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Successful Passivation of Air-Exposed AlGaAs Surfaces by a Silicon Interface Control Layer-Based Technique

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In order to make the recently optimized Si Interface Control Layer (ICL)-based surface passivation technique applicable to air-exposed AlGaAs surfaces,various surface treatments were systematically investigated. The chemical status and quality of the treated surfaces were evaluated by in-situ and ex-situ X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) measurements. It is shown that remarkable reduction of oxide components and enhancement of PL intensity are realizable by a combination of HCl surface treatment and Si ICL formation.

1. Introduction

Surface passivation is an unsolved important technological issue for AlGaAs/GaAs-based electronic and optoelectronic devices such as high electron mobility transistors (HEMTs), hetero-junction bipolar transistors (HBTs) and double-hetero (DH) lasers. Catastrophic damage in cleaved facet mirrors in visible lasers is, for example, known to be related to oxidation enhancement by surface recombination of carriers through surface states. Such surface or interface states are also known to cause pinning of Fermi level at the surface[1] and cause unwanted phenomena in conventional electronic devices such as HEMTs and HBTs. A recent finding[2-4] that the photoluminescence (PL) intensity from AlGaAs/GaAs near-surface quantum wells drops exponentially due to surface states as the well-to-surface distance is reduced, indicates that surface states cause unwanted phenomena in quantum devices utilizing AlGaAs/GaAs nanostructures.

We have recently reported[5] that such PL intensity reduction in near-surface AlGaAs/GaAs quantum wells can be completely suppressed and the PL intensity can be increased by more than 10^3 times by applying a novel surface passivation technique utilizing a molecular beam epitaxy (MBE)-grown ultrathin silicon interface control layer (Si ICL).[5-7] However, this technique requires an in-situ ultra high vacuum (UHV)-based processing sequence and is not readily applicable to air-exposed AlGaAs surfaces due to presence of native oxides. This greatly limits its applicability to conventional devices.

The purpose of the present paper is to carry out a systematic study on surface treatments in order to make the Si ICL-based surface passivation technique applicable to air-exposed AlGaAs surfaces. Various surface treatments were applied to air-exposed AlGaAs surfaces, and the effect of the treatments were evaluated at various stages of passivation using X-ray photoelectron spectroscopy (XPS) and PL measurements. It is shown that a combination of HCl-treatment prior to Si ICL formation is most powerful for successful passivation, resulting in a remarkable enhancement of the surface PL intensity.

2. Experiment

The structure of the sample passivated by the Si ICL-based passivation technology is shown in **Fig.1**. This structure is the optimized version of this technology recently applied to AlGaAs/GaAs near-surface quantum wells using an entirely UHV-based in-situ process.[5] In the present study, this structure was fabricated on air-exposed AlGaAs surfaces after various surface treatments.

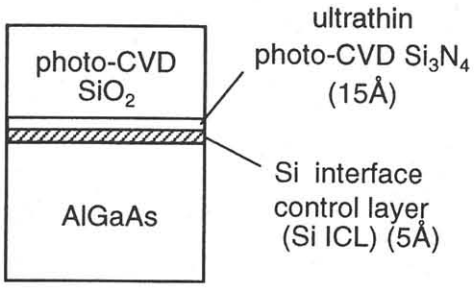

Fig.1. Si ICL-based passivation structure.

Samples were prepared in the following way. First, Si-doped n-$Al_xGa_{1-x}As$ (x=0.3) epitaxial layers with carrier concentration of $1\times10^{17}cm^{-3}$ were grown on n^+-GaAs (100) substrates. Then, the surfaces of the AlGaAs epitaxial layers were exposed to the air which resulted in formation of native oxides. Next, sample surfaces were chemically etched by a conventional wet etchant of H_3PO_4:H_2O_2:H_2O=1:1:38 for 1 minute, and then treated by three different surface treatment methods including (i) UHV thermal cleaning in the MBE chamber, (ii) sulfur (S)-treatment and (iii) HCl-treatment. The conditions for the treatments are summarized in **Table 1**. The S-treatment and HCl-treatment were performed in N_2 atmosphere at room temperature to prevent oxidation of the surfaces during treatments. Then, maintaining N_2 atmosphere, they were carried into a UHV-based growth/fabrication/characterization system. In this system, an MBE chamber, a photo-chemical vapor deposition (CVD) chamber, an in-situ XPS chamber and an in-situ PL chamber were connected among others by a UHV-transfer chamber. A pseudomorphic ultrathin Si ICL (5Å) was grown by MBE at a substrate temperature of 250°C. Finally, a double-layer dielectric consisting of an ultrathin Si_3N_4 layer (15Å) and a thick outer SiO_2 layer (500Å), was deposited by photo-CVD processes using an ArF excimer laser (193nm) as the excitation source. Chemical status and electronic properties of the various surfaces at various passivation steps were characterized by in-situ and ex-situ XPS/PL measurements.

