Self-forming and self-decomposing gallium oxide layers at the GaN/Al2O3 interfaces

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We examine the energy band diagram at the interface between GaN and Al2O3 containing negatively-charged oxygen interstitial (Oi−) defects. At a p-type GaN (p-GaN)/Al2O3 interface, oxygen atoms and electrons are emitted from the Oi− defects causing interfacial oxidation resulting in the self-formation of a p-GaN/Ga2O3/Al2O3 structure. On the other hand, such reactions do not occur at an n-type GaN (n-GaN)/Al2O3 interface. Moreover, when n-GaN/Ga2O3/Al2O3 structures are formed, the Ga2O3 layers spontaneously decompose to form Oi− defects in the Al2O3. Consequently, our proposed Ga2O3 formation mechanism gives completely different results for p-GaN/Ga2O3 and n-GaN/Al2O3 interfaces.

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Gallium Nitride (GaN) power devices can be operated with high electric fields and high power densities, such that devices with lower energy consumption than those using Si or SiC can be realized.1,2 In particular, normally-off GaN metal–oxide–semiconductor field-effect-transistors (MOSFETs) with high threshold voltages can be fabricated, and these have been studied because of their advantages in terms of safety and operational stability.3–5 The deposition of dielectric films on GaN is one of the essential processes required to make MOS structures. To obtain high-performance GaN MOS devices with high carrier mobility and large breakdown fields, it is important to select an appropriate dielectric and to optimize the process by which it is formed. In Si and SiC MOS devices, SiO2 dielectric films are grown by thermal oxidation,6,7 and defect-free Si/SiO2 interfaces can be formed for Si MOS devices. In the case of GaN, the dielectric layers for MOS devices are formed by deposition, and many studies have been done on various materials for this.8–29 Although there are several candidates for the dielectric, it is only with materials that have a large conduction band offset (CBO) or valence band offset (VBO) for GaN that a large threshold voltage can be obtained. Of these, SiO2 and Al2O3 have particularly large bandgaps. Since both SiO2 and Al2O3 have large VBO (3.0 eV~) and CBO (2.0 eV~) for GaN,28,29 it is possible to utilize them for both n-channel and p-channel MOSFETs, and the formation of interfaces with low interfacial state densities have been reported.28,29 GaN/Insulator interfacial structures have been examined in a number of experiments, and the formation of a Ga2O3 interlayer at a GaN/SiO2 interface has been reported.30 In previous work, we proposed a mechanism for the formation of the Ga2O3 interlayer at an n-type GaN (n-GaN)/SiO2 interface.31 In this mechanism, electron transfer from n-GaN to SiO2 and the formation of oxygen vacancy (Vo) defects in the SiO2 induced an energy gain, causing interfacial oxidation and resulting in the spontaneous formation of Ga2O3. As in the case of GaN/SiO2 interfaces, we guess that there are some mechanisms by which a Ga2O3 interlayer spontaneously can be formed at a GaN/Al2O3 interfaces. Therefore, to discuss the reactions and structure arising at the GaN/Al2O3 interface, we focus on oxygen interstitial (Oi) defects in Al2O3, and consider the band offset and the position of the Fermi level (Eform) at the interface. As a result, we find that Ga2O3 layers are spontaneously formed at p-GaN/Al2O3 interfaces, where the Oi defects trigger the interfacial reaction, but are not formed at n-GaN/Al2O3 interfaces. Moreover, we also find that the Ga2O3 layer formed between n-GaN and Al2O3 spontaneously decreases or disappears.

First, we discuss the Oi defects in Al2O3. In this study, we utilize Al2O3 with the corundum structure (α-Al2O3) which is one of the stable forms of the crystal with a bandgap of 8.8 eV. Theoretical calculations have predicted that Oi defects arise in α-Al2O3, and that these defects have a split interstitial structure with O–O bonds in a neutral state.32–34 The formation energy of these defects (EformOi) is given by

\[ E_{\text{form}}^{O_i} = E_{\text{Oi}} - (E_{\text{Bulk}} + \frac{1}{2} \mu_{O_i}) \]

where Ebulk and EOi are the total energies of α-Al2O3 without and with an Oi defect, and \( \mu_{O_i} \) is the chemical potential of the O2 molecules. EformOi is about 4.0 eV.33,34 In addition, it has been reported that an Oi defect traps two electrons and changes its charge state from \( q = 0 \) to \( q = -2 \) (Oi2− defect), resulting in the formation of defect a level at the valence band maximum (VBM) + 1.0 eV.33

