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Platinum-enhanced oxidation of GaAs

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Platinum- (Pt-) enhanced oxidation of GaAs has been investigated using high-resolution x-ray photoelectron spectroscopy (XPS). A thin oxide layer of thickness in the range 0.5–1.6 nm is formed on the GaAs surface and then a Pt layer is deposited on it. Heat treatments at 200 °C in oxygen increase the oxide thickness to 2.4–4.7 nm. Measurements of the take-off angle dependence of the XPS spectra show that the oxide layer has nonuniform layerlike structure, consisting of gallium oxide, arsenic oxide, and elemental arsenic; each oxide component is present between the Pt overlayer and the Si substrate, but is not on the Pt layer. Arsenic oxide is present just below the Pt layer, while gallium oxide and elemental arsenic are present below it. Oxygen atoms produced at the Pt surface are suggested to be the diffusing species through the Pt layer. On the other hand, the moving species in the oxide layer are arsenic and gallium atoms as well as oxygen atoms. The oxide thickness depends on the nature of the oxide layer formed before the Pt deposition, and is mainly attributed to the different composition of the oxide layers. Gallium oxide is suggested to suppress the diffusion of the reacting species. [S0163-1829(97)09136-4]

I. INTRODUCTION

Oxidation of group IV and III-V semiconductors at low temperatures attracts much interest not only from the academic viewpoint but also for the technological application to metal-oxide-semiconductor (MOS) devices. Metal-promoted oxidation is a good candidate for the low-temperature oxidation method. For oxidation of GaAs as well as Si, gold (Au),[1] chromium (Cr),[2,3] aluminum (Al),[4,5] alkali metals,[5–8] and rare-earth metals[9,10] are used as oxidation catalysts. In the presence of a Au overlayer, GaAs and Au react to form GaAu and As, and the oxygen exposure results in the formation of As_2O_3 and Ga_2O_3 on the Au layer.[1] In the case of a Cr overlayer, interdiffusion of Cr occurs, forming arsenidelike species, and the oxygen exposure leads to the formation of As_2O_3-like and Ga_2O_3-like species. However, these techniques cannot be applied to the device technology because the oxide layers are formed on the surface, but not between the metal overlayer and the GaAs substrate.

Alkali metals such as K, Cs, and Na greatly enhance oxygen adsorption on the GaAs surfaces and the enhancement is attributed to the charge transfer from alkali metals to GaAs, which in turn results in the charge transfer from GaAs to oxygen forming $O_2{}^-$ or $O_2{}^{2-}$, i.e., strong oxidizing species.[6,7] Another possibility is the formation of alkali-metal oxide, which easily changes into oxide of GaAs by heating.[6,8] Using rare-earth metals such as Sm (Ref. 9) and Yb (Ref. 10), an oxide layer is also formed between the metal and GaAs. However, the oxide layers formed by these methods are too thin for the device application.[5–10]

We have recently developed a method for the formation of silicon oxide layers between metal overlayers and the Si substrates at low temperatures by use of the catalytic activity of the platinum[11–13] (Pt) or palladium[14] (Pd) overlayers. In this method, a thin oxide layer of ca. 1 nm thickness is formed before the Pt (or Pd) deposition to prevent the direct contact between the Pt (or Pd) layer and the Si substrate, thus avoiding the silicide formation. Heat treatments at 300–400 °C in oxygen increase the oxide thickness to 4–5 nm. The enhanced oxidation is attributed to the formation of oxygen atoms at the Pt (or Pd) surface, which diffuse to the oxide/Si interface and react there. In the present study, this noble method using the catalytic activity of Pt is applied to the oxidation of GaAs at low temperatures.

II. EXPERIMENT

Si-doped n-type GaAs(100) wafers with a donor density of 4.1×10^{16} cm^{-3} were cut into 5×5-mm^2 pieces. The wafers were cleaned in boiling acetone and distilled water and then etched in a 5 wt. % potassium hydroxide (KOH) aqueous solution at room temperature for 3 min. For some specimens, the wafers were heated at 500 °C for 5 min in an oxygen atmosphere. Then, an approximately 3-nm-thick platinum (Pt) layer was deposited by an electron beam evaporation method. The substrate temperature and the evaporation rate were 50 °C and 0.01 nm/s, respectively. In some cases, the specimens were heat treated at 200 °C for 1 h in oxygen after the Pt deposition. The specimens thus fab-