3. Results and Discussion

3.1 Chemical Phases on Air-exposed and Surface-treated AlGaAs surfaces

The Al2p, Ga2p and As2p XPS spectra from the freshly grown MBE $Al_{0.3}Ga_{0.7}As$ surface are shown in **Fig.2**, and this was used as the reference. **Figure 3** shows the XPS Al2p, Ga2p and As2p core level spectra observed at **(a)** initial air-exposed surfaces and **(b)** thermally cleaned surfaces. Large amounts of oxide components exist on the air-exposed surface. By UHV thermal cleaning, As- and Ga-oxides were greatly reduced. However, Al-oxide components still remained together with some AlAs formation. Effect of thermal cleaning quickly disappeared when the surface was re-exposed to the air.

Figures 4 and 5 show the measured XPS spectra of the S-treated and HCl-treated surfaces, respectively. Changes of various components at various steps of processing are summarized in **Fig.6** in terms of the integrated intensity ratio of the XPS spectra. After the S-treatment, As- and Ga-oxides were drastically reduced and As-sulfide phases were formed similarly to the case of GaAs.[8] However, most of Al-oxide component remained, as reported by Oigawa et al.[9] This persisted even after Si ICL formation as seen in **Fig.4**. In contrast to this, all oxide components could be removed almost completely by a combination of HCl-treatment and Si ICL formation as seen in **Fig.5**. The resultant spectra were very similar to those of MBE-grown clean AlGaAs surface as clearly seen by comparing in **Fig.5** with **Fig.2**.

Table 1. Summary of surface treatment conditions.

method	condition	time
(i) UHV thermal cleaning	MBE chamber 650℃ under As_4 flux	60min
(ii) S-treatment	6% $(NH_4)_2S_x$ solution in N_2 ambient	5min
(iii) HCl treatment	3% HCl solution in N_2 ambient	1min

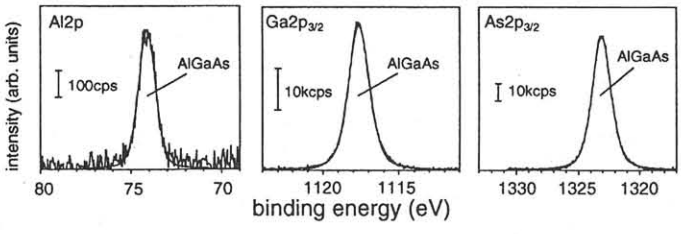

Fig. 2. XPS spectra from the freshly grown MBE AlGaAs surface.

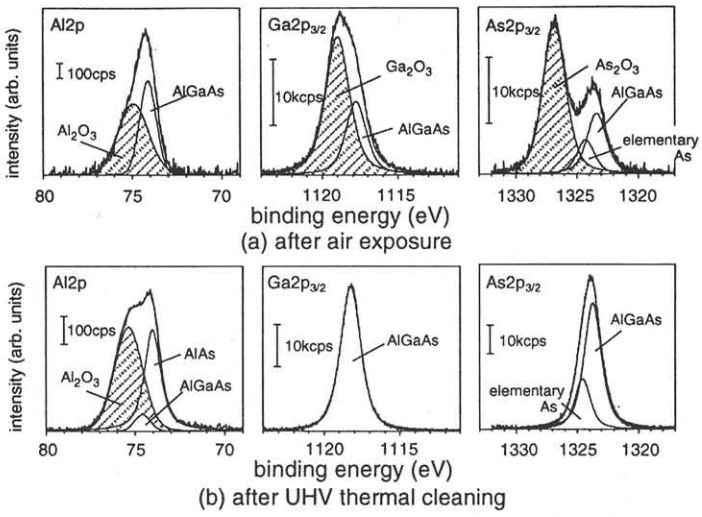

Fig. 3. XPS spectra from AlGaAs surfaces : (a) after air exposure, (b) after UHV thermal cleaning.

