

BULLETIN

OF THE
KOREAN CHEMICAL SOCIETY

VOLUME 18, NUMBER 11
NOVEMBER 20, 1997

BKCS 18(11) 1133-1228
ISSN 0253-2964

Communications

New Buffering Process in Preparation of High Quality GaN Films

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Received April 21, 1997

A great deal of attention in the compound semiconductors has recently been focused on the GaN films because of its optoelectronic and physical properties such as long lifetime, high efficiency, and outstanding reliability with wide band gap energy.^{1,2} The GaN films are currently manufactured by hetero-epitaxy growth and studied for the applications of the short wavelength optoelectronic devices, laser diodes, and etc.³

Generally, three dimensional island structures are inevitably incorporated in the GaN film with the high interfacial energies between GaN layer and hetero-substrate. A two-step growth process has been developed to avoid this problem as well as to promote two-dimensional GaN films growth. This process on sapphire substrate includes the growth of AlN⁴ or GaN⁵ buffer layers at a low temperature followed by the growth of high quality GaN films at a high temperature on as-grown buffer layers. 6H-SiC has been recently suggested as an alternative substrate for high quality GaN films by Sasaki *et al.*⁶ The structural improvement of the GaN films grown on the 6H-SiC substrate owes to the similarity of lattice structure and thermal expansion characteristics along the basal planes of GaN and SiC.⁷

Previous studies have demonstrated that the growth conditions of buffer layers strongly affect the electrical and optical properties of GaN devices.^{5,8,9} The buffer layers play a significant role for the ultimate optimization of GaN device structures on hetero-substrate since they serve as the crystallographic and morphological template for subsequent GaN deposition.

In general, the growth of GaN films on both 6H-SiC and

sapphire can be described by Stranski-Krastnov (SK) mechanism which is characterized by the condition of adhesion. If a free energy for adhesion of crystal-medium interface (2α) is larger than that for substrate-medium adhesion (α_s), a three-dimensional crystal growth is favored whereas a two-dimensional growth is preferred in the opposite condition ($2\alpha < \alpha_s$). The crystals can be strongly adsorbed on the substrates and form a large grain if the changes of surface free energies ($\Delta\alpha = 2\alpha - \alpha_s$) are small.¹⁰

In this communication, a new buffering process in the preparation of GaN films on AlN/6H-SiC is described. The growth system used for this study was a conventional metal organic chemical vapor deposition (MOCVD). In the conventional MOCVD process, the gaseous trimethylgallium (TMG) and NH₃ are carried into a reactor separately and then mixed at the reaction zone. The new process has been carried out by the alternating pulsative supply (APS) of reactant gases TMG, NH₃ and purging gas H₂ for 5 cycles on the AlN buffer layers. The APS is a pretreatment process performed on the buffer layers before the normal MOCVD process to improve the quality of GaN films. The Si faces of 6H-SiC substrate were used for the epitaxial growth of GaN. The surface of substrate was etched by the conventional method. A graphite susceptor coated with SiC was heated by rf induction. The growth temperature was 1060 °C. The AlN buffer layers were prepared using 2.4 μmol/min trimethylaluminum (TMAI) and 2 slm ammonia. The TMAI was delivered into the reactor with H₂ gas. After deposition of AlN buffers, the initial layers were made by following APS process; serial injection of 32 μmol/min of TMG was carried by H₂, followed by purging the system with H₂ gas. Then 2 slm ammonia was supplied, followed

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by H_2 purge. Each gas was alternately supplied into the reactor for every one second. The whole cycle of reactants supply was repeated 5 times. Then, the main GaN films were grown on wetted GaN layers using $32 \mu\text{mol}/\text{min}$ TMG with carrier H_2 , 2 slm ammonia and 0.5 slm N_2 for 20 min. The reactor pressure during growth was maintained at 76 Torr. The growth rate of the GaN films, estimated by high resolution scanning electron microscope (SEM) for lateral view, was about $300 \text{ \AA}/\text{min}$.

