Hydrogen Gas Sensor based on a Single Crystal GaN/AlN/Si(111) Prepared via PAMBE

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Abstract: The growth of an n-type GaN/AlN/Si(111) hetero structure was carried out using molecular beam epitaxy (Gen II MBE System, Veeco). The surface morphology of the as-grown GaN sample showed a high-quality single-crystal GaN epilayer. The obtained crystal in this study showed a clear hexagonal shape, which indicated that the growth process was controlled by a very accurate flux. The energy-dispersive x-ray spectroscopy results indicated that the film is of high quality, without the presence of contaminating elements. The photoluminescence spectrum showed a strong emission and a sharp peak located at 364.5 nm (3.40 eV) as well as full width at half maximum of 8 nm due to the band-edge emission of GaN. The Raman spectra also displayed a strong band at 522 cm^{-1} from the Si(111) substrate. Two Raman active optical phonons were assigned to h-GaN at 139 and 568 cm^{-1} due to E_2 (low) and E_2 (high), respectively. The gas sensor sensitivity increased as a function of the hydrogen flow rate.

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Keywords: GaN; single crystal; molecular beam epitaxy; gas sensor.

1. Introduction

In recent years, processing techniques for III–V nitride groups have been successfully established, particularly for crystal growth; however, the most suitable method is still not concrete due to the excellent chemical stability and high hardness of these compounds [1]. The main techniques used for nitride epitaxial growths are hydride vapor phase epitaxy, liquid phase epitaxy (LPE), metal organic chemical vapor deposition, and molecular beam epitaxy (MBE) [2].

MBE is an advanced technique for growing thin epitaxial layers of semiconductors, metals, or insulators compared with other techniques. In MBE, growth is carried out in an ultra-high vacuum environment (approximately 10^{-10} Torr); therefore, growth is expected to occur far from the thermodynamic equilibrium and is mainly governed by the kinetics of surface processes. By contrast, the growth conditions in other growth techniques, such as LPE, are near the thermodynamic equilibrium and are mostly controlled by diffusion processes near the surface of the substrate [3]. The processes in MBE growth occur at the atomic level in the crystallization zone. The atoms and the molecules that impinge on the substrate are bonded to the surface by weak van der Waals forces and can, thus, have a high surface mobility when the substrate is adequately heated. The thickness, composition, and doping level of the epilayer are precisely controlled by an accurate control of beam fluxes. The MBE technique is environmentally friendly because toxic chemicals are kept inside the growth chamber [4].

Recently, many semiconductors, such as Si, GaN, and 4H–SiC, have been fabricated for hydrogen sensors [5–7]. The Si gas sensor is mature given the relatively small band gap (1.12 eV), which prevents the operation of Si sensors under harsh environments. Particularly, wide-band gap materials, such as GaN (3.4 eV) and 4H–SiC (3.26 eV), overcome this disadvantage because of their higher electron saturation velocity, higher breakdown electric field, and superior thermal stability and chemical stability [8–10].

The detection of hydrogen gas is one of the potential industrial applications of these materials. Hydrogen gas is flammable and explosive when its concentration in the air is more than 4% at room temperature; its detection is thereby one of the most important safety issues. Nitride group semiconductor-based hydrogen gas sensors have also attracted much attention because of an impending need for robust gas sensors operating in harsh environments [5].

The objective of this work is to fabricate a hydrogen sensor based on group III-nitride hetero structure of a single crystal n-type GaN with an AlN buffer layer grown on an n-type Si(111) substrate using a plasma-assisted MBE (PAMBE) system.

