

Initial Oxidation Stage of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and $(\text{Al}, \text{Ga})_{0.5}\text{In}_{0.5}\text{P}$ Surfaces Studied by Photoemission Spectroscopy

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Initial oxidation stage of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and $(\text{Al}, \text{Ga})_{0.5}\text{In}_{0.5}\text{P}$ (100) surfaces has been studied by XPS. Oxygen preferentially interacts with the surface imperfect sites by dissociative chemisorption. The precursor phase of elemental group-V (As,P) was produced as a consequence of preferential oxygen bonding to group-III atoms (Al,Ga,In) even at room temperature. AlGaInP is a more promising visible laser material than AlGaAs in terms of the less oxidized surface property.

1. INTRODUCTION

Surface oxidation of III-V semiconductors is unfavorable from device processing and reliability viewpoints. As far as AlGaAs laser diodes are concerned, the device degradation is accelerated by the facet oxidation, which is marked with increasing Al content.¹⁾ Even though an insulator film deposition prevents the surface from further oxidation, a stable insulator /semiconductor interface has not been always realized due to the existence of unstable native oxide at the interface in practical device processing.²⁾

Although initial oxidation stage has been intensively studied for GaAs ,³⁾ it has not been established yet with respect to oxygen adsorption kinetics and oxygen induced surface products. Still less has been investigated in other III-V ternary semiconductor alloys.

Based on the above background, the initial oxidation stages for $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and $(\text{Al}, \text{Ga})_{0.5}\text{In}_{0.5}\text{P}$, which are candidates for visible light emitting semiconductor laser materials, have been investigated, using X-ray photoelectron spectroscopy (XPS).

2. EXPERIMENTAL

Samples used in this study were (100) oriented GaAs (Te doped, $n=1 \times 10^{17} \text{ cm}^{-3}$), LPE

grown $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ and $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ epi-layers, and MOVPE grown AlAs , $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ and $\text{Al}_{0.5}\text{In}_{0.5}\text{P}$ epi-layers. To prevent air-oxidation on the surface, thin (30-50 Å) GaAs layers were successively grown on both AlAs and AlInP . The samples were loaded into an ESCA LAB5 spectrometer and were cleaned by gentle sputtering of rastered 500 eV Ar^+ beam, during which time they were held at 250-350°C. This heat-up sputtering is superior to the conventional sputtering followed by annealing at 400-600°C, because there is less lattice distortion owing to a smaller amount of imbedded Ar.

Oxygen exposures were carried out by admitting 99.99 % purity oxygen into the preparation chamber. The hot filament ionization gauge was turned off during the exposure to avoid generating excited molecular oxygen, which leads to higher oxygen uptake than unexcited oxygen. XPS measurements were carried out by using $\text{Mg K}\alpha$ ($h\nu = 1253.6 \text{ eV}$) or $\text{Al K}\alpha$ ($h\nu = 1486.6 \text{ eV}$) radiation under 1×10^{-10} Torr base pressure. The photoemitted electrons were energy-analyzed by a 150° hemispherical reflector-type analyzer. To increase the surface sensitivity, the spectra were taken at 62.5° grazing angle with respect to the surface normal.

3. ADSORPTION KINETICS

Figure 1 shows the oxygen sticking coefficients (SCs) as a function of the coverage (θ) for various $\text{Al}_x\text{Ga}_{1-x}\text{As}$ surfaces. The SC (S) is given by following equation;

$$S = \frac{N_s (2\pi mKT)^{-1/2}}{2 \times 10^{-6}} \frac{d\theta}{dL} \dots (1)$$

where N_s is the number of available adsorption sites ($6.3 \times 10^{14} \text{ cm}^{-2}$ for (100) surface), L is langmuir exposure ($1L = 10^{-6} \text{ Torr sec}$) and the other symbols have their usual meaning. The fractional coverage was determined from the relative O 1s peak area intensity with respect to the saturated O 1s peak area intensity which yields one monolayer. As seen in the figure, the SC increases with AlAs mole fraction.

For each AlGaAs , the SC decreases exponentially with the coverage at the lower range and then deviates from exponential dependence, approaching zero at one monolayer coverage. That is, two successive adsorption

stages can be distinguished, as depicted in the inset in Fig. 1. The former exponential dependence can be described by the Elovich equation, as follows;

$$S = S_{01} \exp(-\beta\theta) \dots (2)$$

where irreversible chemisorption, for which activation energy increases linearly with coverage, is assumed.⁴⁾ Elovich kinetics has been empirically applied to the adsorption on heterogenous surface on which defects such as steps, dislocations, lattice vacancies and impurities are present. In fact, Elovich adsorption was enhanced for an intentionally disordered surface. For the latter behavior, on the other hand, SC evolution can be fitted with following Langmuir's expression for dissociative chemisorption of diatomic molecules.

$$S = S_{02} (1-\theta)^2 \dots (3)$$

This expression involves an assumption that the required activation energy for chemisorption is negligibly small.⁵⁾ Similar adsorption behavior to that shown in Fig. 1 was observed for AlGaInP .