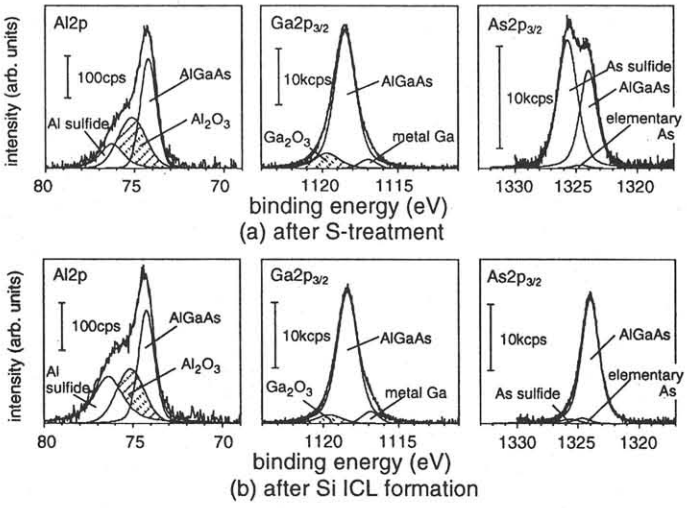

Fig. 4. XPS spectra from AlGaAs surfaces : (a) after S-treatment, (b) after following Si ICL formation.

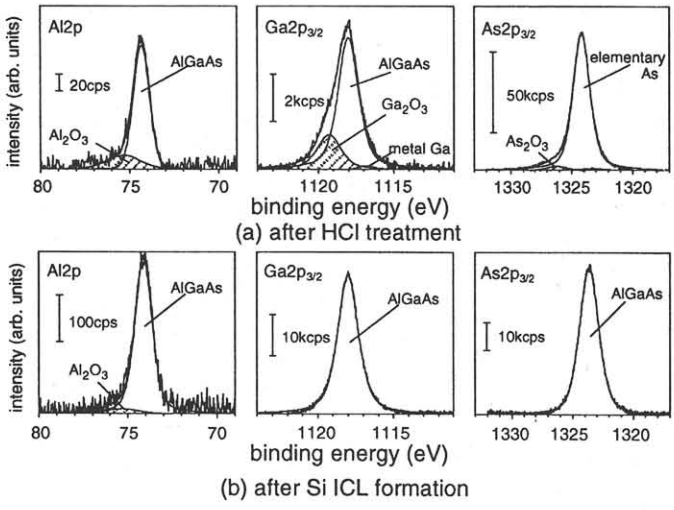

Fig. 5. XPS spectra from AlGaAs surfaces : (a) after HCl-treatment, (b) after following Si ICL formation.

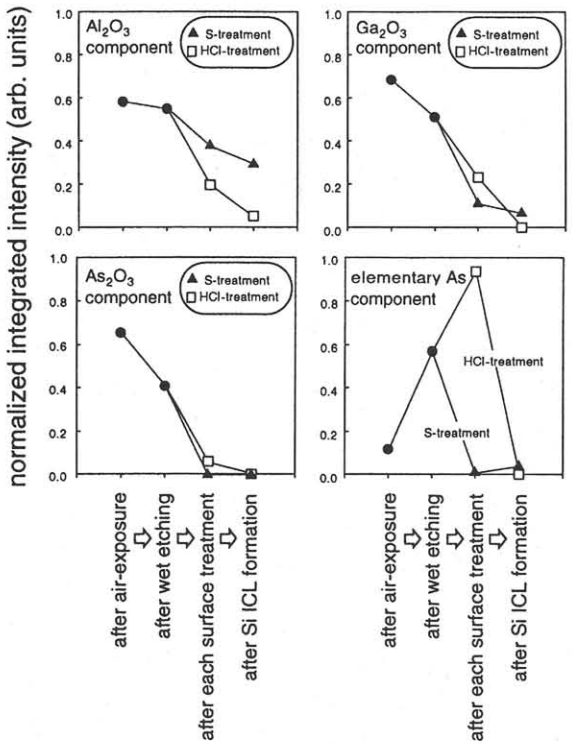

Fig. 6. Normalized XPS intensities obtained from various AlGaAs surfaces.

