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Substrate-polarity dependence of metal-organic vapor-phase epitaxy–grown GaN on SiC

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Single-crystal gallium nitride was grown on each of the two polar {0001} planes of 6H-silicon carbide substrates utilizing metal-organic vapor-phase epitaxy. The substrate polarity is clearly shown to strongly influence the surface morphology and the photoluminescence property of the layer. The examination of the layer surfaces using x-ray photoelectron spectroscopy revealed that {0001} GaN grown on the basal planes of SiC changes its polarity in accordance with the substrate polarity.

I. INTRODUCTION

Gallium nitride is a wide direct band-gap semiconductor with an energy band gap of 3.39 eV at room temperature and has potential applications to light-emitting devices in the visible to ultraviolet region. Usually, GaN has been grown epitaxially on foreign substrates, since it is very difficult to produce large-size wafers of single-crystal GaN, especially on those that induce high densities of defects and cause serious degradation of layers. The selection of a closely matched substrate is crucial for achieving epitaxial layers of high quality.

There have been several attempts to grow GaN on materials other than sapphire, such as silicon, gallium arsenide, gallium phosphide, and silicon carbide. Among these materials, 6H-SiC has the basal-plane lattice constant (a = 3.08 Å) closest to that of GaN (a = 3.19 Å) and is considered to be the most promising substrate. By using SiC, the lattice mismatch can be reduced to 3.4%.

Furthermore, GaN growth on SiC raises another area of interest. It is commonly known that, in compound-semiconductor epitaxies, the substrate polarity often makes distinct changes in layer properties, such as surface morphology, electrical properties, and optical properties. These phenomena are thought to occur because of the difference of the surface-terminating atom affects such growth kinetics as step progression, impurity incorporation, and defect formation. We have presented a tentative model that explains some of the substrate-orientation dependence observed in the growth of GaN on (0001) and (0112) sapphire by the atomic configuration difference between the polar and nonpolar surfaces of GaN. Although the polarity plays an important role in the compound-semiconductor epitaxies as described above, only limited information is available in the literature on the polarity of GaN since most of the workers have used nonpolar sapphire substrates.

It is expected that {0001} GaN on {0001} SiC, both of which have polarity along the (0001) axis, should provide important information on this subject. Although the epitaxial relationship between the GaN layer and the SiC substrate has been established, no authors have referred to the effects of the substrate polarity, nor have the layers been sufficiently characterized. For example, some authors reported that the surfaces of GaN/SiC consist of prominent hexagonal pyramids, while others reported that they show almost featureless morphologies.

The polarity of the compound semiconductors can be determined by an anomalous dispersion effect near the absorption edge; here, the difference in the reflection intensity between the polar planes with opposite orientations is utilized. This method needs x rays with wavelengths near the absorption edge of the material and a technique with high sensitivity detection. Therefore, this method cannot be easily used for every material. Recently, Frommer proposed an alternative method for identifying the surface polarity using x-ray photoelectron spectroscopy (XPS) analysis. This method takes advantage of a binding-energy shift caused by a surface contaminant, oxygen, and makes it possible to determine the surface-terminating atom with a usual XPS system. However, it is only valid when the contaminant adsorbs onto the surface and does not diffuse into the bulk. This gives it limited usefulness, especially for materials in which oxidation readily progresses.

In this paper, we first describe metal-organic vapor-phase epitaxy (MOVPE) of GaN on each of the two polar planes of SiC. Then the polarity of GaN is discussed on the basis of XPS measurements of the layer surfaces. The problem of applying Frommer's method to GaN is also presented.

II. EXPERIMENTS

GaN was grown on {0001}-oriented 6H-SiC by a low-pressure MOVPE technique. The substrates used were low-resistivity n-type SiC grown by the Acheson method. Considering the chemically stable nature of SiC, the substrates were prepared for epitaxial growth as follows: (i) degreasing in organic solvents, (ii) oxidation in an O₂ ambient at 1100 °C for 10 h, (iii) removing the oxide in hydrofluoric acid, and then (iv) heating in a H₂ gas flow at 1150 °C just before growth. The substrate polarity can be determined by the polarity dependence of the oxidation rate.

Growth was performed at ~900–950 °C using tri-
methylgallium (TMGa) and NH₃ as source materials.²¹ To study the substrate-polarity dependence, GaN was simultaneously grown on each {0001} plane of SiC.