Respective initial SC values for Elovich and Langmuir adsorption pertaining to each surface are summarized in Fig. 2 with respect to the energy bandgap. As can be seen in the figure, the SC value for AlGaInP is less than that for AlGaAs by more than one order of magnitude. However, the SC value for $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ is close to that for $\text{Al}_{0.5}\text{In}_{0.5}\text{P}$, compared with the same Al content. Thus, it seems that the SC value is determined by the Al content in these alloys.

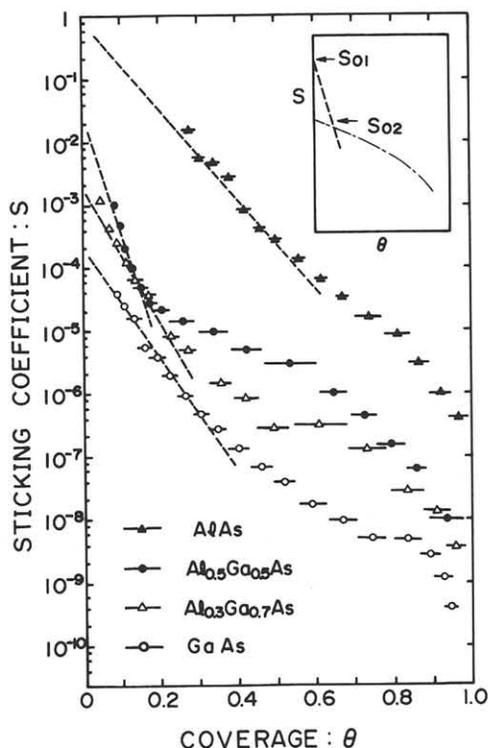


Fig. 1 Sticking coefficient of oxygen as a function of coverage for various AlGaAs surfaces.

4. SURFACE PRODUCTS

Oxygen induced chemical shifts in core levels were revealed by difference spectra between the oxygen adsorbed and the clean surfaces. To eliminate band-bending effect, individual spectra were aligned in energy with respect to the valence band maximum derived from the UP spectrum leading edge. Figure 3 shows the As 3d difference spectra for $10^{10-11}L$ oxidized AlGaAs surfaces. As seen in the figure, at least two different peaks (As_I and As_{II}) are obvious, corresponding to As atoms in different chemical environments. A higher energy peak As_I decreases in intensity and

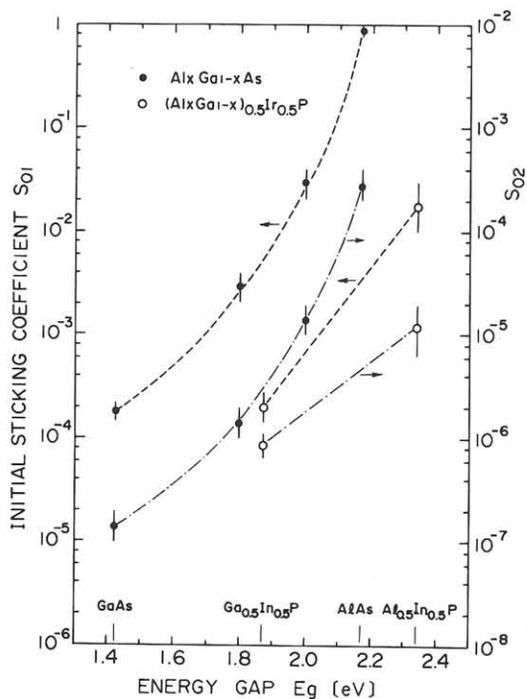


Fig. 2 Oxygen initial sticking coefficients for AlGaAs and AlGaInP.

shifts towards the higher energy side with increasing AlAs mole fraction. A lower energy peak As_{II} is contrary to the As_I peak in behavior. By analyzing chemical shift energies, As_I and As_{II} are assigned to precursor phases for As-oxide and elemental-As, respectively.

It is noteworthy that the As 3d difference spectrum for (100) GaAs shown in Fig. 3 closely resembles that for (110) cleaved GaAs,^{6) 7)} although surface orientation and surface preparation are different each other. Taking into consideration that the difference spectrum is sensitive to the surface configuration, the result clearly demonstrates that oxygen causes surface disorder even at the room temperature adsorption stage. Furthermore, the precursor phase appearance for elemental-As (As_{II}) indicates oxygen's preferential bonding to group-III atoms.

