

Influence of residual Ga₂O₃ and Cs on the increase in the maximum quantum efficiency of NEA-GaAs by a two-step thermal cleaning process

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Abstract

We investigated the relationship between the increase in the maximum quantum efficiency of negative electron affinity (NEA)-GaAs depending on the thermal cleaning conditions and residual species, e.g., Ga₂O₃ and Cs atoms, on the GaAs surface using temperature-programmed desorption. We found that the increase in the maximum quantum efficiency occurs during thermal cleaning at 500–600°C for ~8.5 min. The increase in ratio was maximum when the amount of Ga₂O₃ on the GaAs surface was maximum. In the case that Cs atoms remained, when the thermal cleaning was performed in a temperature range where Ga₂O₃ was not formed, the effect facilitating an NEA surface formation was observed. However, the residual Cs atoms might not be affected at an increased maximum quantum efficiency. From the above results, we considered that the double-dipole structures of Cs-Ga₂O₃ and Cs-O are significant to the high quantum efficiency. The Cs-O dipoles are considered to form easily when Ga₂O₃ is on the GaAs surface before the NEA activation, and the amount of Cs-O dipoles required to reduce the vacuum level below the conduction band minimum increase more than usually NEA surface. As a result, the maximum quantum efficiency increases.

I. Introduction

A negative electron affinity (NEA) surface in which the vacuum level lies below the conduction band minimum is a candidate for the next-generation electron source because of its properties, such as large photoelectron current, ultra-short-pulsed operation, high spin polarization, and low emittance nature. Although various models have been proposed for the NEA surface over more than half a century, the detailed mechanisms of the actual NEA surface are not yet understood.

Generally, an NEA surface is formed by the adsorption of Cs and O atoms on a clean p-type GaAs surface in an ultra-high vacuum condition. After the formation of the NEA surface, the photoelectron current decreases over time because of the adsorption of

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an unexpected residual gas, back bombardment of ionized residual gas, and thermal desorption of the (Cs, O) layer. This sample is repeatedly activated by eliminating the residual species on the surface with thermal cleaning at high temperatures. However, it has been reported that the maximum quantum efficiency of NEA-GaAs increased after thermal cleaning at low temperatures [2nd thermal cleaning (2nd TC)]^{1,2)}. Based on this result, we presumed that new photoemission sites are formed on the NEA surface by the residual species on the surface. In particular, Ga₂O₃ plays an important role in increasing the quantum efficiency; however, the effect of other residues (Cs, As, etc.) on increasing the quantum efficiency have not been discussed.

In this study, 2nd TC was performed at several temperatures to investigate the rate of increase in the maximum quantum efficiency of NEA-GaAs, and the effect of the remaining Ga₂O₃ and Cs on the surface on the above experimental results were evaluated using temperature-programmed desorption (TPD). It was found that the rate of the increase in the maximum quantum efficiency correlates with the amount of residual Ga₂O₃. Moreover, when the 2nd TC was performed at a temperature at which Ga₂O₃ was not formed, residual Cs facilitated the NEA surface formation but did not affect the increase in the maximum quantum efficiency.

II. Experimental Procedures

The samples used were epi-ready Zn-doped p-type GaAs (100) ($\sim 1.0 \times 10^{19} / \text{cm}^3$) substrates. The thermal pretreatment of the samples and the successive NEA activation with alternating supply of Cs and O₂ were performed in a UHV chamber. The base pressure of the chamber was kept at $2.0\text{--}4.0 \times 10^{-8}$ Pa. The sample was soldered on a Mo sample holder by pasting an In seat for thermal conduction. The temperature for the thermal pretreatments was elevated using a carbon heater. The temperatures were measured using a chromel–alumel thermocouple in contact with the backside of the sample holder. The Cs atoms were supplied by sublimation from a Cs dispenser (SAES Getters), and the pressure of O₂ (>99.999995 vol.%) was controlled with a variable leak valve. To measure the emitted photoelectron current, the sample was biased by -100 V. The light source was a Hg–Xe lamp, and a monochromatic light ($h\nu = 1.50$ eV, density = $296 \mu\text{W}/\text{cm}^2$) was illuminated using an optical spectrometer. The quantum efficiency was calculated as a simple ratio of the number of emitted photoelectrons to the number of incident photons.

The thermal cleaning was performed at 700°C for ~ 60 min (1st TC). After the sample was cooled down to room temperature, the NEA activation was performed by the “yo-yo” method (1st NEA activation)³⁾. The photocurrent during the NEA activation exhibited cyclic ups and downs corresponding to the supply of Cs and O₂. The peak value

of the photocurrent gradually increased and finally saturated⁴). As the activation process ended, the thermal cleaning was performed at 150°C, 300°C, 430°C, 460°C, 500°C, 525°C, 575°C, 660°C, and 700°C for ~8.5 min (2nd TC). The NEA activation was performed again when the temperature was naturally cooled to room temperature (2nd NEA activation). When the activation process was completed, the sample surface was cleaned by the 1st TC again. In the 1st and 2nd TC processes, the desorbed substances were also analyzed using TPD at a programmed rate of 10°C/min.