The photoelectron data were collected using MgKα radiation (E = 1.254 keV) of 300 W (15 kV at 20 mA). The XPS system (VG Scientific ADES 500) is equipped with a hemispherical analyzer (CLAM analyzer) and a channeltron detector. The pass energy was set at 20 eV and the energy step at 0.05 eV. The analyzer resolution for this pass energy is higher than 1.0 eV (a full width at half maximum FWHM) for Ag 3d₅/₂ with MgKα radiation. The XPS measurements were carried out at pressures below 3 × 10⁻⁹ Torr with the x-ray take-off angle fixed at 90°.

The film thickness of the samples was ~2–3 μm. For XPS surface analysis, ~0.1-μm-thick GaN epitaxial layers were also prepared to avoid surface roughening.

III. RESULTS AND DISCUSSION

A. Characterization

To assess the crystallographic orientations of GaN, reflection high-energy electron diffraction (RHEED) patterns were taken. Both of the layers on the (0001)₆ are and the (0001)₆ SiC substrates exhibit arrays of spots identical to the layer on (0001) sapphire.⁸ This proves that (0001)-oriented single-crystal films are also grown on the basal planes of SiC.

Surface morphologies of the layers were observed through a scanning electron microscope as shown in Fig. 1. The layer on (0001)₆ SiC shows a featureless, rather smooth surface in contrast with the layer on (0001)₄ SiC. The uneven surface morphology of the layer on (0001)₄ SiC, which consists of numbers of prominent hexagonal pyramids, is very similar to that of the layer on (0001) sapphire.¹³ Such structured surfaces are thought to be ascribed to a sparse surface nucleation and a small lateral growth rate.²¹ The significant change in the surface morphology indicates that the surface nucleation density and/or the lateral growth rate are greatly dependent on the substrate polarity. The disagreement in the description of the surface morphology between Refs. 9 and 13 may be due to this polarity dependence, and it is presumed that the substrates which they used have opposite surface polarity.

Photoluminescence (PL) spectra of the layers measured with a He-Cd laser excitation (λ = 325 nm) at room temperature are shown in Fig. 2. For comparison, this figure also shows the PL spectrum of MOVPE-grown undoped GaN grown on SiC. This result shows that the PL spectrum is improved on (0001) sapphire.

Layer crystallinity was characterized by x-ray rocking-curve (XRC) measurements using an x-ray diffractometer with CuKα radiation (λ = 1.54 Å). Typical widths of the (0004) diffraction of 2–3-μm-thick GaN layers on (0001) SiC and (0001) sapphire are summarized in Table I. In spite of the large difference in the lattice mismatch, the FWHM’s are similar within the experimental accuracy of the XRC measurements (~ 3 min). This result seems to show that the lattice mismatch above a certain value has little effect on the XRC width, or the effect of the decrease in the lattice mismatch might be masked because the growth condition of GaN on SiC has yet to be optimized.

B. Assignment of surface polarity by photoelectron analysis

The substrate-polarity dependence of the surface morphology and photoluminescence property suggests that the layer polarity changes in accordance with the substrate po-

![Figure 1](https://via.placeholder.com/150)  
**FIG. 1.** Surface morphology of GaN; (a) (0001)₆ SiC; (b) (0001)₄ SiC.

![Figure 2](https://via.placeholder.com/150)  
**FIG. 2.** Room-temperature PL spectra of GaN with a He-Cd laser excitation (λ = 325 nm); (a) (0001)₆ SiC, (b) (0001)₄ SiC.

| TABLE I. FWHM's of the (0004) diffraction of ~2–3-μm-thick GaN on (0001)₆ SiC, (0001)₄ SiC, and (0001) sapphire. |
|-----------------|-----------------|-----------------|
|                 | (0001)₆ SiC     | (0001)₄ SiC     | (0001) sapphire |
| (0001)₆ SiC     | 12              | 15              | ~12–15          |
| (0001)₄ SiC     |                 |                 |                 |
| (0001) sapphire |                 |                 |                 |

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larity. To verify this idea, the layer surfaces were examined by an XPS technique.

The energy in the XPS spectrum sometimes needs correction for the charging effect with photoelectron emission. However, energy correction is not necessary here since the total resistivity of the substrate and the epitaxial layer was measured by the van der Pauw method and found to be 1–2 Ω cm.