Next, we discuss the p-GaN/Al2O3 interface. The band offset of this interface is shown in Fig. 1(a). We assume that the Fermi level of p-GaN is located at the VBM. Since the Fermi level is located above the Oi2− defect level, when the p-GaN/Al2O3 interface is formed, electrons can transfer from the GaN to the defect level and the Oi defects become negatively-charged Oi (Oi2−) defects [Fig. 1(b)]. The formation energy of an Oi2− defect is estimated by summing the formation energy of an Oi defect in Al2O3 and the energy gain induced by electron transfer from the Fermi level of the p-GaN layer to the defect level. It is possible to move two electrons per Oi defect, and the energy gain obtained by electron transfer is equal to the difference between the Fermi level and the defect level (about 2.4 eV/electron). Thus, the formation energy of Oi2− defects (EformOi2−) is given by

\[ E_{\text{form}}^{O_i^2-} = E_{\text{Oi}} - (E_{\text{Bulk}} + \frac{1}{2} \mu_{O_i}) + 2.4 \text{ eV} \]
$E_{\text{form}}^{O_2^-} = 4.0 \text{ eV} - 2 \times 2.4 \text{ eV} = -0.8 \text{ eV}$, indicating that the formation of $O_2^{2-}$ defects induces a small energy gain at the p-GaN/Al$_2$O$_3$ interface. In other word, O atoms are released to the interface when p-GaN forms an interface with Al$_2$O$_3$ containing $O_i^2$ defects by giving energy of 0.8 eV. The emission of an O atom, taking electron transfer into account, is described by the following reaction

$$\text{Al}_2\text{O}_3(O_i^2-) \rightarrow \text{Al}_2\text{O}_3 + \frac{1}{2}\text{O}_2 + 2e^-.$$  

(2)

In order to induce this emission reaction, a mechanism to generate energy (0.8 eV) at the interface is required.

Now, we discuss the formation of the Ga$_2$O$_3$ layer. When O atoms are released from the Al$_2$O$_3$, they give rise to oxidation at the interface. The energy gain due to thermal oxidation of GaN ($E_{\text{oxi}}$) shown by the following reaction has been reported as being $E_{\text{oxi}} = 3.20 \text{ eV}^{(2)}$

$$\text{GaN} + \frac{5}{4}\text{O}_2 \rightarrow \frac{1}{2}\text{Ga}_2\text{O}_3 + \text{NO}.$$  

(3)

This energy gain means that thermal oxidation of GaN proceeds spontaneously when the $O_2$ molecules have larger energy than the activation energy. From Eqs. (2) and (3), the complete reaction leading to oxidation at the interface is as follows

$$\text{GaN} + \frac{5}{2}\text{Al}_2\text{O}_3(O_i^2-) \rightarrow \frac{1}{2}\text{Ga}_2\text{O}_3$$

$$+ \frac{5}{2}\text{Al}_2\text{O}_3 + \text{NO} + 5e^-.$$  

(4)

The formation energy for this reaction ($E_{\text{form}}^{\text{all}}$) can be obtained and is $E_{\text{form}}^{\text{all}} = 2.5 \times (0.8 \text{ eV}) - 3.2 \times 0.8 \text{ eV} = -1.2 \text{ eV}$, which means that the energy loss due to electron transfer is compensated by the energy gain by oxidation. Thus, this analysis of the $O_i$ defects in Al$_2$O$_3$ and the electron transfer reveal that an interfacial Ga$_2$O$_3$ layer self-forms at the p-GaN/Al$_2$O$_3$ interface [Fig. 1(c)]. In thermal oxidation of GaN described in Eq. (3), we have considered that GaN is completely oxidized to become Ga$_2$O$_3$. However, when some parts of GaN are not oxidized, there is a possibility that a GaON layer is formed instead of Ga$_2$O$_3$. In this case, oxidation reaction is described as follows

$$\text{GaN} + \frac{5}{4}\alpha\text{O}_2 \rightarrow \frac{1}{2}\text{Ga}_2\text{O}_3\alpha\text{N}_2(1-\alpha) + \alpha\text{NO},$$  

(5)

where $\alpha$ ranges from 0.0 to 1.0, and energy gain by this reaction is $E_{\text{oxi}} = \alpha \times 3.20 \text{ eV}$. By combining Eqs. (2) and (5), the formation energy of all reaction can be obtained and is $E_{\text{form}}^{\text{all}} = 2.5 \times (0.8 \text{ eV}) - 3.2 \times \alpha \text{ eV} = (2.0 - 3.2 \times \alpha) \text{ eV}$. Accordingly, our proposed interfacial oxidation mechanism can form GaON layer instead of Ga$_2$O$_3$ when $\alpha$ is larger than 0.625.