The APS treated samples on AlN/6H-SiC at the nucleation stage were observed by atomic force microscope (AFM) in comparison with those by conventional MOCVD growth. Apparent islands growth in the initial stage of growth can be observed in the surface morphology and microstructure, as shown in Figure 1. The average surface roughness of the films prepared via 5 cycles of APS treatment was 3 nm whereas that by 5 second of conventional MOCVD was 2.4 nm. The number of islands ($1.9 \times 10^{10} \text{ cm}^{-2}$) after 5 cycles of APS (Figure 1a) is less than the one ($3.2 \times 10^{10} \text{ cm}^{-2}$) by MOCVD for 5 sec. on the same AlN buffer layer (Figure 1b). The average island area of the former (12000 nm^2) is larger than that of the latter (2700 nm^2). Therefore, it is considered that the essential role of the APS treatment is the promotion of adhesion in the nucleation stage by lowering the interfacial free energy between film and substrate.

The GaN films fabricated by the APS process demon-

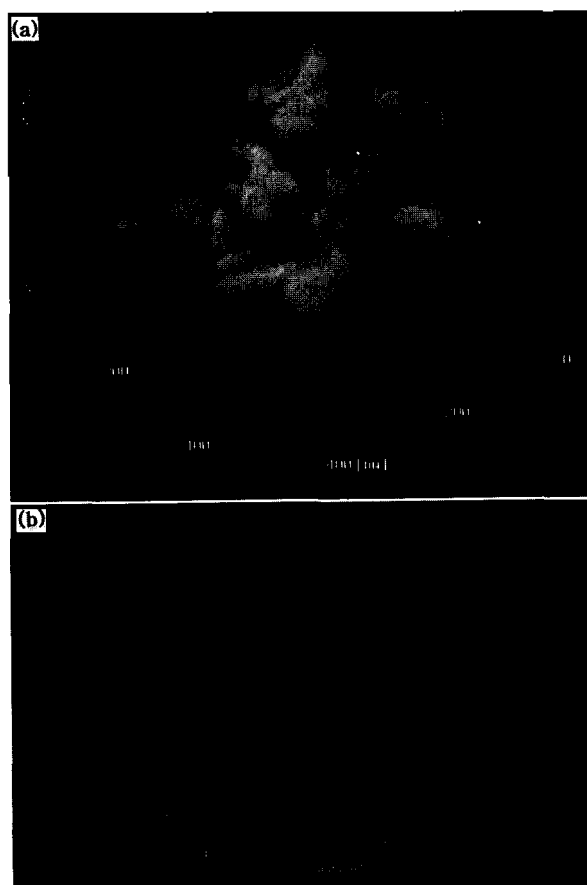


Figure 1. AFM images of GaN films on AlN/6H-SiC at nucleation step: (a) alternating pulsative reactants supply for 5 cycles (b) MOCVD growth for 5 sec.

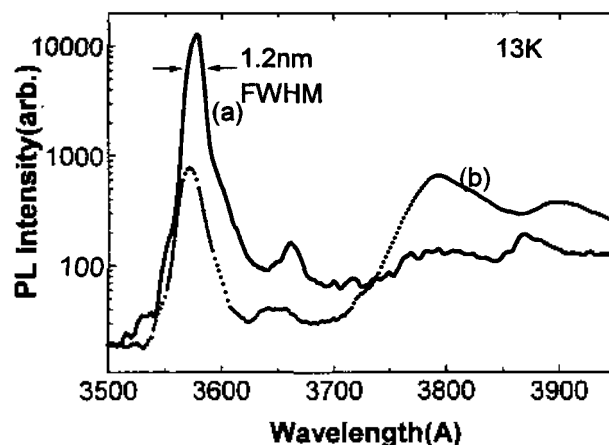


Figure 2. Low temperature photoluminescence spectrum of GaN films: (a) conventional MOCVD growth of 20 min. after 5 cycles of alternating pulsative supply (b) MOCVD growth of 20 min.

strate very low defect density of 10^7 cm^{-2} . As far as we know, this is the lowest defect density ever reported for the GaN films. Double crystal X-ray diffractometer (DCXRD) measurements taken on the $0.6 \mu\text{m}$ GaN films revealed the FWHM of the GaN (0002) reflection having 143 arcsec. whereas that grown without the APS process is 260-300 arcsec. The photoluminescence (PL) spectrum of GaN films at 13 K shows a good optical property, as given in Figure 2. An intense near band-edge emission (I_2) at 357.2 nm with a narrow FWHM of 1.2 nm in Figure 2 (a) was attributed to excitons bound to neutral donors.^{11,12} A defect peak ascribed to a donor-acceptor pair recombination was observed at 380.1 nm and LO-phonon replica at 387.4 nm. It is considered that these patterns of the peaks are caused by impurity contamination, as was also observed by other research groups.¹³⁻¹⁵ As shown in Figure 2 (a) and (b), the relative PL intensity (I_2) has increased more than 10 times after 5 cycles of the APS treatment whereas defect peak has decreased down to 1/10 compare to those of GaN films prepared by conventional MOCVD.