A typical photoelectron spectrum from GaN is shown in Fig. 3. There are observed gallium and nitrogen peaks (Ga 3d, Ga 3p, Ga 3s, N 1s, Ga 2p_{3/2} and Ga 2p_{1/2}) as well as carbon and oxygen peaks related to surface contaminants. The Ga 2p_{3/2} and Ga 3d photoelectron spectra are shown in Fig. 4. It should be noted that both of the gallium photoelectron spectra from the layer on (0001)_c SiC shift towards higher energies. Frommer reported that an additional higher-energy peak appears in the Ga 2p_{3/2} spectrum from (111)_Ga GaP, when the Ga 2p_{3/2} spectrum from (111)_P GaP can be fitted to a single peak. He assigned this higher-energy peak to surface Ga—O bonds and explained this phenomenon by the following model. As shown in Fig. 5, the surface-terminating gallium on the (111)_Ga plane can bond to surface-adsorbed oxygen whereas there is no exposed gallium which can readily make Ga—O bonds on the P-terminated (111)_P plane. It is also reported for GaAs that surface oxidation causes a higher-energy peak in the Ga 3d spectrum from the (111)_Ga plane.

The electronegativity difference between nitrogen and oxygen is significantly smaller than the differences between phosphorus and oxygen and between arsenic and oxygen, as shown in Table II. The insufficient difference in the electronegativity between nitrogen and oxygen leads to a small binding-energy shift and makes it difficult to resolve the present spectra into the contributions from the Ga—N and Ga—O bonds. However, the higher-energy shifts of the gallium spectra are considered to result from the difference of surface oxidation activity between the layers on the (0001)_Si and (0001)_C SiC substrates.

It can be also found in Fig. 4 that the higher-energy shift of the Ga 3d spectrum is smaller than that of the Ga 2p_{3/2} spectrum. The Ga 3d photoelectron has a larger kinetic energy, hence a larger escaping depth, and is less sensitive to the surface than the Ga 2p_{3/2} photoelectron. This also supports the attribution of the higher-energy shifts to the surface Ga—O bonds. As a result, it can be concluded that the GaN surface on (0001)_c SiC is more heavily oxidized than that on (0001)_Si SiC.

![Fig. 3. Photoelectron survey spectrum from GaN on (0001)_Si SiC using MgKα (E = 1.254 keV) radiation.](image)

![Fig. 4. (a) Ga 2p_{3/2} and (b) Ga 3d photoelectron spectra from GaN grown on (0001)_Si and (0001)_C SiC.](image)

![Fig. 5. Frommer's model of the surface oxidation of (111)_Ga and (111)_P GaP.](image)

**Table II. Electronegativities of O, N, P, As, and Ga.**

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>N</th>
<th>P</th>
<th>As</th>
<th>Ga</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.5</td>
<td>3.0</td>
<td>2.1</td>
<td>2.0</td>
<td>1.13</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.64</td>
<td>1.57</td>
<td>1.6</td>
<td>b</td>
</tr>
</tbody>
</table>

*After Pauling (Ref. 28).*

*After Phillips (Ref. 29).*
Next, we will discuss the surface polarity of GaN/SiC based on the XPS data. It is necessary to evaluate the surface oxidation depth in order to see whether the surface oxide is a monatomic layer as Frommer showed for GaP. This can be estimated from the intensity ratio of the O 1s to N 1s photoelectrons, which come from the gallium oxide and GaN, respectively. For this purpose, we suppose a flat and uniform oxide layer with a thickness d, as illustrated in Fig. 6. The intensity ratio of the O 1s to N 1s peaks, $I_{O \, 1s}/I_{N \, 1s}$, is calculated as

$$\frac{I_{O \, 1s}}{I_{N \, 1s}} = \frac{n_{O_{\text{oxide}}}^{\text{oxide}} \lambda_{O \, 1s} \lambda_{O_{\text{oxide}}}}{n_{N_{\text{oxide}}}^{\text{oxide}} \lambda_{N \, 1s} \lambda_{N_{\text{oxide}}}} \exp\left(-\frac{d}{\lambda_{O \, 1s}}\right),$$

(1)

where $\sigma_{O \, 1s}$ and $\sigma_{N \, 1s}$ are the photoionization cross sections of the O 1s and N 1s electrons, respectively, $\lambda_{O \, 1s}$ and $\lambda_{N \, 1s}$ are the mean free paths of the O 1s and N 1s photoelectrons. The superscript on $\lambda$ denotes the material in which the photoelectrons suffer attenuation by inelastic scattering. The N atomic fraction in GaN, $n_{N_{\text{oxide}}}^{\text{oxide}}$, is 0.5. The O concentration in the oxide, $n_{O_{\text{oxide}}}^{\text{oxide}}$, was presumed to be 0.6 from the formula of Ga$_2$O$_3$.