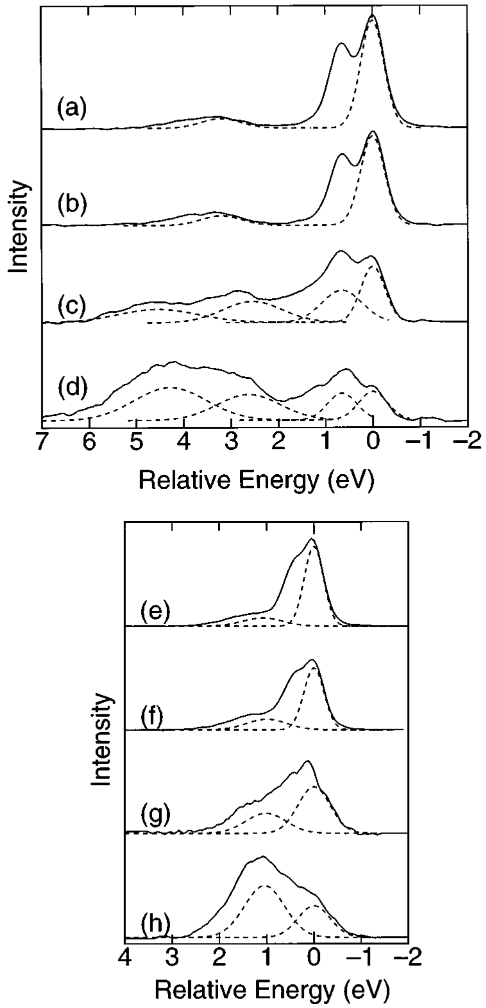

FIG. 1. XPS spectra in the As 3*d* [spectra (a)–(d)] and Ga 3*d* [spectra (e)–(h)] regions for the oxide layers formed in the KOH solution: (a), (e) with no Pt layer and no heat treatment; (b), (f) with no Pt layer after the heat treatment at 200 °C in oxygen; (c), (g) with a Pt layer and no heat treatment; (d) and (h) with a Pt layer after the heat treatment at 200 °C in oxygen.

ricated were exposed to air for ~1 h and then transferred to a UHV chamber with a base pressure of 1.5×10^{-10} Torr for x-ray photoelectron spectroscopy (XPS) measurements.

XPS spectra were measured using a VG SCIENTIFIC ESCALAB 220i-XL spectrometer with a monochromatized Al $K\alpha$ radiation source. X-rays were irradiated at the incident angle of 45° and photoelectrons were collected in the surface-normal direction, i.e., the take-off angle, θ_t of 90°, or at $\theta_t=45°$. The electron pass energy in a semispherical analyzer was set at 10 eV. For measuring the XPS spectra of the specimens with (or without) a Pt overlayer, photoelectron signals were accumulated for ~20 min (or ~5 min). Prolonges x-ray irradiation was found to decompose As oxide, especially in cases where the Pt film was deposited on the KOH-treated GaAs surface.[15] In the XPS measurements of the specimens with the Pt overlayer, the Pt layer was earthed.

III. RESULTS

Figure 1 shows the XPS spectra in the As 3*d* [spectra (a)–(d)] and Ga 3*d* [spectra (e)–(h)] regions for the GaAs surfaces treated with the KOH solution. For the GaAs surface with no heat treatment and no Pt deposition [spectrum (a)], sharp doublet peaks due to As $3d_{5/2}$ and $3d_{3/2}$ levels of the GaAs substrate were observed, and a broad peak was present at 3.3 eV with respect to the substrate As $3d_{5/2}$ peak, which was attributed to As^{3+} of As_2O_3 [hereafter abbreviated to $As^{3+}(As_2O_3)$].[16–19] In the Ga 3*d* region [spectrum (e)], double structure due to the Ga $3d_{5/2}$ and $3d_{3/2}$ levels of the substrate was also observed. A broad shoulder was present in the higher-energy side and attributed to $Ga^{3+}(Ga_2O_3)$.[16,20] The total oxide thickness was roughly estimated to be 0.5 nm. When this surface was heated to 200 °C in oxygen for 1 h, the intensities of the peaks due to As_2O_3 and Ga_2O_3 increased slightly with the peak energies almost unchanged [spectra (b) and (f)]. The total oxide thickness was estimated to be 0.7 nm.

The energies of the substrate peaks depended on the sample preparation methods, mainly due to the change in the band bending in GaAs. In the present report, however, the As $3d_{5/2}$ and Ga $3d_{5/2}$ peaks of the GaAs substrate were taken as the energy references for simplicity. The detailed discussion of the energy of the substrate peaks will be given elsewhere.