So far, we have focused only the p-GaN/Al$_2$O$_3$ interface; now, we focus on the n-GaN/Al$_2$O$_3$ interface and discuss the formation of a Ga$_2$O$_3$ interlayer by the above mechanism. We assume that the Fermi level is located close to the CBO of GaN [Fig. 2(a)]. Since the Fermi level in n-GaN is located 3.3 eV above that in p-GaN, it is considered that the $O_i$ defects trap electrons and change to $O_i^2$ defect structures as with the p-GaN/Al$_2$O$_3$ system [Fig. 2(b)]. However, as the Fermi level rises, the energy loss due to electron transfer from the $O_i^2$ defect level to the Fermi level also increases, resulting in an energy loss of 7.4 eV in Eq. (2), and an energy loss of 15.3 eV occurs for the whole reaction, including interfacial oxidation, given by Eq. (4). Accordingly, a Ga$_2$O$_3$ layer does not self-form at the n-GaN/Al$_2$O$_3$ interface.

On the other hand, this also indicates that Al$_2$O$_3$ on n-GaN can easily form $O_i^2$ defects when O atoms are supplied to the interface due to the energy gained by electron transfer. Now, we consider the n-GaN/Ga$_2$O$_3$/Al$_2$O$_3$ structure formed by surface oxidation during the deposition of Al$_2$O$_3$. We assume that some O atoms are supplied by the following
decomposition reaction of the interfacial Ga\nobreakspace{}2O\nobreakspace{}3 layer, resulting in the formation of $O^{2-}_i$ defects with a large amount of energy gain:

$$\text{Ga}_2\text{O}_3(\text{solid}) \rightarrow \text{Ga}_2\text{O}_3(\text{gas}) + O_2(\text{gas}).$$

The Gibbs free energy of formation in this reaction has been reported to be 1.9 eV.\sup{35} When the emitted O atoms form $O_i$ defects in Al$_2$O$_3$ and these change to $O^{2-}_i$ defects by electron transfer from the Fermi level of n-GaN, the formation energy is calculated to be $E^{\text{form}}_{O^{2-}_i} = 4.0 \text{ eV} - 2 \times 5.7 \text{ eV} = -7.4 \text{ eV}$. The whole reaction is described by the following:

$$\text{Ga}_2\text{O}_3(\text{crystal}) + 2\text{Al}_2\text{O}_3 + 4\text{e}^- \rightarrow \text{Ga}_2\text{O}_3(\text{gas}) + 2\text{Al}_2\text{O}_3(\text{O}^{2-}_i).$$

The formation energy of this complete reaction is $E^{\text{all}}_{\text{form}} = 2 \times (-7.4 \text{ eV}) + 1.9 \text{ eV} = -12.9 \text{ eV}$. This result means that the energy loss of the decomposition reaction is compensated for by the formation of $O^{2-}_i$ defects. Therefore, the Ga$_2$O$_3$ layer between n-GaN and Al$_2$O$_3$ spontaneously decreases or disappears, and further $O^{2-}_i$ defects are formed in the Al$_2$O$_3$. These results clearly show that p-GaN and n-GaN induce completely different interfacial reactions (self-formation/self-decomposition of a Ga$_2$O$_3$ layer) with Al$_2$O$_3$ (Fig. 3). When the GaON layer is formed instead of the Ga$_2$O$_3$ at the interface, decomposition reaction is described as follows:

$$\text{Ga}_2\text{O}_3_{\alpha\beta}N_{2(1-\alpha)}(\text{solid}) \rightarrow \text{Ga}_2\text{O}_3(\text{gas}) + \frac{(3\alpha - 1)}{2}O_2(\text{gas}) + (1 - \alpha)N_2(\text{gas}).$$

