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Surface Nitridation Process of (100) GaAs by NH₃-Plasma Treatment with Planar Magnetic Field

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Plasma-nitridation of (100) GaAs with the magnetic field was performed. X-ray photoelectron spectroscopy as a function of the photoelectron take-off angle shows that the layer formed on GaAs surface is Ga-As-N ternary compounds in the case of a short treatment time or a low treatment temperature. The top layer becomes mainly GaN by desorption of As or N bonded to As with increasing the treatment time or temperature. This plasma-nitridation process is one of the promising candidates for the passivation of (100) GaAs surface.

1. INTRODUCTION

Recently there has been considerable interest in the plasma passivation of GaAs surface using NH3¹² or H2 + N2²³ discharge for improvement in electrical properties of the insulator/GaAs interface, originating from reducing the density of interface states. Such a dry passivation is advantageous for a continuous operation with other dry processes in contrast with the wet passivation using (NH4)2S etc. The surface reaction with the plasma is one of the noteworthy factors to clarify the mechanism for the plasma passivation. This study reports the detailed surface reaction of NH3-plasma with the magnetic field and (100) GaAs observed by X-ray photoelectron spectroscopy (XPS). The oxidation-proof for the plasma-treated samples will be also shown.

2. EXPERIMENTAL

(100) GaAs substrates were placed on the anode electrode, which was grounded, after dipping into the solution of H2SO4 and H2O2. An rf voltage with 13.56 MHz was applied to the cathode electrode, and a magnetic field was also applied parallel to it in order to keep the plasma away from the substrates for avoiding the plasma damage. NH3-plasma was generated under the condition of the pressure of 14 Pa and the rf power density of 0.1 W/cm^2 . The

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plasma-treatment time and temperature were varied from 1 min to 60 min and from 50 $^{\circ}$ C to 300 $^{\circ}$ C, respectively.

Angle-dependent XPS (ADXPS) measurements were carried out with changing the photoelectron take-off angle θ between 90 deg and 20 deg in order to study the depth profile from the surface. θ was defined as the angle between the XPS detector and the sample surface.

3. RESULTS AND DISCUSSION

Figure 1 shows Ga 3d and As 3d XPS spectra observed at θ of 90 deg for samples treated using NH3 plasma at 250 °C for various treatment times. The circular symbols signify the signal due to GaAs substrate. Before plasma treatment, GaAs substrates were dipped in the H2SO4/H2O2 solution. This chemical treatment almost completely etches the surface oxide, which shows the XPS signal with higher binding energy (BE) than GaAs, as also shown in Fig. 1. It is found from Fig. 1 that the NH3-plasma treatment brings about the new signal with a high BE shown by triangular symbols in both Ga 3d and As 3d spectra. The difference in BE observed in Ga 3d spectra between the new signal with a high BE and the original signal due to GaAs gradually becomes larger as the treatment proceeds, and saturates after the treatment for 20 min. Such differences in BE observed in both Ga 3d and As 3d are, however, smaller than those between the signal due to oxides and that due to GaAs. Therefore



Fig. 1. Change in Ga 3d and As 3d XPS spectra for samples through NH₃-plasma treatment at 250 $^{\circ}$ C for various times. The spectra before treatment are also shown.



Fig. 2. NH₃-plasma treatment time dependence of normalized N 1s intensity.

signals shown by triangular symbols are not ascribed to oxide but nitride. Disappearance of the As-N signal by the plasma treatment more than 20 min in As 3d spectra is obvious. Change in the XPS intensity of N 1s, whose BE is about 398.5 eV, with the treatment time shown in Fig. 2 is also consistent with that in the intensity of As 3d due to As-N bond. Here the intensity of 1 min-treated sample is normalized to 1. The enhancement of the energy difference in two Ga 3d spectra and the reduction of As-N signal, both of which tend to saturate by the treatment for 20 min, suggest a surface reaction that the NH3-plasma forms Ga-As-N layer on GaAs in the early stage, and then GaN is mainly formed by desorption of As and N bonded to As from such ternary compounds.

Figure 3 shows the normalized XPS intensity of As 3d due to nitride against the photoelectron take-off angle θ obtained by the ADXPS which gives the depth profile without destruction. The smaller θ gives information in the region nearer from the surface. The intensities of the signal at various θ are divided by the signal intensity of As 3d in the bottom GaAs substrate at the same θ , and the values are normalized to 1.0 at θ of 90 deg. We stated in detail the normalization method elsewhere.³⁾ The samples shown in Fig. 3 were plasma-treated at 250 °C for 5, 10 and 20 min. It is revealed from Fig. 3 that the intensity of As 3d due to nitride decreases near the surface region with increasing the treatment This fact also suggests that GaN layer is time. gradually formed as the NH3-plasma treatment proceeds and that the surface layer through the treatment for longer than 20 min is GaN almost without As.



Fig. 3. Normalized XPS intensity of As 3d due to nitride against photoelectron take-off angle in samples plasma-treated for 5, 10 and 20 min at 250 °C.

The depth profiles for samples treated by NH3-plasma for 20 min at various treatment temperatures are shown in Fig. 4. θ dependence of the XPS intensities of Ga 3*d* and As 3*d* both due to nitride and N 1*s* are presented. The intensities are normalized in the same manner as those shown in Fig. 3. These results suggest that the plasma treatment forms the surface layer which mainly consists of As-N binary compounds at 50 °C and Ga-As-N ternary compounds at 100 °C. Raising the treatment temperature above 200 °C makes the surface layer mainly consisting of GaN. Therefore, it turns out that increases both in treatment-time and temperature play the equivalent role for forming GaN layer.

Finally, the oxidation-proof in this plasma-treatment is presented. XPS spectra at θ of 90 deg for the sample after plasma-treatment at 250

°C for 45 min and for one only dipped into the H2SO4/H2O2 solution are shown in Fig. 5. Both of the spectra were observed after the air-exposure at room temperature for 20 days. As shown in Fig. 1, the XPS spectra after the wetor the plasma-treatment show almost no signal due to the oxide in either case. The air-exposure brings about no signal due to the oxide in the plasma-treated sample. On the other hand, the signal due to the oxide, shown by the arrow, is clearly seen in the sample only dipped into the solution. These results support that the NH3-plasma treatment is one of the promising techniques for the passivation of GaAs surface.



Fig. 4. Normalized XPS intensities against photoelectron take-off angle in samples plasma-treated for 20 min at various temperatures.



Fig. 5. As 3d XPS spectra for the sample (a) through plasma treatment and (b) only dipped in the solution. Both of the spectra were observed after exposure to the air for 20 days.

4. CONCLUSIONS

NH3-plasma passivation of (100) GaAs with planar magnetic field was carried out. ADXPS study elucidates that GaN is formed on the GaAs surface with the appropriate treatment time and temperature. This process is one of the effective methods for the passivation of GaAs surface.

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