The dotted lines in the As 3*d* and Ga 3*d* spectra show the As $3d_{5/2}$ and Ga $3d_{5/2}$ components obtained from the curve decomposition. In the curve decomposition method, the background was subtracted using the Shirley method, i.e., the method in which the inelastic background intensity at binding energy E_b was assumed to be proportional to the integration of the signal intensity with the energy lower than E_b. For the spectra in the As 3*d* region of the specimens with the Pt overlayer, a broad background due to the Pt overlayer in this energy region was measured and this background was subtracted from the As 3*d* spectra. Then, the observed spectra were fitted by several peaks considering that the intensity ratio of the $3d_{5/2}$ component was $\frac{2}{3}$ and the energy splitting between these components was 0.70 eV for As 3*d* and 0.44 eV for Ga 3*d*. (The peaks only due to the As $3d_{5/2}$ and Ga $3d_{5/2}$ components are included in the figure for simplicity.) The peak energies shown below were determined by the curve decomposition.

When a Pt layer was deposited on the KOH-treated GaAs surface, prominent changes occurred in the XPS spectra. In the As 3*d* region, new peaks appeared at 4.5 and 0.65 eV [spectrum (c)], and they were attributed to As^{5+} of As_2O_5 and As^0 of elemental As, respectively.[16–18] The structure of the Ga 3*d* spectrum changed because of an increase in the intensity of the $Ga^{3+}(Ga_2O_3)$ peak [spectrum (g)].

When the Pt-covered GaAs surface was heated at 200 °C in oxygen for 1 h, the intensity of the $As^{5+}(As_2O_5)$ peak increased markedly, and that due to GaAs decreased [spectrum (d)]. The intensity of the $Ga^{3+}(Ga\ _2O_3)$ peak became much stronger than that of the substrate peak [spectrum (h)]. The total thickness of the oxide layer after the heat treatment at 200 °C was estimated to be 4.7 nm, as described later. Comparison of spectra (d) and (h) with spectra (b) and (f), i.e., the spectra for the specimens with and without a Pt layer after the heat treatment at 200 °C in oxygen, clearly shows that the Pt overlayer greatly enhanced the oxidation of GaAs.

The first row in Table I shows the XPS intensity ratio R_{ox} of the oxide species to that of the GaAs substrate measured at the take-off angle θ_t of 90° for the specimens in which

TABLE I. Ratio of the areal intensity of the oxide peak to that of the substrate peak R_{ox} and the thickness of the oxide layer d for the ⟨Pt/KOH oxide/GaAs(001)⟩ specimens with no heat treatment.

	As	As_2O_3	As_2O_5	Ga_2O_3
$R_{\mathrm{ox}}(90°)$	0.95	0.93	0.81	0.54
$R_{\mathrm{ox}}(45°)/R_{\mathrm{ox}}(90°)$	1.1	1.5	1.8	1.6
d (nm)	1.0	0.8[c]	0.6	0.5[c]
Calc. $R_{\mathrm{ox}}(45°)/R_{\mathrm{ox}}(90°)$[a]	1.6	1.9	2.2	1.9
Calc. $R_{\mathrm{ox}}(45°)/R_{\mathrm{ox}}(90°)$[b]	1.6	1.9	4.6	1.9

[a] Values for the ($Pt/As_2O_5/As_2O_3+Ga_2O_3/As/GaAs$) structure.
[b] Values for the ($As_2O_5/Pt/As_2O_3+Ga_2O_3/As/GaAs$) structure.
[c] Partial oxide thickness for the ($As_2O_3+Ga_2O_3$) layer (see the text for details).

they were treated with the KOH solution and no heat treatments were performed after the Pt deposition. The second row in Table I shows R_{ox} for $\theta_t = 45°$ divided by that for $\theta_t = 90°$, $R_{\mathrm{ox}}(45°)/R_{\mathrm{ox}}(90°)$. It can be concluded from the $R_{\mathrm{ox}}(45°)/R_{\mathrm{ox}}(90°)$ values that the oxide layer has nonuniform layerlike structure composed by various oxide species, as described below. For oxide layers consisting of several layers, R_{ox} of a certain oxide species increases with a decrease in θ_t for the following two reasons: (i) Enlarged path of photoelectrons in the oxide layer due to the oblique incidence and (ii) enlarged path of photoelectrons in the layers present between the oxide layer and the GaAs substrate. Therefore, it is expected that due to effect (ii), the larger the distance between the GaAs substrate and the oxide layer, the larger the $R_{\mathrm{ox}}(45°)/R_{\mathrm{ox}}(90°)$ value.

