Interfacial solid-state reaction at thermally oxidized $In_{1-x}Ga_xAs_yP_{1-y}$ alloys

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The interfacial reaction between thermally oxidized $In_{1-x}Ga_xAs_yP_{1-y}$ and an $In_{1-x}Ga_xAs_yP_{1-y}$ epilayer was studied using Raman and x-ray photoelectron spectroscopy (XPS) analyses. In Raman spectra, it was found that the appearance of the phonon modes, i.e., the first-order longitudinal (LO) and transverse-optical (TO) modes for crystalline arsenic, was due to the $In_{1-x}Ga_xAs_yP_{1-y}$-oxide interfacial reaction. The XPS analyses showed that this reaction corresponded to the GaAs-oxide interfacial reaction, i.e., $As_2O_3 + 2GaAs \rightarrow Ga_2O_3 + 4As$. Furthermore, the reaction depends on the composition y of $In_{1-x}Ga_xAs_yP_{1-y}$, which may be due to the enhancement in the initial transient reaction by thermal damage of $In_{1-x}Ga_xAs_yP_{1-y}$ occurring at the interface.

I. INTRODUCTION

$In_{1-x}Ga_xAs_yP_{1-y}$/InP systems have been used for many optoelectronic devices in optical-communication fields. Moreover, its high mobility makes this material very promising for high-speed transistors.[1,2] For example, recently numerous metal-insulator-semiconductor (MIS) devices fabricated have been reported.[3-5] However, the successful preparation of high quality devices is difficult to achieve with consistency.[6] Some of the problems arise because the chemical, physical, and electrical properties of the oxide-semiconductor interface are not sufficiently understood or controlled. Many authors have reported that[7-10] when the oxide is grown on GaAs by means of heat treatment, the Raman signal of crystalline and amorphous arsenic appears. This may suggest that the thermally induced solid-state interfacial reaction, i.e., $As_2O_3 + 2GaAs \rightarrow Ga_2O_3 + 4As$, is responsible for the appearence of the arsenic at the oxide-semiconductor interface.

In this paper, we present for the first time the characterization of the thermally induced solid-state interfacial reaction at the $In_{1-x}Ga_xAs_yP_{1-y}$-oxide interface using XPS and laser Raman spectroscopy.

II. EXPERIMENT

About 1-μm-thick undoped $In_{1-x}Ga_xAs_yP_{1-y}$ epilayers have been grown on (100) InP substrates by the liquid phase epitaxy (LPE) technique. The samples studied were InP and $In_{1-x}Ga_xAs_yP_{1-y}$ ($y = 0.30$, 0.55, 0.79, and 1.00) lattice matched to the InP substrate. The compositions y were estimated by the x-ray double-crystal diffraction method and photoluminescence (PL) measurement.

The oxidation of the samples was done in $N_2 + O_2$ ambient at 400 °C. Raman spectra were measured at room temperature using the 5145 Å line of Ar ion laser as an exciting source. The Raman signal was collected in the near back-scattering configuration and analyzed with a monochromator. The XPS measurements were made on a ESCALAB-5 electron spectrometer using unmonochromatized Al*Kα* radiation. The mean free path of an inelastic electron is a function of the electron kinetic energy and material. It is estimated that the mean-free path of an electron excited with Al*Kα* x-ray is approximately 3.5 Å of As2*p*, 5.5 Å of Ga2*p*, 15 Å of Ga3*p*, and 19 Å of As3*d*, respectively. Deconvolution of the unresolved spectra and the following determination of the spectrum intensity was accomplished after smoothing and subtracting a smooth background.

III. RESULTS AND DISCUSSION

A. InGaAs-oxide systems

Figure 1 shows Raman spectra for the thermally oxidized InGaAs epilayers. The spectrum for the InGaAs epi-

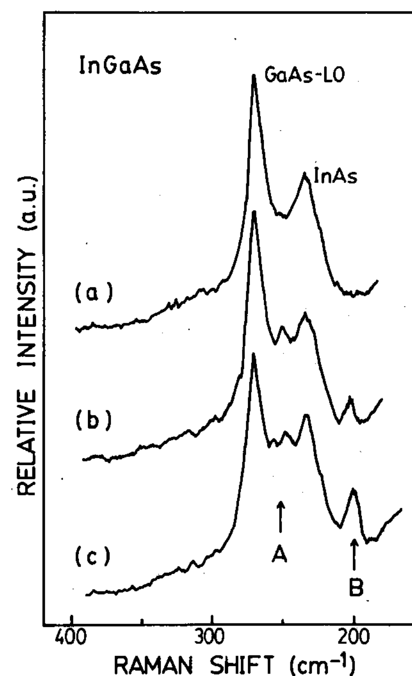

FIG. 1. Raman spectra of InGaAs thermally oxidized at various conditions. (a) InGaAs epilayer, (b) InGaAs thermally oxidized at 420 °C for 20 min, and (c) InGaAs thermally oxidized at 420 °C for 50 min.

