phys. stat. sol. (c) **0**, No. 1, 124–128 (2002)

Growth of GaN Thin Films on Silicon Using Single Source Precursors and Development of New Patterning Technology by Combination of MOCVD and Micro-Contact Printing Methods

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(Received July 22, 2002; accepted October 1, 2002)

PACS: 68.55.Jk; 81.15.Gh

We have grown the GaN thin films on silicon substrates using the newly developed single source precursors by thermal MOCVD method. Highly oriented GaN thin films in the [002] direction with hexagonal structure were deposited on Si(111) substrates at 800 °C and 1 Torr with Triazido(triphenylphosphine oxide) gallium. XRD pattern and pole-figure analysis proved that the highly oriented GaN film has a single-crystalline nature. PL data of this film show that a strong emission peak but with some large FWHM of 100 meV could be observed at 3.4 eV (365 nm). Patterning of GaN thin films was also successfully performed by MOCVD onto Si(100) substrates of which surface was modified by organic thin film. The organic thin film of SAMs was in first obtained by μCP method. The deposition of GaN thin films has then been carried out onto those modified Si(100) substrates using the single molecular precursor by thermal MOCVD without carrier and bubbler gases. In addition, a buffer layer of thin TiO_2 film was applied into the modified Si(100) substrates to understand a possibility of selective deposition of GaN film.

1. Introduction III–V nitride compound semiconductors have attracted attention due to special applications such as blue/UV light emitting diodes (LED), laser diodes (LD), high-temperature/high-power electronic devices [1].

Among several film deposition techniques, metal organic chemical vapor deposition (MOCVD) method, which is the most widely used, is growing method of GaN films using thermal-decomposing metal-organic compounds, single precursors have strong reactivity and can control composition and quality of films. An ideal GaN single source precursor would be a non-pyrophoric, air-stable liquid with a high vapor pressure, because it can enable us to avoid hazardous and pyrophoric gaseous precursors (for example, $Ga(CH_3)_3$ or NH_3) and very harsh conditions to deposit GaN. Recently, organometallic gallium azides of several types, $(R_3N_2)Ga(N_3)$, $(N_3)_2Ga\{N[CH_2CH_2\ (NEt_2)]_2\}$, and $(R_3N_2)Ga(N_3)$ have been reported to act as single source precursors for the GaN growth, in which the azide group behaves as a major nitrogen source [2–6].

Micro-contact printing (μCP) [7, 8] is a non-photolithographic technique for generating patterned self-assembled monolayers (SAMs) [9] on the surfaces of a variety of substrates. This method is a useful variant of "soft lithography". The microstructure formations in these depositions are in turn directed by SAMs of octadecyltrichlorosi-

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lane (OTS) that are themselves patterned by contact printing. The patterned deposition is thus achieved without the use of photolithography or reactive ion etching. This method provides a wide process window for the selective CVD and exploits the advantages inherent in CVD by carrying out the reaction under conditions of kinetic control. Regions of the substrate modified with OTS SAMs are essentially inert while the unmodified regions are reactive.

In this paper, we have synthesized new precursors for the GaN thin film deposition and then applied it into the GaN growth and Si patterning technology by combination of MOCVD and Micro-contact printing (μCP) methods.

2. Experimental Procedure To synthesize the new single GaN precursor (Triazido(triphenyl phosphine oxide) gallium (III), TATPPOG), which contains gallium and nitrogen atom in the same compounds, using phosphine (PR_3) compounds, not anime and alkyl group, as ligand.

$$GaCl_3 + 3NaN_3 \rightarrow Na[Ga(N_3)_4] + 3NaCl \quad \text{(in THF, 25 °C)}$$

$$Na[Ga(N_3)_4] + (O{=}PPh_3) \rightarrow (O{=}PPh_3)Ga(N_3)_3 + NaN_3$$

$(O{=}PPh_3)Ga(N_3)_3$ is solid at room temperature with melting point of 85–90 °C and boiling point of about 250 °C. The precursors were kept in a constant temperature (about 250 °C). The substrates were heated during the deposition.

To synthesize another organic gallium-azide compound (Bisdimethylethylethylene diamidogallium azide, BDEEDAG) that has a coordination number of gallium more than 4, we also used nitrogen functional group that can act Lewis base as ligand. Coordination numbers of gallium increase into 4 or 5 from 3, because these functional group coordinate gallium. Thus, the new compound is more thermal-stable and gallium-azide functional group can efficiently act on MOCVD.

$$(Me_2N)CH_2CH_2(Et)NH + \text{n-BuLi} \rightarrow (Me_2N)CH_2CH_2(Et)Li - BuH$$

$$(Me_2N)CH_2CH_2(Et)Li + GaCl_3 \rightarrow (Me_2N)_2(CH_2CH_2(Et)N)_2GaCl - 2LiCl$$

$$(Me_2N)_2(CH_2CH_2(Et)N_2GaCl + NaN_3 \rightarrow (Me_2N)_2(CH_2CH_2(Et)N)_2GaN_3 - NaCl.$$

With these newly developed precursors, in this study, we have firstly grown the GaN thin films on Si(111) and Si(100) substrates at the deposition temperature and pressure in the ranges of 500–900 °C and 1–2 Torr, and then performed the patterning of GaN thin films by MOCVD onto Si(100) substrates of which surface was modified by organic thin film of OTS.