It is seen from Table I that $R_{\mathrm{ox}}(45°)/R_{\mathrm{ox}}(90°)$ had different values for different oxide components, i.e., almost unity for As^0, ~1.5 for $As^{3+}(As_2O_3)$ and $Ga^{3+}(Ga_2O_3)$, and ~1.8 for $As^{5+}(As_2O_5)$, verifying the nonuniform layerlike structure. On the basis of this result, the above consideration shows that the most probable structure is ($Pt/As_2O_5/As_2O_3+Ga_2O_3/As/GaAs$). Once the structure of the oxide layer is determined, the thickness of each oxide component, d, can be estimated using the following equation:

$$R_{\mathrm{ox}}(90°) = \frac{D_{\mathrm{oxide}}\sigma_{\mathrm{oxide}}\int_0^d \exp(-x/\lambda_{\mathrm{oxide}})dx}{D_{\mathrm{GaAs}}\sigma_{\mathrm{GaAs}}\exp(-d/\lambda_{\mathrm{oxide}})\exp\left[\sum_i(-d_i/\lambda_i)\right]\int_0^\infty \exp(-x/\lambda_{\mathrm{GaAs}})dx}, \tag{1}$$

where D is the number of As (or Ga) atoms per unit volume, σ is the ionization cross section, λ is the mean free path of photoelectrons, and subscripts GaAs, oxide, and i denote the values for the GaAs substrate, the oxide species, and the ith component present between the oxide layer and the GaAs substrate, respectively. Assuming that $\sigma_{\mathrm{oxide}}/\sigma_{\mathrm{GaAs}}$ is unity and adopting 2.5 nm for λ of all the species,[21,22] Eq. (1) reduces to

$$R_{\mathrm{ox}}(90°) = \frac{D_{\mathrm{oxide}}}{D_{\mathrm{GaAs}}}\left[e^{(a+d)/2.5} - e^{a/2.5}\right], \tag{2}$$

where a is the thickness of the layer between the oxide layers and the GaAs substrate in nm.

For the layer of oxide mixture such as the ($As_2O_3+Ga_2O_3$) layer, the oxide thickness can be determined using the following equations:

$$R^1_{\mathrm{ox}}(90°) = \frac{D^1_{\mathrm{oxide}}c}{D^1_{\mathrm{GaAs}}}\left[e^{(a+d)/2.5} - e^{a/2.5}\right], \tag{3}$$

$$R^2_{\mathrm{ox}}(90°) = \frac{D^2_{\mathrm{oxide}}(1-c)}{D^2_{\mathrm{GaAs}}}\left[e^{(a+d)/2.5} - e^{a/2.5}\right], \tag{4}$$

where superscripts 1 and 2 denote oxide species 1 and 2, respectively, and c is the concentration of oxide species 1 in the mixture. The partial oxide thickness d_p of species 1 is defined as

$$d_p = cd. \tag{5}$$

Using Eqs. (2)–(5), the thickness of each oxide component is estimated from the intensity ratio, $R_{\mathrm{ox}}(90°)$, shown in the first row of Table I and it is depicted in the third row. The total oxide thickness was estimated to be 2.9 nm, much larger than that before the Pt deposition (0.5 nm).

Once the thickness of each oxide species and the structure of the oxide layer are determined, $R_{\mathrm{ox}}(45°)/R_{\mathrm{ox}}(90°)$ can be calculated using the following equation:

$$\frac{R_{\mathrm{ox}}(45°)}{R_{\mathrm{ox}}(90°)} = \frac{e^{\sqrt{2}(a+d)/2.5} - e^{\sqrt{2}a/2.5}}{e^{(a+d)/2.5} - e^{a/2.5}}. \tag{6}$$

TABLE II. Ratio of the areal intensity of the oxide peak to that of the substrate peak R_{ox} and the thickness of the oxide layer d for the ⟨Pt/KOH oxide/GaAs(001)⟩ specimens after the heat treatment at 200 °C in oxygen.

	As	As_2O_3	As_2O_5	Ga_2O_3
$R_{\mathrm{ox}}(90°)$	0.95	1.96	2.87	2.05
$R_{\mathrm{ox}}(45°)/R_{\mathrm{ox}}(90°)$	1.3	2.4	2.7	1.4
d (nm)	0.7[b]	1.0	1.1	1.9[b]
Calc. $R_{\mathrm{ox}}(45°)/R_{\mathrm{ox}}(90°)$[a]	1.9	2.5	2.9	1.9

[a] Values for the ($Pt/As_2O_5/As_2O_3+Ga_2O_3/As/GaAs$) structure.
[b] Partial oxide thickness for the (Ga_2O_3+As) layer.

The calculated values are shown in the fourth row in Table I. They were larger than the experimental values but not very different. The most probable cause for the difference between the experimental and calculated values is the presence of roughness at the interfaces, i.e., the interface roughness makes R_{ox} less take-off angle dependent. On the other hand, the uncertainty of the photoelectron mean free path was found to cause only a small error in the calculation of $R_{ox}(45°)/R_{ox}(90°)$. For example, a change in λ_{oxide} from 2.5 to 3.0 nm with λ_{GaAs} of 2.5 nm decreases the ratio only by ~5% for the total oxide thickness of 3 nm.