2. Experiment

The III-nitride hetero structure of an n-type GaN with an AlN buffer layer was grown on an n-type Si(111) substrate using a PAMBE system. The growth of III-nitrides on a 3 in Si(111) substrate was started after a standard cleaning procedure using the RCA method. The substrate was then mounted on the wafer holder and loaded into the MBE system. The Si substrate was then outgassed at a temperature of 200 °C for 1 h in a load-lock and for 20 min in buffer chambers. After outgassing, the Si substrate was transferred to a growth chamber. Prior to the epilayer growth, the Si substrate surface was treated to remove the SiO_2 layer. The Si substrate was heated at 850 °C, and a few monolayers of Ga were deposited on the substrate to remove the SiO_2 via the formation of Ga_3O_2. Reflection high-energy electron diffraction (RHEED) showed a typical Si(111) 7×7 surface reconstruction pattern with the presence of prominent Kikuchi lines, which indicated a clean Si(111) surface. Before the growth of the nitride epilayers and the introduction of N_2, a few Al monolayers were also deposited (1 to 3 monolayers) at 850 °C on the Si surface until the 7×7 surface reconstruction disappeared. This step was conducted to avoid Six Ny formation, which is harmful for the growth of subsequent epilayers. The buffer or wetting layer, AlN, was first grown on the Si substrate. The substrate temperature was increased to 870 °C, and both the Al and N shutters were opened simultaneously for 15 min to grow the AlN buffer layer. Subsequently, the GaN epilayer was grown on top of the buffer layer for 60 min with the substrate temperature set to 850 °C. Details on the fabrication of the gas sensor were reported by Asmiet *et al*. [5].

3. Results and Discussion

Figure. 1 shows the RHEED pattern of the evolution of the epilayer GaN. The result showed a smooth, single-crystalline surface with a series of streaks running perpendicular to the surface of the crystal, consistent with two-dimensional diffraction. A regular flat array of atoms transformed into line arrays, and spotty RHEED patterns were not present throughout the growth formation [11]. These observations confirmed that the grown sample had high-quality single-crystalline structures. These structures correspond with the scanning electron morphology (SEM) image in Fig. 2. The SEM image showed that the average crystal size obtained was about 1 μm. The obtained crystal in this study showed a clear hexagonal shape, which indicated that the growth process was controlled by a very accurate flux [12]. Fig. 3 shows the energy-dispersive X-ray spectroscopy (EDX) spectra and the atomic composition of the film elements for the unintentionally doped n-type GaN/AlN/Si(111) film. The peak intensity refers to the concentration of the element in the sample and the atomic composition by percentage. In contrast to those of other research groups, the results in this paper indicated that the film are of robust quality and have no contaminating elements [13, 14]. The PL spectrum was dominated by an intense and sharp peak at 364.5 nm (3.40 eV), with a full width at half maximum (FWHM) of 8 nm due to the band-edge emission of GaN, as shown in Fig. 4. The strong intensity of the band-edge PL emission of GaN indicated its high optical quality. Reducing the dimensions to nanometers drastically changed the physical properties of the GaN film. The quantum confinement effects in nanostructured semiconductors play an important role in their electrical and optical properties. The quantum confinement effect can be qualitatively explained using effective mass approximation. An estimate of the nanocrystallite sizes was determined using the following relation. Assuming infinite potential barriers for a spherical particle with radius *R*, the effective band gap E_g^{nano} (*R*) is given by the following equation [15, 16]:

$$E_g^{nano}(R) = E_g^{bulk} + \frac{h^2\pi^2}{2R^2}\left(\frac{1}{m_e^*}+\frac{1}{m_h^*}\right) - \frac{1.786e^2}{\varepsilon R}, \quad (1)$$