By considering the difference in the Gibbs free energy between the O$_2$ and N$_2$ molecules (0.2 eV at 1500 K),\sup{36} formation energy in this reaction is estimated to be $1.9 \text{ eV} + 2(1 - \alpha)/2 \times 0.2 \text{ eV}$. In addition, since the number of $O^{2-}_i$ defects in Al$_2$O$_3$ decrease, the formation energy of whole reaction described in Eq. (7) changes to $E^{\text{all}}_{\text{form}} = (3\alpha - 1) \times (-7.4 \text{ eV}) + 1.9 \text{ eV} + 2(1 - \alpha)/2 \times 0.2 \text{ eV} = (9.5 - 22.4 \times \alpha) \text{ eV}$ and becomes smaller than the case of Ga$_2$O$_3$ interlayer. Accordingly, when $\alpha$ is larger than 0.424, GaON decomposition reaction at the n-GaN/Al$_2$O$_3$ interface can occur, but when it is smaller than 0.424, GaON can exist stably at the interface. In some experimental reports, Ga$_2$O$_3$ on the n-GaN has been studied by XPS spectra and they showed the reduction of the peak derived from Ga-O bond by forming n-GaN/Ga$_2$O$_3$/Al$_2$O$_3$, which is consistent with our prediction on Ga$_2$O$_3$ decomposition.\sup{37,38}
Finally, we discuss the formation of interfacial dipoles induced by electron transfer at GaN/Al2O3 interfaces. As shown in Fig. 1(b), electron transfer from the Fermi level of GaN to the Oi defect level induces interfacial dipoles. However, in the case of p-GaN/Al2O3 interfaces, since a Ga2O3 interlayer is formed and electrons return from the Oi defect level to the Fermi level of p-GaN, the interfacial dipoles disappear and the band bending is eliminated [Fig. 1(c)]. On the other hand, the interfacial dipoles are not eliminated from n-GaN/Al2O3 interfaces [Fig. 2(b)]. The magnitude of the interfacial dipoles depends on the number of electrons transferred from GaN to the O2− defect level, which is determined by the density of O defects in Al2O3. The Oi defect density is extremely high, the electron transfer stops when the O2− defect level reaches the Fermi level due to the band bending. Since the Fermi level of n-GaN is located 5.7 eV above the O2− defect level, a large number of electrons can be transferred, resulting in large band bending [Fig. 2(c)]. In other words, we can obtain n-GaN/Al2O3 interfaces with larger CBO by forming Al2O3 with higher Oi defect densities on n-GaN, and this can lead to lower gate leakage currents in MOSFETs.

In this paper, we have focused on the Oi defects and interfacial reactions caused by them, and revealed that p-GaN and n-GaN shows completely different interfacial structures. On the other hand, it is considered that V0 defects also cause large effects for the electronic characteristics at the interfaces and in the oxides. In our previous work, we proposed interfacial reaction mechanism induced by the V0 defect formation at the n-GaN/SiO2 interfaces. However, since formation energy of the V0 defects in Al2O3 is very large, such the interfacial reaction do not occur at the n-GaN/Al2O3 interfaces. Thus, although the V0 defects are very important, they do not cause different interfacial reactions for both p-GaN and n-GaN.

In conclusion, on the basis of an examination of the Oi defects in Al2O3 and the position of the Fermi level at p-GaN/Al2O3 and n-GaN/Al2O3 interfaces, we have proposed a mechanism for interfacial oxidation and revealed the differences between the reactions taking place and the structures formed at these two different interfaces. For p-GaN/Al2O3 interfaces, O atoms forming the O2− defects are released and induce interfacial oxidation, resulting in the formation of a p-GaN/Ga2O3/Al2O3 structure. This reaction does not occur at n-GaN/Al2O3 interfaces due to the large energy required to transfer electrons from the O2− defect level to the Fermi level. On the contrary, when an n-GaN/Ga2O3/Al2O3 structure is formed, the Ga2O3 layer spontaneously decomposes to form O2− defects. Electron trapping at the O2− defect level causes interfacial dipoles and this makes the CBO between n-GaN and Al2O3 large, so that larger CBO is obtained by forming Al2O3 with a higher Oi defect density. This suggests that we can reduce the gate leakage current in n-GaN MOSFETs by using O-rich Al2O3.