Atom-Probe Study of Al-Ga Exchange Reaction at Al-GaAs Interfaces

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An atomically abrupt Al-GaAs interface was observed for Si-doped GaAs at 200 K by atom-probe mass spectroscopy. At 300 K an Al-As mixed layer having a low As concentration and containing no Ga was formed. Formation of the mixed layer at 200 K for Zn-doped GaAs could be attributed to a promoted reaction by Zn. A decrease in the thickness of the unreacted Al layer, an increase in the As concentration in the mixed layer with temperature, and the abrupt AlAs-GaAs interface indicate Al diffusion into GaAs and stable Al-As bonding.

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A great deal of interest in the structure of Al-GaAs interfaces has induced extensive studies. However, the occurrence of the Al-Ga exchange reaction at room temperature is still controversial.[1] While studies by Auger-electron spectroscopy[2-4] and x-ray photoemission spectroscopy[5] concluded that no exchange reaction takes place under 300 K, the result with angle-integrated photoemission spectroscopy indicates the formation of AlAs by the exchange reaction.[6]

The disagreement may be caused by the rather macroscopic methods employed for the study of a few atomic layers at the interfaces. Thus, the pertinent approach is to utilize an ultramicroscopic technique which allows mass analysis of each interfacial atomic layer. The atom-probe technique[7,8] was expected to be an instrument which would satisfy this requirement because it successfully demonstrated its unique capability by mass analysis of the metal-Si interfaces on an atomic scale.[9-11]

The high-mass-resolution atom probe technique[8] was used for the present study. The specimen tips of Si-doped and Zn-doped GaAs ($n=2\times10^{18}$ cm^{-3} and $p=2\times10^{19}$ cm^{-3}, respectively) were prepared by cutting 0.3-mm-thick GaAs wafers into square rods of dimensions $0.3\times0.3\times10$ mm^3. Needle-shaped specimens for the atom-probe study were made by etching one end of the rod in the solution H_2SO_4:H_2O_2= 2:1 at 60 °C until a tip radius of less than 1000 Å was obtained. The other end of the rod was inserted into a Pt tube which was spot welded on a Mo loop. The specimen could be heated by resistive heating of the Mo loop and its temperature was measured by a Chromel-Alumel thermocouple inserted into the Pt tube.

The domain mass analyzed by the atom-probe instrument was a small area on the hemispherical apex of a specimen needle. At the early stage of the mass analysis its diameter was usually 1–2 nm and the number of atoms detected from a monoatomic layer was about ten.[8] This number increased gradually to over twenty as the tip radius increased.

Figure 1 is a typical histogram of the mass spectrum of an Al-deposited GaAs tip. The mass resolution is high enough to identify each detected ion as Al, As, As_2, As_3, and the isotopes of ^{69}Ga and ^{71}Ga without ambiguity. C^+, O^+, CO^+, and CO_2^+ were detected during field evaporation of the contaminated surface layers before the Al deposition.

The abscissa of Fig. 2 is the total number of detected ions and the ordinate is the number of Al, Ga, and As ions plotted respectively in the order of detection. The specimen temperature was maintained at 200 K while the Al deposition and atom-probe mass analysis proceeded from the deposited Al layer to the substrate of Si-doped GaAs through the interface. The first ten atoms are Al and then a few As atoms are detected, which indicates that the Al coverage is approximately a monolayer. Note that the interface is abrupt and no mixed layer, which would be noticed by the disordered detection of Al, Ga, and As, was found. The slopes of the plotted lines represent the local concentration of each element. Thus, the slopes of Ga and As should be parallel for GaAs. The steeper slope of As could be due to the preferential field evaporation of some Ga atoms at the field exerted by the dc voltage applied to the tip.[12]

When Al-deposited GaAs was heated at 300 K for 60 min and mass analyzed at 200 K, one As atom was detected after the detection of sixteen Al atoms and then seven more As atoms were detected with nineteen more Al atoms, indicating the formation of a Al-As mixed layer with a low As concentration (Fig. 3). After the detection of the last Al atom, five As atoms were detected successively be-