In the calculation, the interfaces between oxide layers are assumed to be sharp although the real interfaces are not probably so sharp, with the concentrations of the oxide species changing gradually with the depth. However, this assumption increase $R_{ox}(45°)/R_{ox}(90°)$ for one oxide species but decreases that for other oxide species. The calculated $R_{ox}(45°)/R_{ox}(90°)$ values for all the oxide species are larger than the experimental values, and hence, the errors cannot be attributed to this assumption but to the interface roughness as described above.

The calculated $R_{ox}(45°)/R_{ox}(90°)$ value assuming a structure in which some species is present on the Pt surface is always far from the experimental values, e.g., the fifth row for the (As_2O_5/Pt/As_2O_3+Ga_2O_3/As/GaAs) structure, verifying that all the oxide species are present between the Pt layer and the GaAs substrate.

Table II shows $R_{ox}(90°)$ (first row), $R_{ox}(45°)/R_{ox}(90°)$ (second row), the oxide thickness (third row), and calculated $R_{ox}(45°)/R_{ox}(90°)$ (fourth row) for the KOH oxide layer with the Pt film after the heat treatment at 200 °C in oxygen. The ratio, $R_{ox}(45°)/R_{ox}(90°)$, abbreviated to R, was in the following order:

$$R(As_2O_5) > R(As_2O_3) > R(Ga_2O_3) \approx R(As).$$

This result indicates that the oxide has a (Pt/As_2O_5/As_2O_3/Ga_2O_3+As/GaAs) structure. Comparison of Table II with Table I shows that the heat treatment in oxygen increased the thickness of Ga_2O_3 and As_2O_5 greatly, and increased that of As_2O_3 slightly, while that of As decreased. The total oxide thickness increased to 4.7 nm.

The $R_{ox}(45°)/R_{ox}(90°)$ value for elemental As contains a large error of ±20% because the As $3d_{3/2}$ peak due to the GaAs substrate overlaps the As $3d_{5/2}$ peak of As^0. However, measurements of the ratio for many specimens confirmed that the As layer (or As+Ga_2O_3 layer) was always present just above the GaAs substrate.

Figure 2 shows the XPS spectra for the thermal oxide-covered GaAs(100) substrate in the As $3d$ [spectra (a)–(c)] and Ga $3d$ [spectra (d)–(f)] regions. The thermal oxide layers were formed by heating the GaAs(100) substrate at 500 °C in oxygen for 5 min. In the As $3d$ spectrum for the specimen with no Pt layer, a weak peak due to As^{3+}(As_2O_3) was observed, but no peak due to As^{5+}(As_2O_5) was seen [spectrum (a)]. In the Ga $3d$ spectrum, a peak due to Ga^{3+}(Ga_2O_3) was present with a considerably high intensity [spectrum (d)]. These results show that the thermal oxide layer was composed mainly by Ga_2O_3, in agreement with the previous studies.[23,24] The total oxide thickness was estimated to be 1.6 nm.

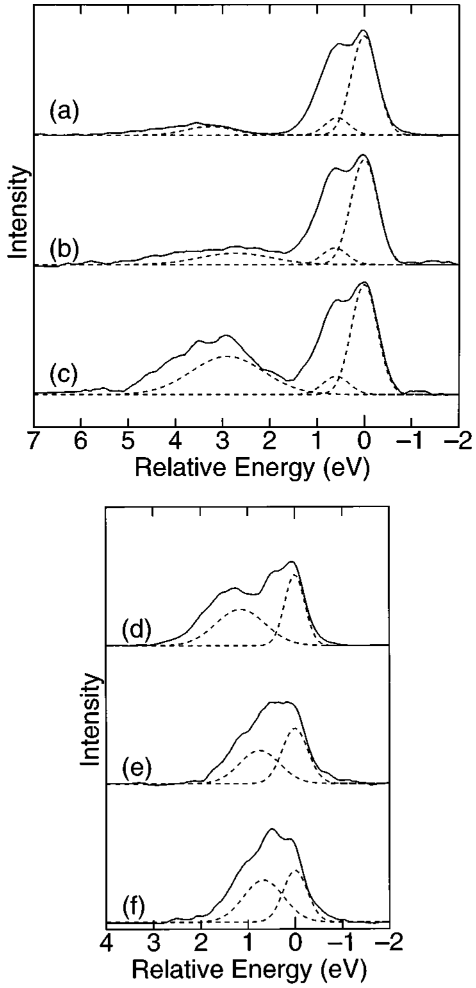

FIG. 2. XPS spectra in the As $3d$ [spectra (a)–(c)] and Ga $3d$ [spectra (d)–(f)] regions for the thermal oxide layers formed at 500 °C: (a), (d) with no Pt layer and no heat treatment; (b), (e) with a Pt layer and no heat treatment; (c), (f) with a Pt layer after the heat treatment at 200 °C in oxygen.