The P 2p spectra in AlGaInP exhibited similar behavior to that for the As 3d in AlGaAs, as shown in Fig. 4. However, the thermal stability of the surface products is

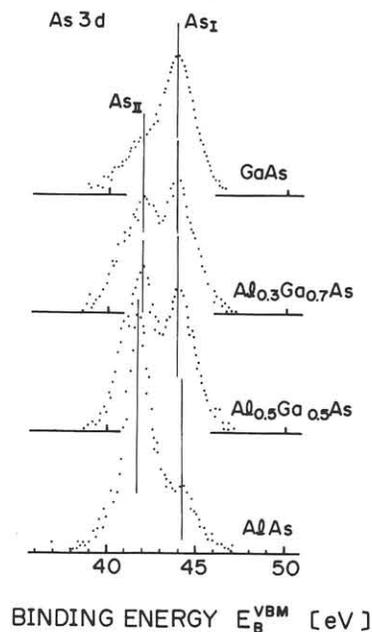


Fig. 3 The As 3d difference spectra between spectra for clean and oxygen exposed AlGaAs surfaces.

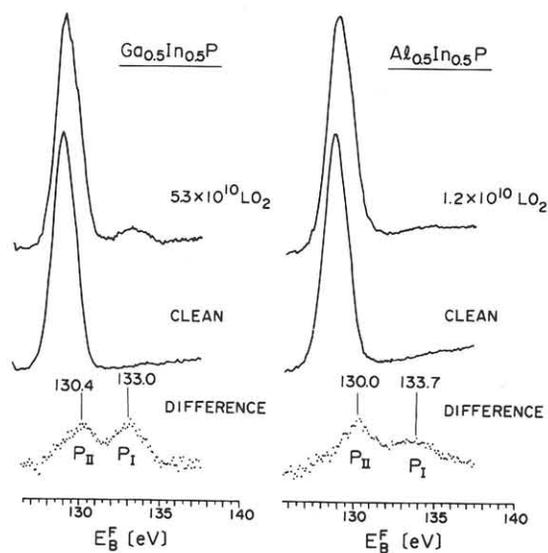


Fig. 4 Oxygen induced P 2p spectra for $Ga_{0.5}In_{0.5}P$ (left) and $Al_{0.5}In_{0.5}P$ (right) surfaces. Solid line: The P 2p spectra of clean and oxygen exposed surfaces. Dotted line: The P 2p difference spectra.

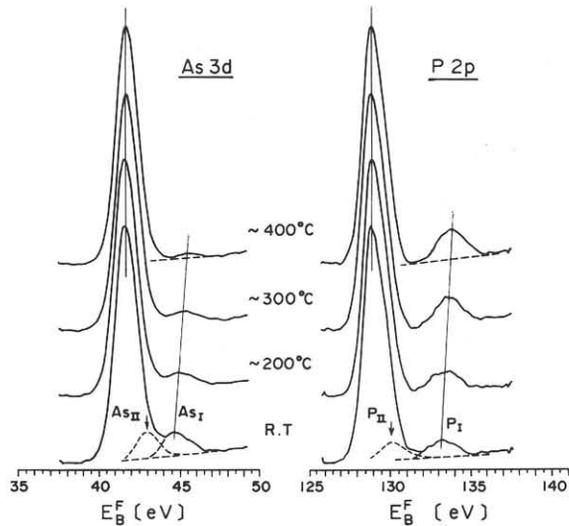


Fig. 5 Changes in the As 3d (left) and the P 2p (right) spectra upon successive annealing for 10^{10} - 10^{11} oxygen exposed surfaces in UHV.

different. After 10^{10} - 10^{11} oxygen exposure, the samples were annealed successively up to 400 °C in UHV. As can be seen in Fig. 5, oxidic phase As_I shifts towards higher energy and both As_I and As_{II} decrease in intensity with increasing annealing temperature. On the other hand, the oxidic phase P_I develops in intensity, shifting towards higher energy with increasing temperature, whereas the P_{II} peak decreases. Shifted P_I peak at 400 °C corresponds to $(In,Ga,Al)PO_4$ in energy.

5. CONCLUSION

Two successive adsorption stages were found from oxygen uptake measurements. The first stage corresponds to Elovich kinetics (adsorption to surface imperfections) and the second stage corresponds to Langmuir kinetics (dissociative chemisorption). Oxygen preferentially interacts with surface group-III atoms, resulting in the precursor phase appearance for elemental-V (As,P), and thus causes surface disorder.

Considering that $(Al_xGa_{1-x})_0.5In_0.5P$ has a larger bandgap than $Al_xGa_{1-x}As$ with the same Al content, $(Al_xGa_{1-x})_0.5In_0.5P$ is a promising

visible laser material 8) 9) because of the less oxidized property and the less instability for the oxidized surface.

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