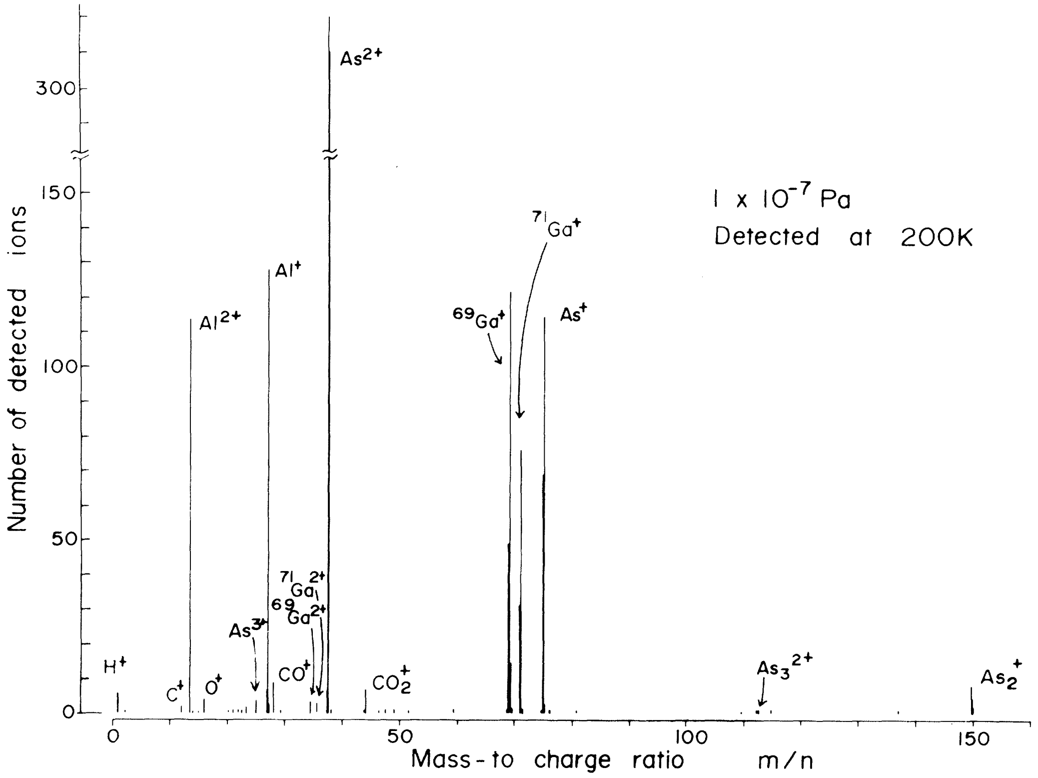

FIG. 1. Mass spectrum of Al-deposited GaAs.

fore the detection of the first Ga atom. The mixed layer is one or two atomic layers thick and contains no Ga atoms. The mixed-layer–GaAs boundary is also clear.

Heating the tip at 500 K for 60 sec resulted in the formation of a mixed layer with a higher As concentration and one Ga atom (Fig. 4). In this case, As atoms also were detected after the detection of the last Al atom, which suggests that Al replaces Ga of the first layer of GaAs at the boundary and directly interacts with As of that layer, and that the replacement of Ga of the second layer[13] is not likely.

At higher temperatures the diffusion of Al into

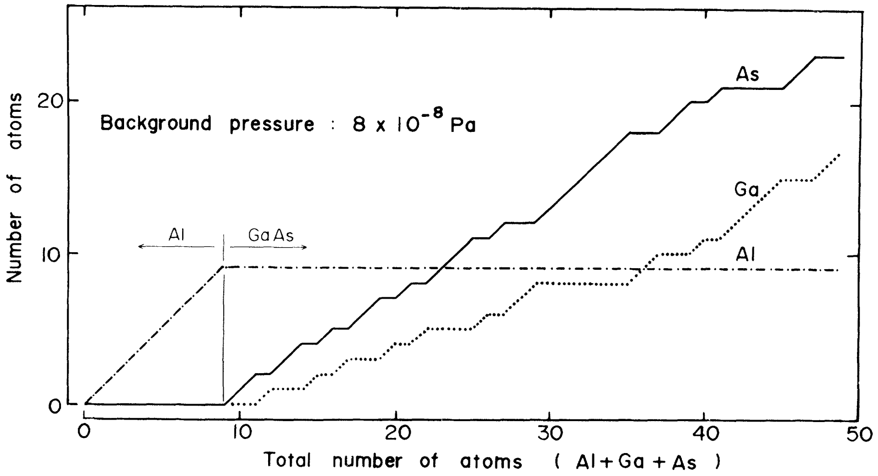

FIG. 2. The cumulative number of Al, Ga, and As atoms vs that of each element detected by mass analysis of Al-deposited, Si-doped, [011]-oriented GaAs at 200 K. The vertical line indicates the Al-GaAs interface.