3.2 Photoluminescence Properties of Treated Surfaces

In order to examine the relation between surface structures of AlGaAs surfaces and their optical properties, PL measurements were performed at various stages of passivation. PL spectra obtained from various surfaces are summarized in **Fig.7**. As shown in this figure, PL intensity was drastically decreased after air-exposure compared with that of the in-situ MBE-grown surface. The PL intensity was enhanced by UHV thermal annealing, corresponding to the reduction of oxide components. However, PL intensity was strongly decreased by re-exposing the thermally cleaned surface to the air again.

The change of PL intensity is summarized in **Fig.8** for S- and HCl-treated surfaces. In the case of S-treatment, the intensity became so weak after the treatment, unlike the case of S-treated GaAs surface.[10] By applying the Si ICL-based passivation, significant recovery of the PL intensity was obtained, but it is far from that of initial MBE surface. On the other hand, the PL intensity was drastically recovered near to the level of the freshly MBE-grown AlGaAs surface by a combination of HCl-treatment, Si ICL formation and subsequent deposition of insulating films.

The overall PL behavior of various surfaces seems to exhibit strong correlation with the presence of Al-oxide components. Such a correlation seems to be consistent with the DIGS model for surface state formation at insulator-semiconductor interface[1] since selective oxidation inevitably destroys two-dimensional order of the interface. The recovery of PL intensity by the S-treatment was low, and this seems to be related to persistence of the Al-oxide component throughout the processing as shown in **Figs.4 and 6**. On the other hand, reduction of all the oxide components by a combination of HCl-treatment and Si ICL formation probably gives rise to realization of ordered and stoichiometric AlGaAs surface with low-density of surface and interface states.

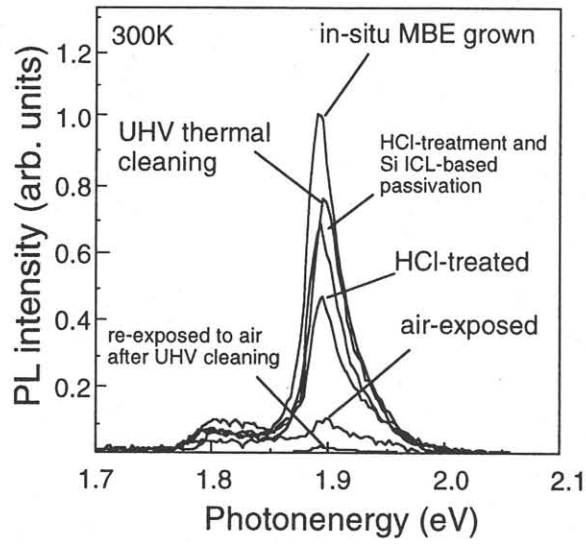

Fig. 7. PL spectra from various AlGaAs surfaces.

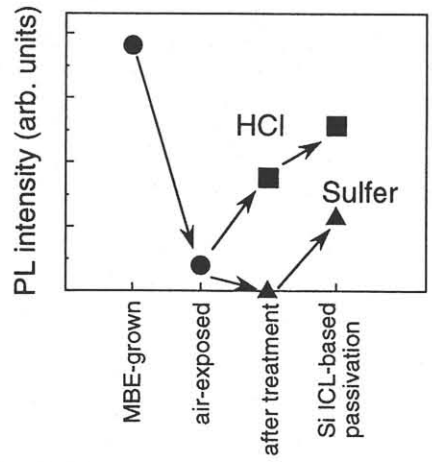

Fig. 8. Change of PL intensity from S-treated and HCl-treated AlGaAs surfaces.

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