Monolayer patterning via the μCP of OTS was performed using previously reported procedures [10–12]. Si substrates were washed with high-purity deionized (DI) water, acetone and methanol and then dried in a stream of filtered argon. A solution of OTS in dry hexane was used as the "ink". The OTS solution was applied to the polydimethylsiloxane stamp using a photoresist spinner and the inked stamp was dried in a stream of Ar for ~30 s. The stamp was brought into contact with the substrate by hand and held in place for ~30 s. This procedure routinely yields OTS thin films that are about 25–30 Å thick. The OTS patterned substrates were cleaned with methanol and finally dried with a stream of argon before being loaded into the CVD reactor. The depositions of GaN films were carried out with BDEEDAG, as precursor.

3. Results and Discussion GaN thin films grown on silicon substrates at the deposition temperature and pressure in the ranges of 500–900 °C and about 1–2 Torr using the newly developed single source precursor, TATPPOG, by thermal MOCVD method.

Figure 1a shows the typical XRD pattern of a GaN thin film grown on Si(111) substrate at 800 °C and 1 Torr with TATPPOG. The X-ray diffraction pattern shows a highly oriented GaN thin film in the [002] direction with hexagonal structure. In order to investigate the detailed film structure, the X-ray pole figure analysis using the grazing incidence X-ray diffractometry was performed. The result confirmed that the highly oriented GaN thin film has a similar property of single-crystalline hexagonal GaN. Figure 1b shows the six-fold symmetry attributing to h-GaN. However, there are some other poles near the dots, indicating that the as-grown film has not perfect single crystalline property. Plan-view SEM image (Fig. 1c) of the GaN film of Fig. 1a shows no cracks and quite large crystals more than 1 μm with spatially periodic shapes such as closed orbits. The film thickness calculated by the cross-sectional SEM image (not shown) is 2.5 μm. However, the higher film growth rate (or thickness) as well as the more rough films could be grown on Si(111) substrates under high deposition pressure. For an application test into the optical devices, photoluminescence (PL) measurement are also carried out at room temperature. Fig. 1d shows the obtained PL spectrum using the same GaN film as Figs. 1a and 1b. The PL data shows that a strong emission peak at 365 nm (3.4 eV) is onserved, suggesting a possibility of visible (blue) light display applications. However, the FWHM of the emission peak is some large to be 100 eV due to no profect crystalline and considerable carbon impurity (10%) in the film layers.

Figure 2a shows the XRD pattern of a GaN thin film grown on Si(110) substrate with BDEEDAG precursor under the same deposition condition of Fig. 1. The XRD data shows only a hint of polycrystalline h-GaN crystal formation on Si(110), suggesting

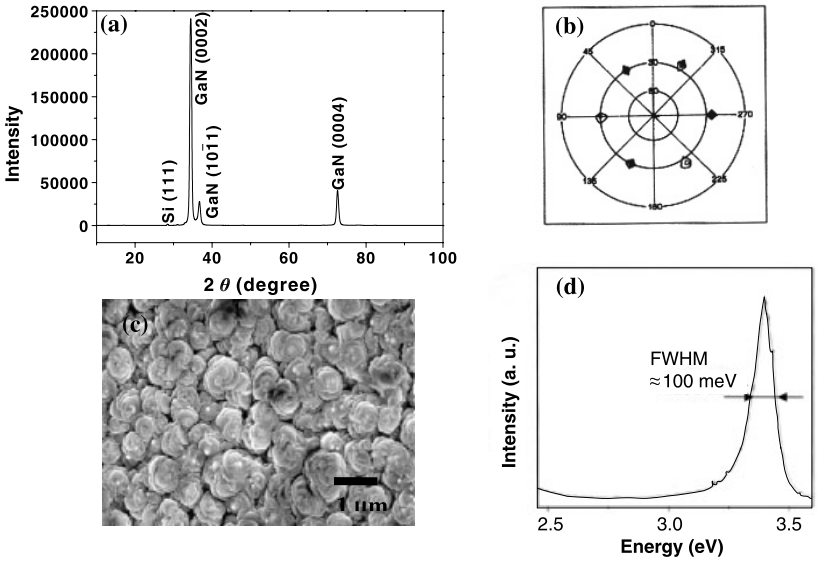

Fig. 1. X-ray diffraction pattern, pole figure and SEM image of a GaN thin film grown on Si (111) substrate at 800 °C and 1 Torr with TATPPOG: a) XRD, b) X-ray pole figure, and c) SEM, d) shows a PL spectrum of the GaN film of a)