When a Pt layer was deposited on the thermal oxide layer, the spectral feature was changed mainly because of lower energy shifts of the peaks due to As_2O_3 [spectrum (b)] and Ga_2O_3 [spectrum (e)]. The ratios, $R_{ox}(90°)$, for Ga_2O_3 and As_2O_3 were nearly unchanged by the Pt deposition. The total oxide thickness was estimated to be 1.6 nm.

By heating the ⟨Pt/thermal oxide/GaAs(100)⟩ specimen at 200 °C in oxygen for 1 h, the intensity of the peak due to

TABLE III. Ratio of the areal intensity of the oxide peak to that of the substrate peak R_{ox} and the thickness of the oxide layer d for the ⟨Pt/thermal oxide/GaAs(001)⟩ specimens after the heat treatment at 200 °C in oxygen.

	As	As_2O_3	As_2O_5	Ga_2O_3
$R_{ox}(90°)$	0.17	0.96		1.35
$R_{ox}(45°)/R_{ox}(90°)$	1.2	1.9		1.2
d (nm)	0.2[b]	0.7		1.5[b]
Calc. $R_{ox}(45°)/R_{ox}(90°)$[a]	1.7	2.0		1.7

[a] Values for the (Pt/As_2O_3/Ga_2O_3+As/GaAs) structure.

[b] Partial oxide thickness for the (Ga_2O_3+As) layer.

$As^{3+}(As_2O_3)$ increased markedly [spectrum (c)], and that due to Ga_2O_3 increased only slightly [spectrum (f)].

Table III shows $R_{ox}(90°)$ (first row), $R = R_{ox}(45°)/R_{ox}(90°)$ (second row), the oxide thickness (third row), and calculated $R_{ox}(45°)/R_{ox}(90°)$ (fourth row) for the thermal oxide layer with the Pt film after the postdeposition heat treatment at 200 °C in oxygen. The ratio R was in the following order:

$$R(As_2O_3) > R(Ga_2O_3) \approx R(As).$$

This indicates that the oxide has ($Pt/As_2O_3/Ga_2O_3 + As/GaAs$) structure. Assuming this layered structure, the thickness of each oxide component was calculated to be 0.7 nm for As_2O_3, 1.5 nm for Ga_2O_3, and 0.2 nm for As, and thus, the total oxide thickness was 2.4 nm.

IV. DISCUSSION

The thickness of the oxide layer formed in the KOH solution is ~0.5 nm before the Pt deposition. The heat treatment of this specimen at 200 °C in oxygen increases the oxide thickness only slightly to ~0.7 nm. On the other hand, after the deposition of the Pt overlayer, the oxide thickness increases to 2.8 nm just by leaving the specimen in the air at room temperature. For this specimen, the heat treatment at 200 °C in oxygen markedly increases the oxide thickness to 4.7 nm. These results show that the oxidation of GaAs is promoted greatly by the Pt overlayer.

Comparison of the XPS spectra measured at the take-off angle of 90° and 45° clearly shows that all the oxidized species are present between the Pt overlayer and the GaAs substrate, but not on the Pt layer. This result is in strong contrast to the cases of the noble metal– or transition metal–promoted oxidation of GaAs,[1–3] where the oxide layer is formed on the metal surfaces, and thus, the moving species through the metal layers are As and Ga formed by the decomposition of GaAs due to the interaction between metal atoms and the GaAs substrate. In the present study, the direct contact between the GaAs substrate and the Pt overlayer is prevented by the thin oxide layers formed before the Pt deposition, thus avoiding the interaction between them. In the cases of Pt- or Pd-enhanced oxidation of Si, a thin oxide layer is also found to prevent the direct contact between the metal overlayer and the Si substrate, avoiding the silicide formation, and consequently, the silicon oxide layer is formed between the metal layer and the Si substrate.[11–14]

Since the Pt film increases the thickness of the oxide layer between the Pt film and the GaAs substrate but no oxide is formed on the Pt, it can be concluded that the moving species through the Pt layer is an oxidizing species but is not Ga or As atoms. We think that the moving species through the Pt layer is oxygen atoms or oxygen ions (O^- or O^{2-}) initially produced at the Pt surface. It is well known that oxygen is adsorbed dissociatively on the Pt surface at room temperature.[25,26] Oxidation of GaAs by these species proceeds much faster than that by oxygen molecules because of a low activation energy.