DCXRD and PL data suggest that the APS process improves the quality of crystallinity and optoelectronic properties. The APS treatment is thought to enhance adhesion on the surface in the nucleation stage since it induce the formation of large size GaN grain as shown in AFM images. Further investigations, such as binding energies of precursor molecules to the growing GaN surfaces and buffer-surfaces are in progress for the systematic explanation of these results.

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Hydrogen Evolution from Water with Colloidal CdS Particle-Agarose Gel System

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Received July 8, 1997

The search of an alternative energy system for fossil fuel is of extremely important. For the alternative energy the solar energy storage system is a popular and possible candidate.¹ There are two kind of the storage system: thermal and quantum conversion. The photosynthetic system of green plants is an example of the quantum conversion. We are interested in an artificial photosynthetic system, particularly in the colloidal semiconductor particle system. Several artificial photolysis systems of water by sun light have been studied.²⁻⁵ Hydrogen was produced by irradiating suspension of or colloidal particles of CdS or TiO₂ containing a catalyst with a sacrificial electron donor in aqueous solution.⁶⁻⁸ However, most of these systems such as vesicle system are more mobile phase. Thus, we initiate a rather fixed system, such as the colloidal particle-agarose system. Here we report, for the first time, an artificial hydrogen evolution system from water or aqueous alcohol with CdS colloidal semiconductor particle-agarose gel system.

CdS colloidal particle-agarose gel system was prepared as follows: agarose (200 mg, Aldrich) and CdS powder (40 mg, Aldrich, <5 μ) were suspended in water (10 mL) by sonicating for 5 minutes and boiling; the boiling mixture (2 mL) was transferred into the photocell (30 mL, with pyrex window) and cooled down on the one side of the window of the photocell. The system was completed by adding 18 mL of water or aqueous alcohol and then deaerating with argon. Rh catalyst could be attached² on the CdS-agarose wall in the photocell by illuminating the colloidal CdS-agarose system containing 30 μL of RhCl₃ (0.1 M stock solution, Figure 1) for 20 minutes with 450-550 nm light (450 W Xe-lamp) and then the system were deaerated again.

When the colloidal CdS-agarose gel system containing Rh catalyst with ethanol as electron donor was irradiated by using 450-550 nm light through 0.4 M CuSO₄ filter solution

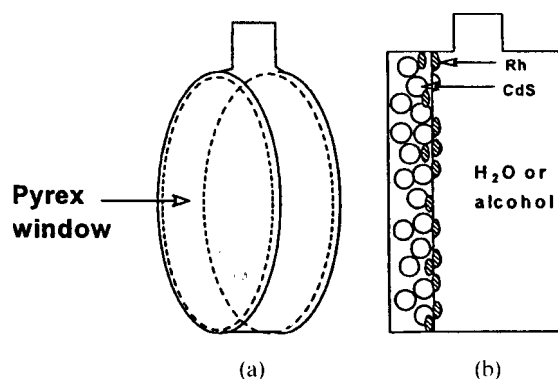


Figure 1. (a) Photocell used. (b) Colloidal CdS particle-agarose gel system with Rh catalyst.

(5 cm length),⁹ hydrogen was detected by Gas Chromatograph (Hewlett Packard 5890, Molecular sieve 5A, 80-100 mesh, 1/8 in 6 ft column, TCD). The GC spectral profile of the gaseous portion of the colloidal CdS-agarose system on illumination for 4hrs is shown in Figure 2. The hydrogen produced in the colloidal CdS-agarose system is readily recognized (Retention time 0.73 min) and analyzed quantitatively. Oxygen and nitrogen peaks could be seen in the GC spectra (Retention times 1.56 and 3.21, respectively) but could not be measured quantitatively, because of the interference of oxygen in air. However, when aqueous ethanol is used as electron donor, acetaldehyde was detected in GC. Retention time of acetaldehyde is 0.63 min on GC (HP-1 capillary column, FID). The amounts of hydrogen evolution in several condition were measured by GC and summarized in Table 1.¹⁰

No hydrogen was formed from the photolysis of water with colloidal CdS-agarose system in the absence of Rh catalyst. However, hydrogen was formed from the photolysis