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layer in Fig. 1(a) agrees well with those reported earlier.[11] Two main peaks are corresponding to the LO phonon mode based on GaAs and the LO-TO mixed phonon mode based on InAs. Spectra (b) and (c) in Fig. 1 show the relative intensity of the InGaAs layers thermally oxidized for 20 and 50 min at 420 °C, respectively. One can find the appearance of two peaks, peak A and peak B, for which the intensities depend on the time of the thermal oxidation process. In spectrum (c), peak A is not sufficiently separated from two main peaks. The recent works[7-10] on oxide-GaAs interfacial reaction revealed the Raman signals of two peaks as well as the LO and TO modes of GaAs. They reported that some signals, due to the crystalline arsenic, might be for the LO(257 cm^{-1}) and TO(198 cm^{-1}) modes of the arsenic, and the structureless Raman scattering near 200–250 cm^{-1} was due to amorphous arsenic. Therefore, we speculate that the appearance of two peaks, A and B, are corresponding to the LO and TO phonons for crystalline arsenic, respectively.

In order to clarify the origin of these peaks, we have analyzed the thermally oxidized samples by XPS, as shown in Fig. 2. Spectra (a) and (b) in Fig. 2 show the relative intensity of as-grown epitaxial samples and thermally oxidized samples following the removal of oxide by HF etching, for constituent atoms, respectively. Spectra (c) in the same figure represents the intensity for a thermally annealed sample of spectra (b) at 300 °C for 20 min. It is difficult to accurately estimate the oxide film thickness. Since the mean-free path of an inelastic electron is approximately 5–20 Å, we removed the surface oxide by HF with special care in order to observe the interfacial reaction. The peaks related to InGaAs, As, As_2O_3, As_2O_5, and Ga_2O_3 are shown in the same figure. Although these peaks are not sufficiently separated from one another, we have some information from slight differences of the peak shapes. Therefore, we carried out the deconvolution of those unresolved spectra to determine the peak intensity of the peak in the spectra. Those treatments were accomplished after smoothing and subtracting a smooth background. The typical deconvoluted XPS spectra for As2*p* are shown in Fig. 3. For simplicity, it

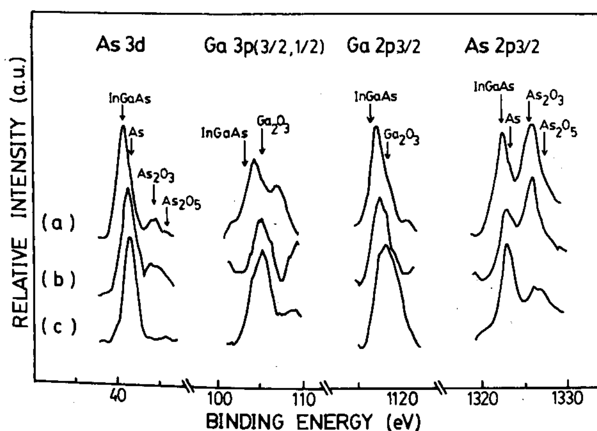

FIG. 2. XPS spectra of As3*d*, Ga3*p*, Ga2*p*, and As2*p* for InGaAs at various process conditions. (a) as-grown InGaAs epilayer, (b) thermally oxidized InGaAs following HF etching, and (c) thermally annealed sample (b) at 300 °C for 20 min.