where m_e*, m_h* are the effective masses of the electron in the conduction band and of the hole in the valence band, respectively, and ε is the dielectric constant. The second term on the right hand side shows that the effective band gap is inversely proportional to R^2 and increases as the particle size decreases. The third term in Eq. (1) represents the Coulombic interaction. An estimate of the GaN Nano crystallite sizes was identified using Eq. (1) with the radius of the Nano crystallite E_g^{nano} at 11 nm. Fig. 5 shows the micro-Raman spectrum of the n-GaN thin film at room temperature. The spectrum was normalized with respect to the maximum intensity at 522 cm^{-1}. This maximum point was attributed to the crystalline silicon. The sample showed peaks at 139 and 568 cm^{-1}, corresponding to the E_2 (low) and E_2 (high) modes of GaN, respectively [5]. The result confirmed that the crystals obtained were wurtzite-structured GaN single crystals with a high crystallite. This result was also confirmed by x-ray diffraction. Fig. 6 shows that the x-ray rocking curve diffraction peak located at 17.34° was identified as wurtzite GaN(0002). The FWHM of the diffraction result was calculated to be 22.8 arcsec, suggesting a low dislocation density and a high-quality single crystal. Fig. 7 shows the I–V characteristics of the Pt/as-grown GaN hydrogen gas sensors operating at different flow rates of 2% H_2 in N_2 gas at room temperature. The sensors exhibited viable Schottky behavior when they were operated in air. Upon exposure to hydrogen gas, the Schottky behavior of the sample became ohmic, and the device maximum current increased and saturated at a flow rate of 80 sccm as a function of the flow rates of 2% H_2 in N_2 gas. The series resistance decreased as a function of the flow rates of 2% H_2 in N_2 gas, as shown in Fig. 8. The hydrogen sensing mechanism started with the dissociation of hydrogen molecules on the Pt surface, forming atomic hydrogen, which subsequently diffused through the bulk Pt layer until being absorbed at the Pt/n-type GaN interface. This effect showed to be decreasing in the effective Schottky barrier height (SBH), causing the change in the electrical characteristics of the device [17–18]. The flow current mechanism governed by the thermionic emission conditions was assumed to confirm the drop in the effective Schottky barrier height as a function of the hydrogen flow rate. The SBHs were obtained from the I–V measurements based on the following equation [16]:

$$\phi_B = \frac{KT}{q}\ln\left(\frac{AA^*T^2}{I_\circ}\right), \qquad (2)$$

where ϕ_B is the barrier height, $I_\circ$ is the saturation current density, q is the electron charge, K is Boltzmann's constant, T is the absolute temperature, A^* is the effective Richardson coefficient, and A is the contact area. The theoretical value of A^* was calculated using

$$A^* = 4\pi m^* K / h^3, \qquad (3)$$

where h is Planck's constant. For the n-type GaN, $m^*=0.20\, m_o$ is the effective electron mass for GaN. The effective SBH decreased from 7.8 to 5.2 eV when the gas flow rate increased and saturated at a flow rate of 80 sccm.

Sensitivity is one of the important parameters normally used to gauge the performance of a gas sensor. The hydrogen detection sensitivity, S, is defined as [19]

$$S = \frac{I_{H_2} - I_{Air}}{I_{Air}}, \qquad (4)$$

where I_{H2} and I_{Air} are the current levels in H_2 containing ambient and ambient air, respectively. Fig. 9 shows that at a constant voltage of 3 V, the maximum sensitivity of the gas sensor is approximately 5.5. This value corresponds with that in other research and is significantly higher than the reported value for the n-GaN commercial sample, which is only 0.86 at room temperature [19–21]. The increase in the hydrogen detection sensitivity is due to the high crystallinity (low defect), which leads to the enhancement and control of the current transport at the Pt/n-type GaN interface.

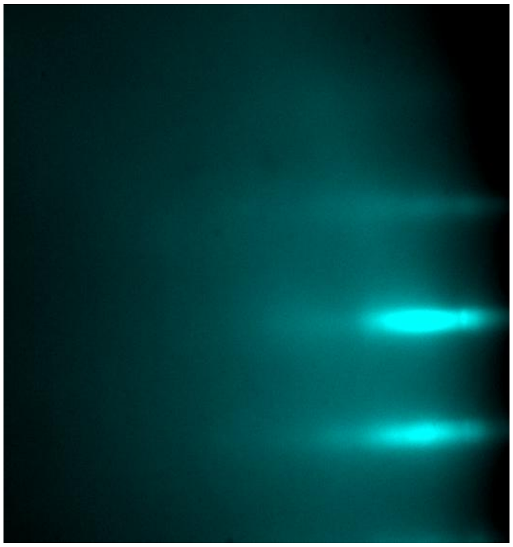


Fig. 1. RHEED pattern of GaN layer.