III. Results and Discussions

Figure 1 shows the TPD spectra of Cs, As₂, Ga₂O from the 1st NEA-GaAs surface during the 1st TC, and we determined the temperatures of Ga₂O₃ formation and desorption. The horizontal axis represents the temperature of the GaAs sample. The left vertical axis shows the intensity of Cs desorption, and the right vertical axis shows the intensities of As₂ and Ga₂O desorption. In the case of 1st TC, the thermal cleaning was performed at 700°C for ~1 h. The solid, dashed, and dotted lines represent Cs, As₂, and Ga₂O, respectively. The Cs desorption at 600–660°C was not observed because the Cs desorption from other samples except the GaAs sample was removed.

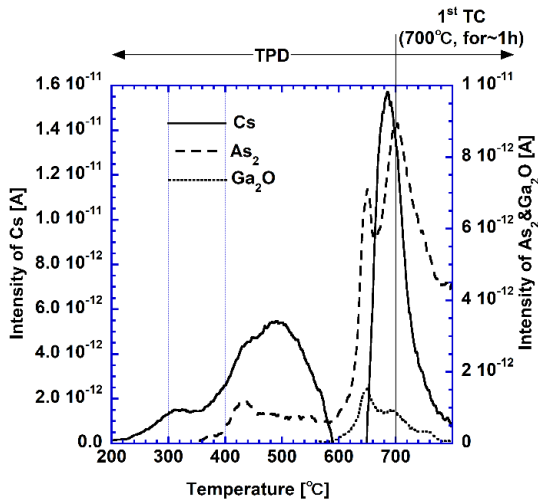
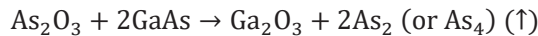


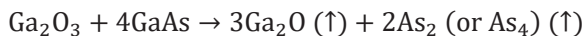
Fig. 1 TPD spectra of Cs (solid line), As₂ (dashed line), and Ga₂O (dotted line) from the 1st NEA GaAs surface during the 1st TC (700°C, for ~1 h).

The Cs desorption began at 200°C, and the As₂ desorption was observed at 350°C. The desorption peaks of Cs and As₂ from 350°C to 600°C were derived from the Cs-O-As compounds^{5,6}. First, an As oxide, As₂O₃, was formed simultaneously with the desorption of Cs. However, As₂O₃ is unstable at a temperature higher than 250°C; therefore, Ga₂O₃ was formed with As₂ desorption according to the following process:



The As₂ and Ga₂O signals were observed in the same temperature range (600–660°C).

This indicates that the following reaction occurred:



Consequently, we considered that Ga_2O_3 was formed at 350°C and desorbed at 600°C in this experiment.

Next, to investigate the relationship between the increase in the maximum quantum efficiency and the amount of residual Ga_2O_3 on the GaAs surface, we discuss the relationship between the increased rates of the maximum quantum efficiency and the amount of As_2 desorbed simultaneously with the formation of Ga_2O_3 . Figure 2 shows the 2nd TC temperature dependence of the rate of increase of the maximum quantum efficiency and the amount of As_2 desorbed at $350\text{--}600^\circ\text{C}$. The horizontal axis represents the temperature of the 2nd TC. The left vertical axis shows the increased rates of the maximum quantum efficiency. When this rate was more than 1, the maximum quantum efficiency of NEA-GaAs increased due to the 2nd TC. The right vertical axis shows the amount of As_2 desorbed after the 2nd NEA activation normalized by the As_2 desorption after the 1st NEA activation at $350\text{--}600^\circ\text{C}$. The smaller the As_2 desorption, the larger the amount of Ga_2O_3 formed on the GaAs surface by the 2nd TC. As shown in Fig. 2, the increase in the maximum quantum efficiency was closely related to the amount of Ga_2O_3 on the GaAs surface. The increased rate of quantum efficiency indicated the maximum value when the amount of As_2 desorbed was minimum, that is, the maximum amount of Ga_2O_3 remained on the GaAs surface and decreased at 660°C and 700°C when Ga_2O_3 was desorbed. Based on the above results, it was concluded that the rate of the increase in the maximum quantum efficiency correlates with the amount of residual Ga_2O_3 .

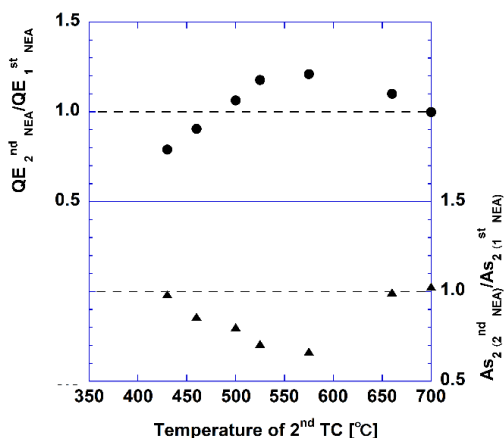


Fig. 2 The 2nd TC temperature dependence of the increasing rates of the maximum quantum efficiency (left vertical axis) and the amount of As_2 desorbed at $350\text{--}600^\circ\text{C}$ normalized by As_2 desorbed after the 1st NEA activation at $350\text{--}600^\circ\text{C}$ (right vertical axis).