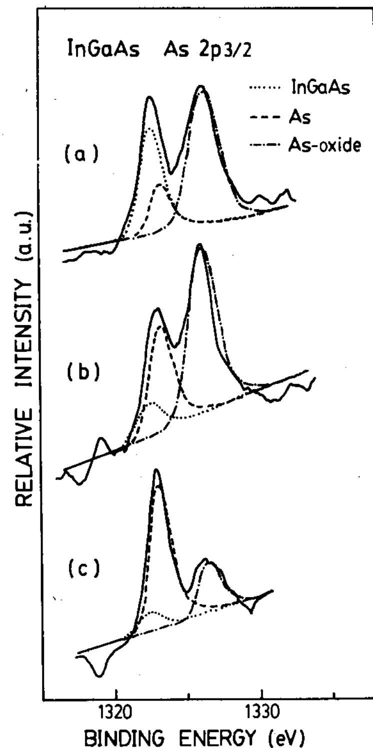

FIG. 3. Deconvoluted XI spectra of As2*p* fi InGaAs.

was defined that the As-oxide peak is composed of As_2(and As_2O_5. From the results in Fig. 3, it is clear that tl intensities corresponding to the constituent atoms are diffe ent for these samples. With the thermal oxidation and a nealing, the intensity of arsenic increased; however, those InGaAs and As-oxide decreased. The depth concentratic and the chemical state profile at various process conditio: are shown in Fig. 4. These are derived from the intensities the deconvoluted spectra for the unresolved ones in Fig. From taking account of each mean-free path for As2*p*, Ga2 As3*d*, and Ga3*p*, it seems that the accuracy of estimat depth profiles is within 20%. The figure shows that the m tallic As exists at all samples, and that both concentrations the As-oxide and InGaAs decrease as those of the Ga_2O_3 ai metallic As increase with the thermal oxidation and the fc lowing annealing process. It is noted that the solid-state i terfacial reaction is being thermally enhanced for t InGaAs-oxide system, e.g., by following the reactic

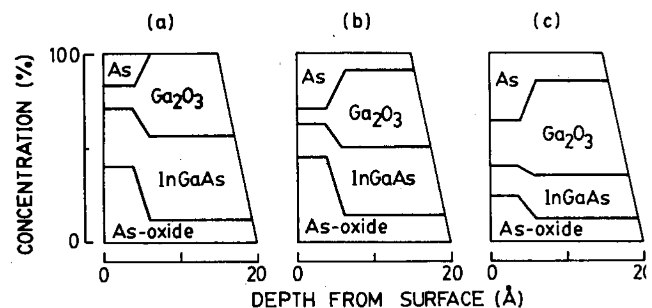

FIG. 4. Depth concentration and chemical state profile at various proc conditions described in Fig. 2. The inelastic electron mean-free path is proximately 3.5 Å of As2*p*, 5.5 Å of Ga2*p*, 15 Å of Ga3*p*, and 19 Å of As respectively.

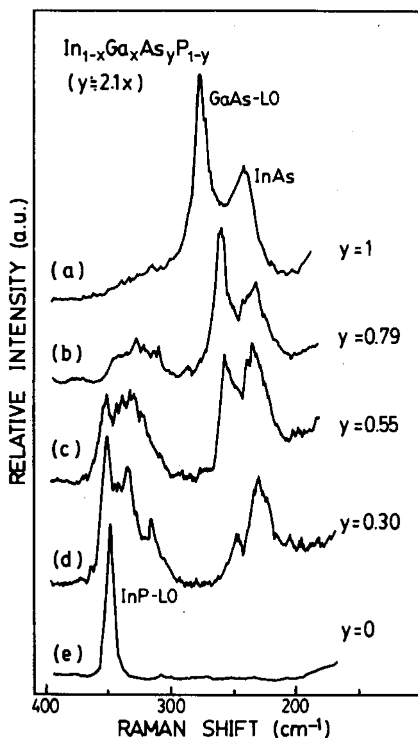

FIG. 5. Raman spectra of $In_{1-x}Ga_xAs_yP_{1-y}$ epilayer. The compositions y of Raman spectra (a)–(e) are 1.00, 0.79, 0.55, 0.30, and 0, respectively.