After the Pt deposition, the oxide layers have layerlike nonuniform compositions. If the oxidation reaction were to proceed at the GaAs/oxide interface, the oxide layer would possess a more uniform composition because both Ga oxide and As oxide would be formed simultaneously. The nonuniform oxide composition is likely to be caused by the oxidation reaction at the Pt/oxide interface and in the oxide bulk. Namely, in cases where the diffusion of As atoms in the oxide layer is faster than that of Ga atoms, As oxide is formed above Ga oxide. This expectation is supported by the experimental result that after the heat treatment of the specimens with the Pt layer in oxygen, the oxide layers have ($Pt/As_2O_5/As_2O_3/Ga_2O_3 + As/GaAs$) and ($Pt/As_2O_3/Ga_2O_3 + As/GaAs$) structures for KOH oxide and thermal oxide, respectively. Therefore, it can be concluded that As and Ga formed by the decomposition of GaAs diffuse toward the Pt/oxide interface, and react with oxygen atoms injected from the Pt layer. The proposed oxidation mechanism is shown schematically in Fig. 3.

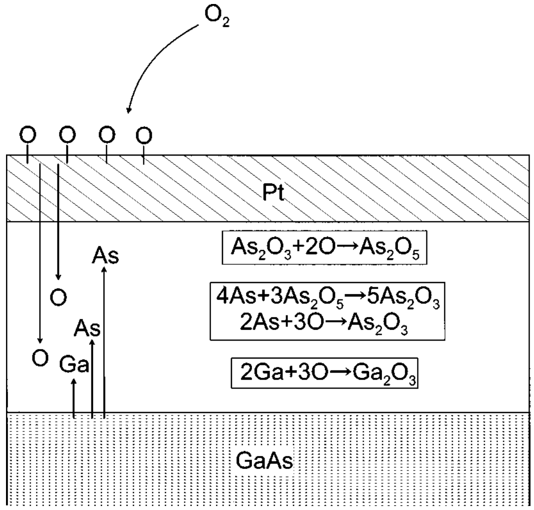

FIG. 3. Model of the mechanism for the Pt-enhanced oxidation of GaAs.

The oxidation mechanism of GaAs is in contrast to that of Pt-enhanced oxidation of Si where the diffusion species in the silicon oxide layer is oxygen atoms.[11–13] The different mechanism is likely to be caused by the higher diffusion rate of As (and Ga) atoms in the oxide layer than that of Si atoms. Namely, in the case of Si oxidation, oxygen atoms are needed to diffuse to the Si/silicon oxide interface because of the low diffusion rate of Si in the oxide layer. For the oxidation of GaAs, on the other hand, As and Ga atoms diffuse in the oxide layer at low temperatures. This expectation is supported by the result that the thickness of the GaAs oxide layer formed at 200 °C using the catalytic activity of the Pt film is 4.7 nm, thicker than that of the silicon oxide layer formed at the same temperature (3.8 nm).[11,13]

When the (Pt/KOH oxide/GaAs) specimen is heated at 200 °C in oxygen, the thickness of As_2O_3 increases, while that of As slightly decreases. This result can be explained by the following mechanism (cf. Fig. 3): the decomposition of GaAs is enhanced by heating. Elemental As present just above GaAs diffuses toward the oxide/Pt interface, and reacts with oxygen atoms near the Pt/oxide interface, forming As_2O_3. The decrease in the thickness of the As layer shows that the diffusion and reaction of As atoms are more enhanced by heating than the decomposition of GaAs. The formation of As_2O_3 occurs by the following reactions:

$$\text{(i)}\quad 2\,\mathrm{As}+3\mathrm{O}\rightarrow \mathrm{As_2O_3},\qquad \Delta H=-1403\ \ \mathrm{kJ\,mol^{-1}},\tag{7}$$

$$\text{(ii)}\quad \tfrac{4}{5}\mathrm{As}+\tfrac{3}{5}\mathrm{As_2O_6}\rightarrow \mathrm{As_2O_3},\qquad \Delta H=-100\ \ \mathrm{kJ\,mol^{-1}}.\tag{8}$$

The changes of enthalpy are estimated simply from the heat of formation. For reaction (i), As atoms react with oxygen atoms in the oxide layer that are injected from the Pt layer. For reaction (ii), on the other hand, As atoms react with As_2O_3, and consequently, the As_2O_3 layer is formed beneath the As_2O_5 layer, in good agreement with the experimental result.

When As_2O_3 is formed near the Pt/oxide interface, it is further oxidized to As_2O_5 by the reaction with oxygen atoms injected from the Pt layer:

$$\mathrm{As_2O_3}+2\mathrm{O}\rightarrow \mathrm{As_2O_5},\qquad \Delta H=-768\ \ \mathrm{kJ\,mol^{-1}}.\tag{9}$$

As_2O_5 is likely to be formed only where the concentration of oxygen atoms is sufficiently high. Namely, the concentration of oxygen atoms in the oxide layer decreasing with the distance from the Pt/oxide interface may be another reason for the oxide structure in which As_2O_5 is above As_2O_3.

