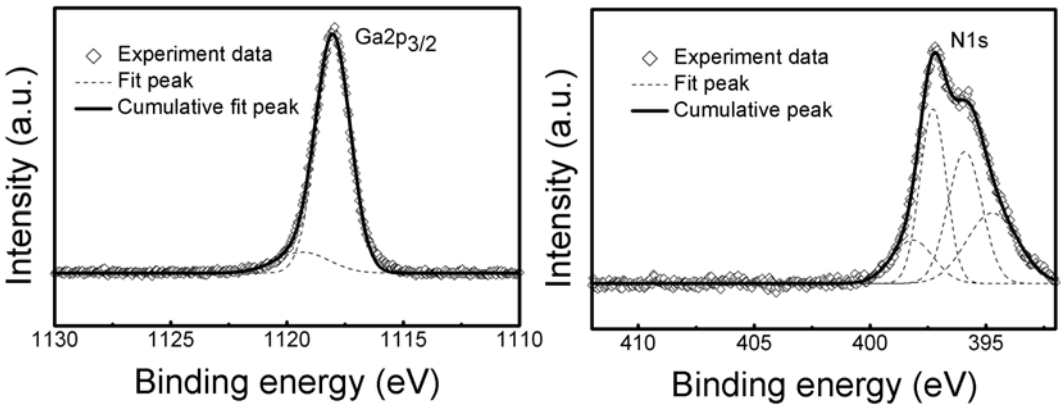

Fig. 4. XPS spectra of the Ga2p$_{3/2}$ and N1s core levels of the GaN epi-layers.

of the Ga2p$_{3/2}$ core-level, there were two peaks detected at 1,118.00 and 1,119.33 eV, respectively. The dominant peak at 1,118.00 eV was identified as the Ga-N bonding, while the second small peak at 1,119.33 eV was attributed to Ga-O bonding [11]. In the N1s spectrum, several peaks were observed at 394.73, 395.88, 397.27, and 398.14 eV. The cumulative peak of these peaks was centered at 397.22 eV, which was assigned to Ga-N bonding [12,13]. The asymmetry of the N1s peak was supposed to represent the presence of chemisorbed nitrogen, along with nitrogen in GaN [14,15].

Fig. 5 shows the X-ray diffraction pattern of the GaN epitaxial films grown on Si substrates. From Fig. 5, the (0002) and (0004) GaN peaks were identified at 2θ=34.3° and 2θ=73.4°, respectively. The diffraction pattern shows that a highly oriented GaN film with hexagonal structure was formed on Si substrate. The high resolution XRD (HRXRD) measurement ($\omega/2\theta$ scan mode) was carried out around the (0002) GaN peak to investigate the single crystalline quality. The GaN (0002) peak position was 17.30868°, with the full width at half maximum (FWHM) value of 428.6 arcsec. This value indicates that the GaN epitaxial films grown on Si substrates by the developed technique of this study have device-level crystallinity.

The SEM surface image and cross-sectional view are shown in Fig. 6. A dense but relatively rough surface was observed in the GaN films. Thickness of the films was approximately 3.0 μm, and growth rate was calculated to be 6.0 μm/h. From the results of XRD and SEM, the GaN seed layer was found to play an important role in growing high-quality GaN epitaxial layers on Si substrates. It is as if island-like seeds acted as effective defect sinks, absorbing dislocations that form in the early-stage of epitaxial growth, thus making a major portion of epi-layers free from dislocations [8,9]. Surface roughness, however, has to be further improved for commercial application of the developed technique to LED or LD fabrications.

Fig. 7 shows the room temperature PL spectrum of the GaN films grown on Si substrates using the liquid source GaN seed layer technique. The PL spectrum exhibits strong and sharp peak at 3.41 eV

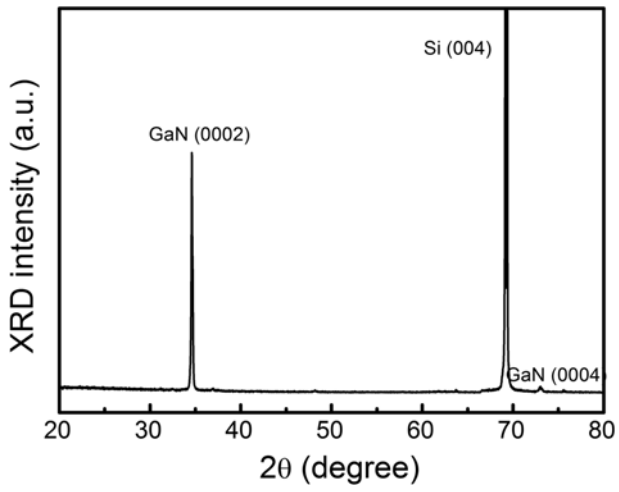

Fig. 5. XRD pattern of the GaN film on the (100) Si substrate.