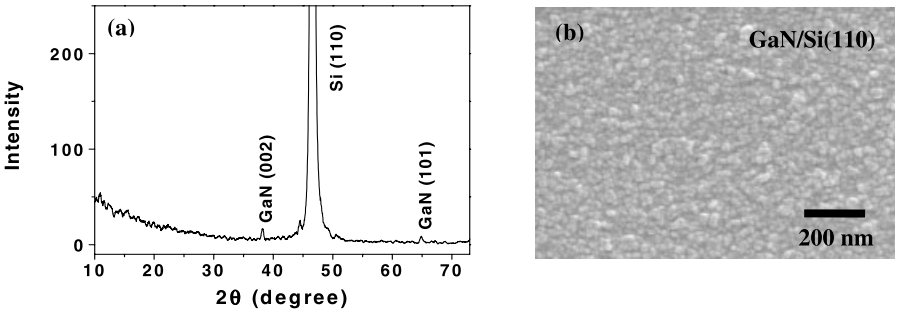

Fig. 2. XRD and SEM data of a h-GaN thin film grown on Si (110) substrate with BDEEDAG precursor: a) XRD and b) SEM

that the BDEEDAG precursor may have more high activation energy than that of TAPPOG. This indicates the different bond strengths between gallium and other fuctuinal groups such as phosphine-related groups or nitrogen-related groups. The SEM image of Fig. 2b thus shows poor crystallity with sub-micron size crystals. When the deposition temperature is decreased to 500 °C, however, near similar deposition behavior as Fig. 2a was observed. In this moment, we don't know this in details. One possibility is that since the BDEEDAG precursor has quite low vapor pressure, a diffusion process by mass transfer of the precursor in the gas phase is preferable rather than surface reactions between the substrate and precursor. Based on these differences in deposition temperature, we used the BDEEDAG precursor for the patterning of modified Si(100) substrates. Since the modified Si substrate by organic film can only endure up to 500 °C, it is very important for us to select proper GaN source for the Si patterning.

A buffer layer of thin TiO_2 film was applied into the modified Si(100) substrates to understand a possibility of selective deposition of GaN film. Since the modified Si(100) substrates with organic film has both hydrophilic and hydrophobic surfaces on bare silicon part and SAMs regions, respectively, the TiO_2 can only be deposited on the bare silicon area while the GaN will have an another selectivity. This indicates that a micro-patterning is possible for the GaN films on silicon substrates with a buffer layer by combining the MOCVD and μCP methods. Without TiO_2 buffer layer, the GaN film was existed on either the bare silicon surface or SAMs area, respectively. In the case of GaN/TiO_2/patterned Si(100) films, GaN thin film of hundreds Å is deposited both on pattern and base (see Fig. 3). However, nitrogen diffusion in the patterned TiO_2 film

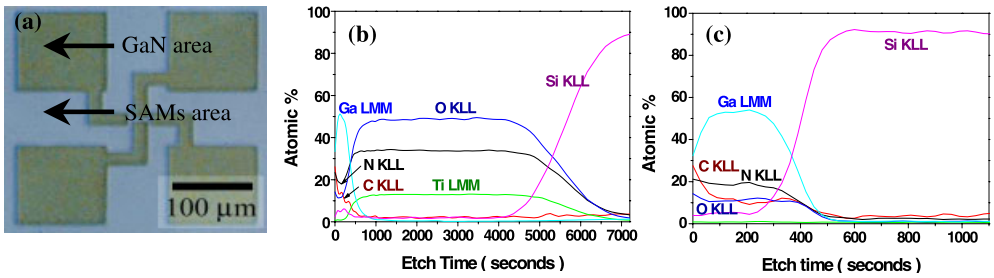

Fig. 3 (online colour). a) SEM image and Auger sputter depth-profiles of b) depth profile of base part and c) depth profile of pattern part acquired from a GaN/TiO_2/patterned Si(100) sample

layer effect the overlapping of N KLL (389 eV) of GaN and Ti LMM (390, 421 eV) of TiO_2. With this reason, the magnitude of nitrogen is less than that of gallium in the GaN film layer, so besides TiO_2, TiON is also shown by diffusion of nitrogen.

4. Conclusions The MOCVD grown GaN layer on Si(111) substrates is hexagonal single-crystalline textured. Highly oriented crack-free GaN thin film in the [002] direction with hexagonal structure was deposited on Si(111) substrate at 800 °C and 1 Torr with TATPPOG. XRD pattern and pole-figure analysis proved that the highly oriented GaN film has a single-crystalline nature.

A micro-patterning of GaN thin films was also performed by MOCVD onto Si(100) substrates of which surface was modified by organic thin film of OTS. The deposition of GaN thin films has then been carried out onto the those modified Si(100) substrates by thermal MOCVD. To avoid a destruction of the organic film of SAMs, we did the GaN deposition at relatively low temperature as low as 500 °C with BDEEDAG rather than TATPPOG. In addition, a buffer layer of thin TiO_2 film was applied into the modified Si(100) substrates to understand a possibility of selective deposition of GaN film.

Acknowledgements Support of this research by the 2000 BSRI project (Grant No. 2000-015-DP0195) of Korea Research Foundation and by the BK 21 project of Ministry of Education, Korea is gratefully acknowledged.

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