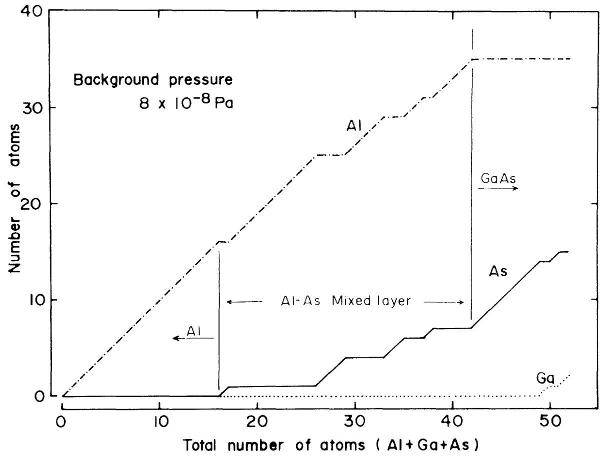

FIG. 3. Field-evaporation sequence of Al, As, and Ga ions from the [011]-oriented GaAs. The two vertical lines delineate the Al-As mixed layer formed by heating at 300 K for 60 min.

GaAs became more active, the thickness of the unreacted Al layer decreased, and the As concentration in the mixed layer increased. However, few Ga atoms released by the Al-Ga exchange reaction were detected on the surface and at the interfacial region. The released Ga atoms may have diffused to the tip surface and migrated away to the tip shank or desorbed from the surface.[5]

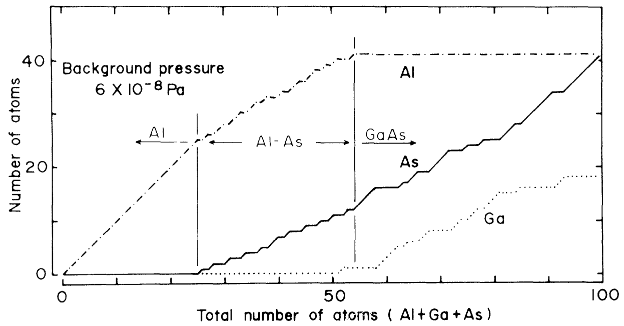

FIG. 4. Detection sequence of field-evaporated ions from the Al-deposited, [001]-oriented GaAs tip heated at 500 K for 60 sec. The As concentration of the Al-As mixed layer is higher than that at 300 K. The mixed layer has clear boundaries with the unreacted Al layer and the GaAs substrate as indicated by vertical lines.

At 900 K all Al atoms were bound with As atoms, forming a mixed layer with the stoichiometry of AlAs (Fig. 5). The abrupt AlAs-GaAs interface may be due to the stable Al-As bonding which suppresses the further diffusion of Al into GaAs.

For Zn-doped GaAs, the Al-Ga exchange reaction took place at a lower temperature than that for Si-doped GaAs. The Al-As mixed layer was formed at 200 K (Fig. 6), and the evidence of the exchange