Ga atoms diffuse toward the Pt/oxide interface to some extent, and react with oxygen atoms that are injected from the Pt layer and diffuse in the oxide layer:

$$2\,\mathrm{Ga}+3\mathrm{O}\rightarrow \mathrm{Ga_2O_3},\qquad H=-1837\ \ \mathrm{kJ\,mol^{-1}}.\tag{10}$$

The oxide structure in which Ga oxide is located below As oxide results from the lower diffusion rate of Ga atoms in the oxide layer than that of As atoms.

The decomposition of GaAs may be caused by the following mechanism: since the oxide layer is thin initially, a small number of oxygen atoms (or oxygen ions) reach the oxide/GaAs interface, and the following reaction occurs:

$$2\,\mathrm{GaAs}+3\mathrm{O}\rightarrow \mathrm{Ga_2O_3}+2\,\mathrm{As},\qquad \Delta H=-1655\ \ \mathrm{kJ/mol^{-1}}.\tag{11}$$

This reaction is most likely because elemental As and Ga_2O_3 are present near the GaAs substrate after the oxidation, as described before. Due to the largely exothermic reaction, Ga-As bonds (bond energy 1.7 eV) are broken, forming As and Ga atoms. Once these atoms are produced, the decomposition of GaAs is enhanced by the oxidation of these atoms [reactions (7)–(10)] because all the reactions are exothermic.

The thickness of the KOH oxide layer with the Pt film is ~2.9 nm before the heat treatment, and it increases markedly to ~4.7 nm after the heat treatment at 200 °C. On the other hand, the thickness of the thermal oxide layer with the Pt film is ~1.6 nm before the heat treatment and it increases to only ~2.4 nm by the heat treatment. The thermal oxide layer consists mainly of Ga_2O_3, while the KOH oxide layer contains only a small amount of Ga_2O_3 [cf. Figs. 2(e) and 1(g)]. Therefore, the above results can be well explained by assuming that Ga_2O_3 retards the diffusion rates of the reacting species. Namely, once a thick Ga_2O_3 layer is formed, the Pt-enhanced oxidation does not proceed any more. It is also likely that the KOH oxide layer has a lower atomic density than the thermal oxide layer, which enhances the diffusion, and consequently, after the heat treatment, the KOH oxide layer becomes thicker than the thermal oxide layer. A similar phenomenon is observed for the Pt-enhanced oxidation of Si; i.e., when the oxide layer formed before the Pt deposition has a low atomic density due to the presence of high amounts of suboxide species, the increase in the oxide thickness caused by the Pt-enhanced oxidation is large.[13]

After the Pt deposition, all the observed oxide peaks shift by 0.4–0.7 eV toward the lower binding energy with respect to the substrate peaks. In the absence of the Pt overlayer, positive charges are accumulated in the oxide surface region due to photoemission. The positive charges induce a potential drop across the oxide layer, shifting the oxide bands downward toward the oxide surface, and consequently, the core levels of the oxide shift in the higher-binding-energy direction. In the presence of the Pt overlayer, on the other hand, such a charge-up effect does not occur because the Pt layer is earthed, and consequently, the oxide peaks are observed at the lower binding energy. The effect of final-state screening by electrons in the Pt layer may also contribute to the lower-energy shifts.

V. CONCLUSIONS

A Pt layer formed on the thin oxide-covered GaAs enhances the oxidation of GaAs. The heat treatment of the ⟨Pt/thin oxide/GaAs(100)⟩ specimens at 200 °C in oxygen increases the oxide thickness to 2.4–4.7 nm. The take-off-angle–dependent XPS measurements show that the oxide layer has a nonuniform layerlike structure, consisting of As oxide, Ga oxide, and elemental As, and all the oxide components are present between the Pt layer and the GaAs substrate. The diffusing species through the Pt layer is oxygen atoms initially produced at the Pt surface. As atoms formed by the decomposition of GaAs diffuse in the oxide layer toward the oxide/Pt interface and react with oxygen atoms near the interface. Ga atoms do not diffuse far from the GaAs/oxide interface, and thus react with oxygen atoms in the oxide bulk, which are injected from the Pt layer. Consequently, Ga oxide is formed below As oxide. It is suggested that Ga oxide suppresses the diffusion of the reacting species. The thermal oxide layer consists mainly of Ga oxide and hence the oxide thickness increases only slightly by the Pt-enhanced oxidation, while the thickness of the oxide layer initially formed in the KOH solution increases markedly because the oxide layer contains only a small amount of Ga oxide.

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