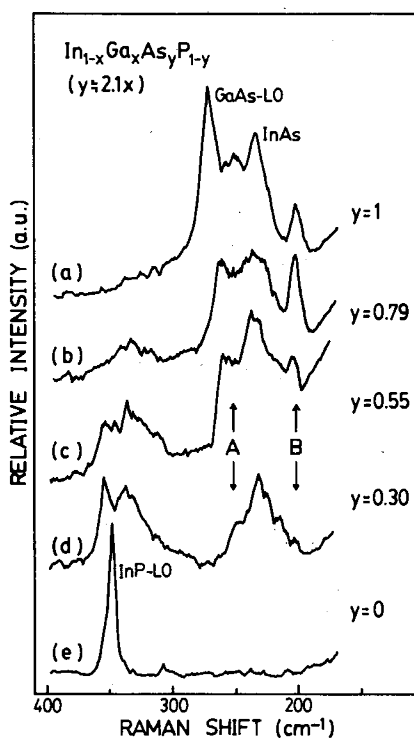

FIG. 6. Raman spectra of thermally oxidized $In_{1-x}Ga_xAs_yP_{1-y}$.

$As_2O_3 + 2GaAs \rightarrow Ga_2O_3 + 4As$, as reported for the GaAs-oxide systems.[7–10] For the InGaAs-oxide systems, the influence of an In atom, one of the constituent atoms, upon the oxide reaction was not made clear. The XPS analysis was also carried out, especially for In3d. Results show that In is almost thermally oxidized to In_2O_3, indicating that the In oxidation is not related to the intensity of the excess arsenic produced by the interfacial solid-state reaction.

From these results, therefore, it is found that the origin of the Raman peaks, A and B, may be the excess arsenic due to the thermally induced solid-state reaction at the InGaAs-oxide interface.

B. $In_{1-x}Ga_xAs_yP_{1-y}$-oxide system

In order to study the influence of the composition of quaternary $In_{1-x}Ga_xAs_yP_{1-y}$ upon the thermally induced solid-state reaction occurring at the quaternary-oxide interface, we have measured the Raman spectra of various compositions of quaternary alloys. Figure 5 shows the Raman spectra of the $In_{1-x}Ga_xAs_yP_{1-y}$ epilayers. Many peaks for various LO and TO phonons are seen in this figure and the data agrees with that which what was reported earlier.[12,13] Then, Raman analyses were carried out for these epilayers following their thermal oxidation at 420 °C for 50 min, as shown in Fig. 6. It is clearly seen that peaks A and B appear in Figs. 6(a)–6(c), but not in Fig. 5. These peaks correspond to the LO and TO phonons due to the crystalline arsenic. In Fig. 6(d), peaks A and B are not clearly seen because of the small amount of the arsenic ($y = 0.30$), and in Fig. 6(e) neither of these peaks appears. These results indicate that the origin of the excess crystalline arsenic depends on the composition of the $In_{1-x}Ga_xAs_yP_{1-y}$ quaternary alloy. In the comparison of spectra (a) and (b) in Fig. 6, both intensities of peaks A and B in Fig. 6(b) are larger than those of Fig. 6(a), although the As composition ($y = 1$) of Fig. 6(a) is larger than that of Fig. 6(b). However, after these samples were more thermally annealed, these intensities in Fig. 6(a) became largest in all samples. These results show that the solid-state interfacial reaction may be influenced by the thermal damage introduced near the semiconductor-oxide interface at the oxidation and annealing process. This is because the thermal damage which is related mainly to the evaporation of the phosphorous atoms in the quaternary alloys may enhance the solid-state reaction at the semiconductor-oxide interface when the transient reaction starts in $In_{1-x}Ga_xAs_yP_{1-y}$-oxide systems. Finally, it has been found, from the detected signal of the excess arsenic, that the thermally induced solid-state interfacial reaction strongly depends on the composition y of the $In_{1-x}Ga_xAs_yP_{1-y}$ alloy.

IV. SUMMARY

We have characterized the thermally oxidized $In_{1-x}Ga_xAs_yP_{1-y}$-oxide interfacial reaction by both Raman and XPS analyses. It has been found that the appearance of the crystalline arsenic-related signals in Raman spectra may be due to the thermally induced solid-state interfacial reaction, as is reported for GaAs, i.e., $As_2O_3 + 2GaAs \rightarrow Ga_2O_3 + 4As$. Furthermore, this reaction strongly depends on the As composition y of the $In_{1-x}Ga_xAs_yP_{1-y}$ alloy, and then initial transient reaction is enhanced by the thermally induced damage. Our results suggest that the key parameters to obtain an excellent oxide-$In_{1-x}Ga_xAs_yP_{1-y}$ alloy interface are the composition y,

the conditions of thermal oxidation and annealing, and the thermal damage induced by the evaporated phosphorous in the alloy.

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