The mean free paths and photoionization cross sections of species relating to the present experiments are listed in Table III. From Penn’s formulas, $\lambda_{N \, 1s}$ and $\lambda_{O \, 1s}$ are estimated to be 21.82 and 9.2 Å, respectively. The O 1s and N 1s photoionization cross sections are 0.063 and 0.039 Å$^2$. By substituting these data in Eq. (1), d is calculated at 9 Å when $I_{O \, 1s}/I_{N \, 1s}$ is 0.8 from the survey spectrum in Fig. 3.

This result means that oxygen diffuses into GaN layers to a depth of a few atomic layers, in contrast to Frommer’s model. Consequently, Frommer’s model cannot be directly applied to GaN. To determine the surface polarity from the XPS measurements mentioned above, there is need to examine the mechanism of the surface oxidation: (i) adsorption onto the surface and (ii) diffusion into the bulk. These are considered as follows.

### TABLE III. Kinetic energies, mean free paths, and photoionization cross sections of the photoelectrons relating to the present study.

<table>
<thead>
<tr>
<th>Kinetic energy (eV)</th>
<th>Mean free path (Å)</th>
<th>Photoionization cross section (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga 3d</td>
<td>1236</td>
<td>29</td>
</tr>
<tr>
<td>N 1s</td>
<td>855</td>
<td>21</td>
</tr>
<tr>
<td>O 1s</td>
<td>722</td>
<td>19</td>
</tr>
<tr>
<td>Ga 2p$_{1/2}$</td>
<td>138</td>
<td></td>
</tr>
</tbody>
</table>

*MgKα radiation.*

*Calculated by Penn’s formulas (Refs. 30 and 31).*

*After Ref. 32.*

1. Oxidation of elements is determined by their ionization tendencies; an element with a stronger tendency to donate an electron more readily makes bonds with oxygen. Judging from the ionization potentials and electronegativities of gallium and nitrogen, $^{33}$ gallium has a stronger electron-donating tendency than nitrogen. Consequently, it is plausible that the surface-terminating gallium more readily bonds to oxygen than does the surface-terminating nitrogen.

2. The diffusion constant of oxygen in GaN is considered to be determined by the concentration of the nitrogen vacancy. This is based on the assumption that the group-VI impurity, oxygen, preferentially occupies the group-V sites. As described in Ref. 21, GaN layers grown in the [0001]$_{Ga}$ direction are deduced to have larger nitrogen vacancies than those grown in the [0001]$_N$ direction. Therefore, the layer terminated with gallium is thought to have a larger oxygen diffusion constant than the layer terminated with nitrogen.

From the above considerations, GaN terminated with gallium can be expected to suffer more surface oxidation than GaN terminated with nitrogen. In conclusion, GaN layers on (0001)$_C$ and (0001)$_Si$ SiC substrates are terminated with gallium and nitrogen, respectively.

### IV. SUMMARY

GaN was grown on the basal planes of SiC by MOVPE. The surface morphology and luminescence property are strongly dependent on the substrate polarity. Differences in the binding-energy shifts of the Ga photoelectron spectra lead to the conclusion that GaN epitaxial layers on (0001)$_Si$ and (0001)$_C$ SiC are terminated with nitrogen and gallium, respectively. This seems to show that the surface morphology and the photoluminescence property are influenced by the layer polarity. This will be an important result for improving crystal quality and clarifying the growth mechanism of GaN.

Frommer’s assignment method is not universally applicable in that it assumes a monatomic layer surface oxide. However, by comparing the ionization tendency between the constituent elements and the oxygen diffusion constant between the two polar surfaces, we can determine the surface polarity by the XPS analysis even when Frommer’s assumption is not applicable.

### ACKNOWLEDGMENTS

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