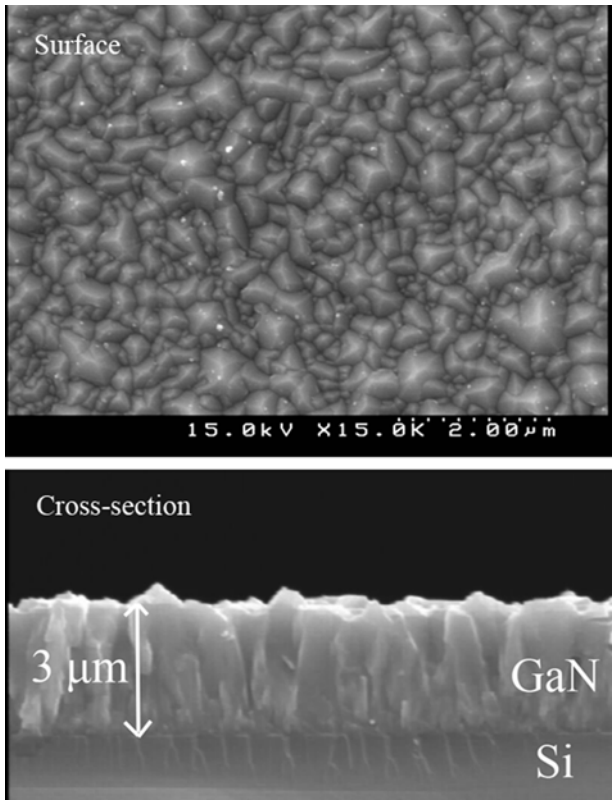

Fig. 6. Surface morphology and cross-section of the GaN epitaxial film.

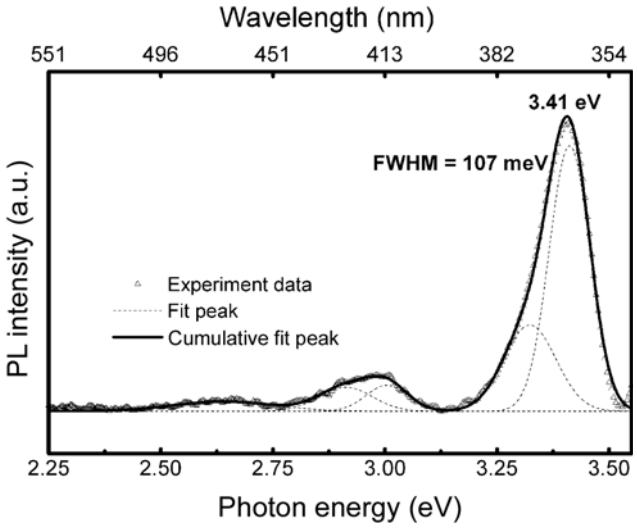

Fig. 7. Room temperature PL spectrum of the GaN films on the (100) Si substrate.

with the FWHM value of 107 meV. In addition, there are broad peaks with low intensity located at lower energy side of 3.41 eV peak. Overlapping with the main peak at 3.41 eV on the left shoulder, there was a weak transition at 3.32 eV, which is attributed to the N vacancy [15,16]. The other three peaks observed at 3.00, 2.91, and 2.64 eV were believed to originate from impurities or deep level defects [17]. The defect related peaks were, however, minimal for most of the samples obtained in this study.

CONCLUSIONS

Gallium nitride (GaN) epitaxial layers have been successfully deposited on Si substrates by the MHVPE technique with a GaN seed-layer formed from liquid source precursor. The structure of the GaN films was hexagonal with a (0002) preferred orientation. The FWHM value of the (0002) GaN peak was 428.6 arcsec. The PL spectrum shows a strong and sharp peak at 3.41 eV with a FWHM value of 107 meV, together with some lower energy level peaks coming from impurities and defects. It implies that introduction of the GaN seed-layer formed by a solution precursor method has improved the properties of GaN epi-layers to a device-level quality. Therefore, the developed GaN seed-layer technique of this study proved to be a promising and comparable method for the deposition of GaN epi-layers on Si substrates.

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