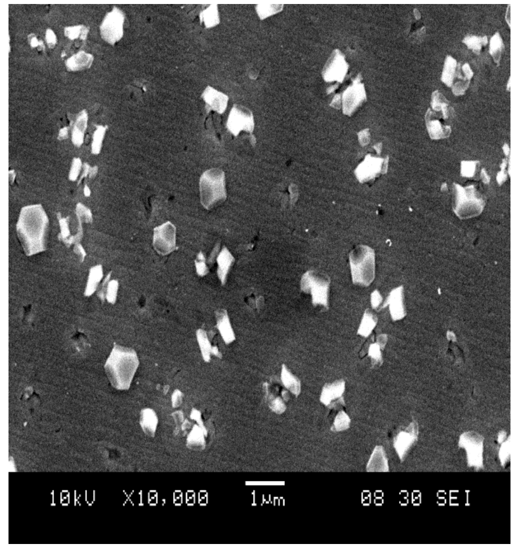


Fig. 2. SEM image of single crystal GaN layer.

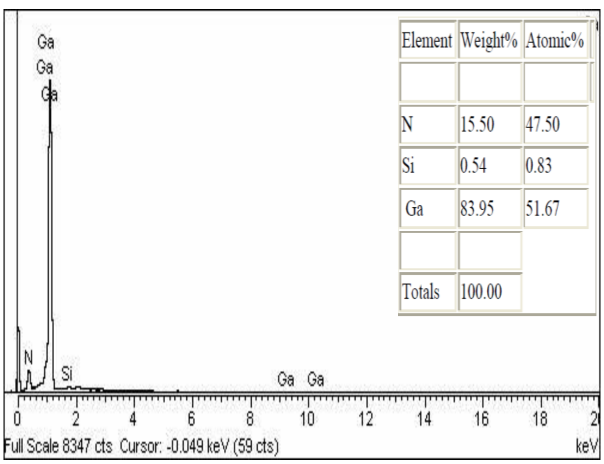


Fig. 3. EDX spectra and the atomic composition elements of GaN/AlN/Si(111) film.

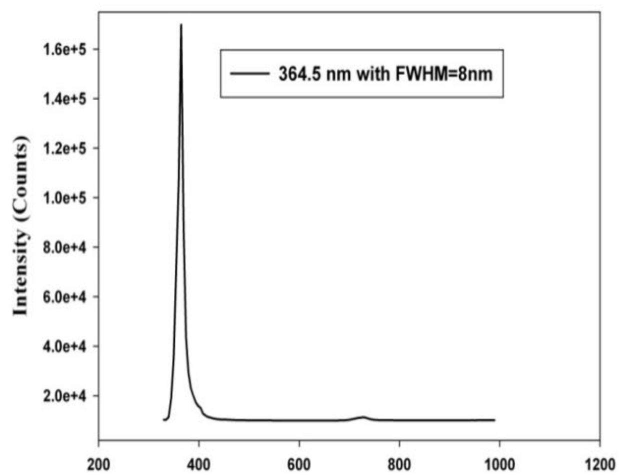
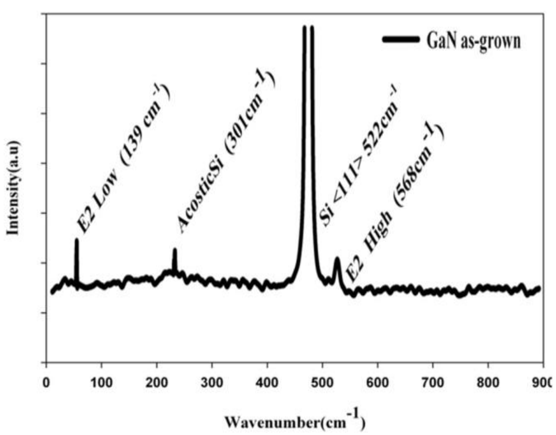


Fig. 4. PL spectra of the GaN layer on Si substrate.