Finally, to investigate the effect of residual Cs species on the GaAs surface, we discuss the quantum efficiency during the NEA activation when the 2nd TC was performed

at temperatures at which Cs remained sufficiently. Figure 3 shows the peak quantum efficiency values during the NEA activation when the 2nd TC was performed at 150°C and 300°C for 8.5 min. The horizontal axis represents the number of peaks. Only the first peak was obtained by the Cs supply; the others were obtained by the O₂ supply. The vertical axis shows the peaks of quantum efficiency. The shape of the plot classifies the thermal cleaning conditions; circular plot for 150°C of the 2nd TC, square plot for 300°C of the 2nd TC, and triangular plot for the 1st TC (700°C for 1 h), respectively. Note that in the case of the 2nd TC, the first peaks of quantum efficiency due to the Cs supply were higher than those observed at the 1st TC. According to previous works ³⁾, the NEA surface on GaAs was not formed at the first peak of quantum efficiency and was formed at the other peaks formed by the O₂ supply in the 1st NEA activation. As can be observed in the first peaks at 150°C and 300°C of the 2nd TC in Fig. 3, both the values were higher than the second peak of 1st NEA activation. Therefore, the NEA surface on GaAs was formed by due to only the Cs supply at the 2nd TC at 150°C and 300°C. As the reason for this, it was considered that the Cs species which influence photoelectron emissions, such as Cs-O-Ga and Cs-O-As, etc., sufficiently remained on the GaAs surface. Wu *et al.* reported that Cs-O-Ga and Cs-O-As were desorbed at more than 350°C ⁶⁾. Therefore, it is presumed that the Cs species facilitated the formation of the NEA surface on GaAs. However, no increase in the maximum quantum efficiency was observed. At present, we consider that the residual Cs on the NEA surface does not contribute to the increasing maximum quantum efficiency of NEA-GaAs.

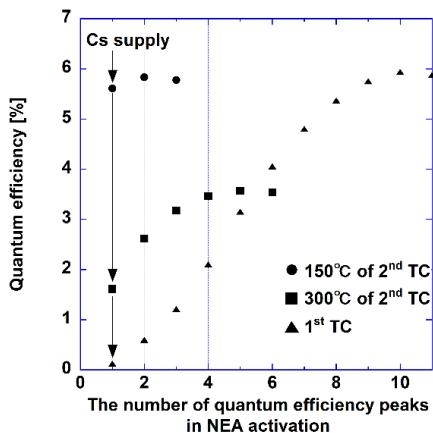


Fig. 3 Peak values of quantum efficiency during the NEA activation when the 2nd TC was performed at 150°C (circular plot) and 300°C (square plot) for 8.5 min, and the 1st TC (triangle plot) was also performed.

The above results indicate that the increase in the maximum quantum efficiency resulted in the residual Ga₂O₃ on the GaAs surface. The double-dipole model, Cs-GaAs or Cs-O-GaAs dipole and (Cs, O) dipole, has been well known as a model of the NEA surface ⁷⁻⁹⁾. In the two dipoles mentioned above, the (Cs, O) dipole is suggested to reduce

the vacuum level below the conduction band minimum. In the case of Ga₂O₃ existing on the surface before the NEA activation, Cs-Ga₂O₃ is formed when Cs is first supplied during the activation process. During the following O₂ exposure, the O atoms dissociated from O₂ react with the Cs atoms and/or GaAs surface. However, it is predicted that the formation of the Cs-O dipole is facilitated rather than the reaction of O atoms and GaAs surface by residual Ga₂O₃. Therefore, the number of Cs-O dipoles increases compared to that in the 1st NEA activation, leading to an increase in the maximum quantum efficiency.

IV. Conclusion

We investigated the relationship between the increase in the maximum quantum efficiency of NEA-GaAs depending on the thermal cleaning conditions and residual Ga₂O₃ and Cs on the GaAs surface. It was found that the increase in the maximum quantum efficiency necessitated Ga₂O₃, and the increasing rate was maximum when the amount of Ga₂O₃ on the GaAs surface was maximum. In the case of residual Cs, when the 2nd TC was performed at a temperature at which Ga₂O₃ was not formed, the residual Cs facilitated NEA surface formation; however, it might not affect the increase in the maximum quantum efficiency. At present, we consider that the Cs-O dipole reduces the vacuum level below the conduction band minimum and is formed easily when Ga₂O₃ is present on the GaAs surface before the NEA activation, which leads to an increase in the maximum quantum efficiency.

ACKNOWLEDGMENT

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