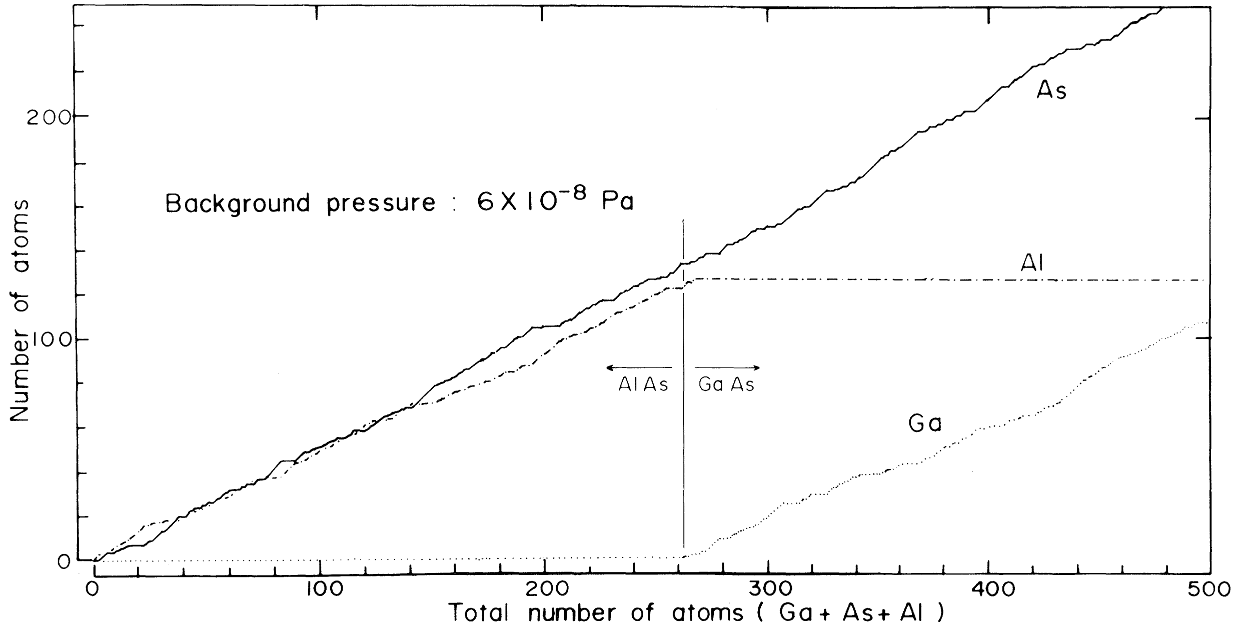

FIG. 5. Detection sequence of field-evaporated ions from the Al-deposited [001]-oriented tip heated at 900 K for 70 sec. The abrupt AlAs-GaAs interface is indicated by a vertical line.

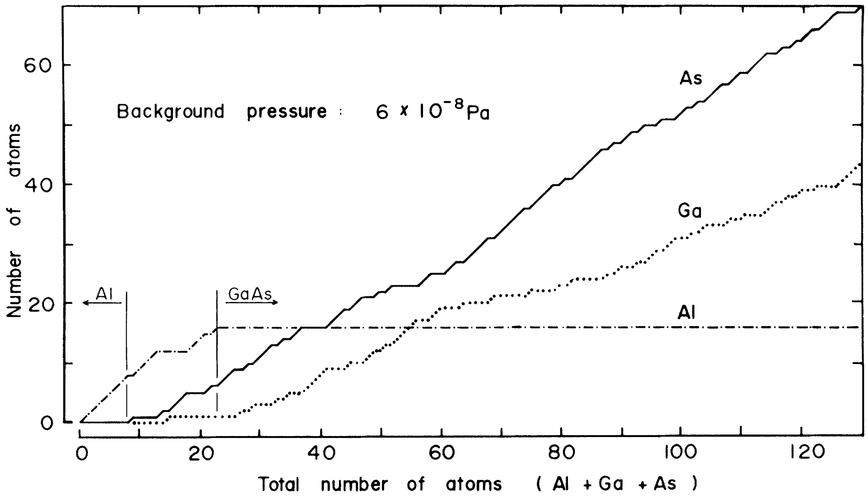

FIG. 6. Formation of an Al-As mixed layer at the interface of the unreacted Al layer and the Zn-doped, [011]-oriented GaAs at 200 K. The mixed layer is indicated by vertical lines.

reaction was noticed even at 120 K. The occurrence of the exchange reaction at the low temperatures could be attributed to a promoted reaction by Zn which greatly advances the interdiffusion of Ga and Al.[14] However, no Zn atoms were detected during the atom-probe mass analysis because the Zn concentration in GaAs is so low that the probability of finding Zn atoms in the present small number of detected atoms is extremely low.

The experiment was repeated many times with more than ten Si-doped and several Zn-doped GaAs specimen tips. Although the thickness of deposited Al layer could not be well controlled, the variation of the As concentration in the mixed layer with temperature and the abruptness of the interfaces were reproducible.

The observed effect of dopants on the exchange reaction suggests that the disagreement on the occurrence of the exchange reaction at room temperature might be caused by an extremely small amount of dopant or impurity in the specimen and that the detailed study of the interfacial reaction requires an ultramicroscopic technique which can depict the interfacial composition on an atomic scale.

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