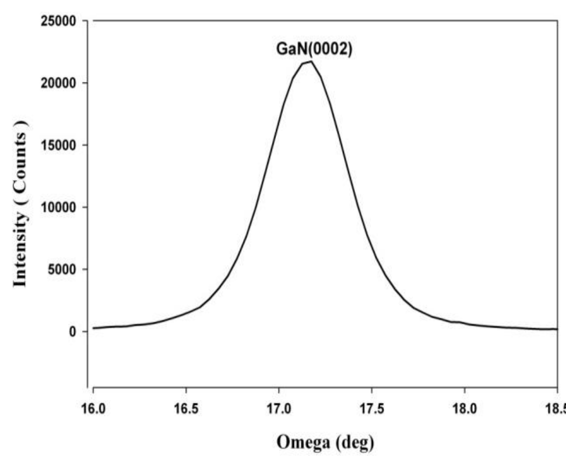
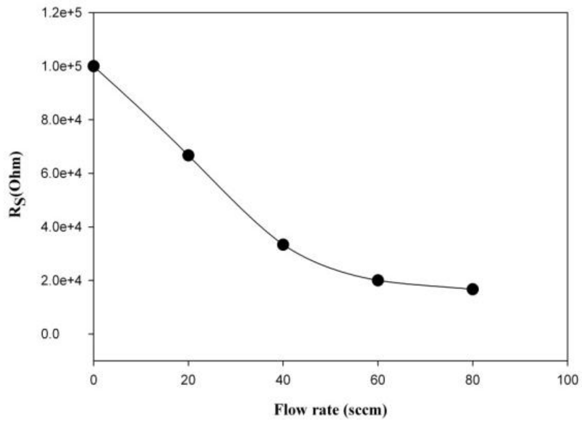


Fig. 5. Raman spectra of the GaN layer on Si substrate.

Fig. 6. RC spectra of the GaN layer on Si substrate.



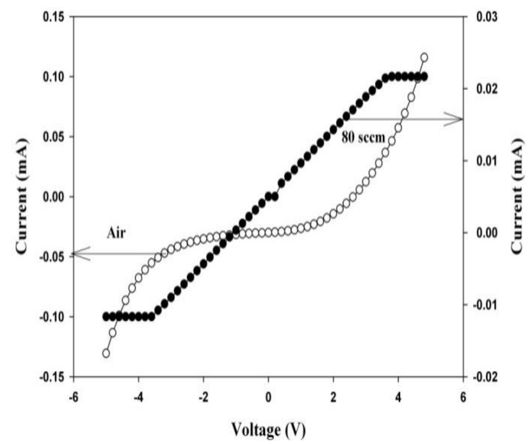


Fig. 7. I–V measurement of GaN gas sensor with different H_2 gas flow rates.

Fig. 8. Hydrogen series resistance as a function of hydrogen flow rate at 3 V.

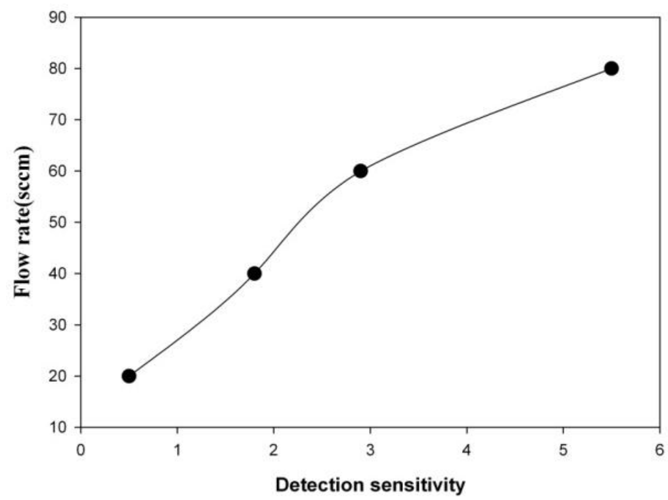


Fig. 9. Hydrogen detection sensitivity as a function of hydrogen flow rate at 3 V.

4. Conclusions

In this paper, high-quality single-crystalline structures of GaN/AlN/Si(111) were prepared via PAMBE. The obtained crystal showed a clear hexagonal shape, indicating that the growth process was controlled by a very accurate flux. EDX and Raman spectroscopy results indicated that the obtained crystals are wurtzite-structured GaN single crystals with high crystallinity. The increase in hydrogen detection sensitivity is due to the high crystallinity (low defect), which leads to the enhancement and control of the current transport at the Pt/n-type GaN interface.

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