

Correlation between Chemical and Electrical Properties of n-InGaP Surfaces Grown by MOVPE

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ABSTRACT

Correlation between chemical and electrical properties of n-InGaP surfaces grown by metal-organic chemical vapor epitaxy (MOVPE) was investigated by x-ray photoelectron spectroscopy (XPS), current-voltage (I-V) and UHV contactless capacitance-voltage (C-V) methods. An air-exposed surface exhibited highly In-rich phase where the InPO_4 -like natural oxide was dominant. Poor I-V characteristics appeared in Schottky contacts fabricated on the air-exposed surfaces. Chemical treatments in HCl and HF solutions were found to be effective in reducing natural oxide and in recovering the surface stoichiometry. The UHV contactless C-V results showed no pronounced Fermi level pinning at the chemically treated InGaP surfaces. Furthermore, such treatments improved Schottky I-V properties.

INTRODUCTION

InGaP and lattice-matched InGaP/GaAs heterostructures are promising materials for the production of high-power/high-frequency devices such as heterojunction bipolar transistors (HBTs) and high-electron mobility transistors (HEMTs). For the reproducibility of the device fabrication process and the reliability of the device operation, it is indispensable to understand and control surface properties of the base materials. However, surface chemistry of InGaP has not been explored in detail.

In this paper, we present a investigation on surface chemistry as well as its correlation with surface electrical properties of InGaP grown by MOVPE, especially focusing on chemically processed surfaces which actually act as an initial surface for the device fabrication process.

EXPERIMENTAL

Si-doped $\text{In}_{0.49}\text{Ga}_{0.51}\text{P}$ epitaxial layers were grown on n^+ GaAs (001) substrates at 580°C by MOVPE with trimethylindium (TMI), triethylgallium (TEG) and phosphine (PH_3). The layer thickness of InGaP was approximately 600 nm, and the carrier concentration of the grown layer determined by a Hall measurement was $6 \times 10^{16} \text{ cm}^{-3}$. The band-edge photoluminescence at room temperature (RT) was found at 1.85 eV which corresponds to an ordering parameter, α , of 0.35-0.40 [1]. Preliminary deep level transient spectroscopy (DLTS) study showed that no pronounced electron trap with the density higher than $1 \times 10^{14} \text{ cm}^{-3}$ was found in the InGaP layer.

Properties of natural oxide on as-grown and air-exposed InGaP surfaces were investigated at first. In order to control the InGaP surface, the effects of the wet chemical treatments using the following three kinds of solutions were investigated: (i) an NH_4OH solution at 50°C for 10min, (ii) an $\text{HCl}:\text{H}_2\text{O} = 1:1$ solution at RT for 1min, and (iii) $\text{HF}:\text{C}_2\text{H}_5\text{OH}=1:5$ solution at RT for 2min.

The surface chemical properties of InGaP layers were characterized by XPS using Perkin Elmer PHI 1600C system with a spherical capacitor analyzer and a monochromated Al $K\alpha$ x-ray source ($h\nu=1486.6 \text{ eV}$). I-V measurements were done using HP 4156A semiconductor parameter analyzer.

RESULTS AND DISCUSSION

1. Air-exposed InGaP surface

Figure 1 shows XPS spectra of the In $3d_{5/2}$, Ga $2p_{3/2}$, P $2p$, and O $1s$ core levels for the air-exposed InGaP surface. For comparison, the peak intensities were adjusted at each spectra. The In $3d$ signal with an electron escape angle of 15 deg exhibited broad spectra with the peak shift to the higher binding energies in comparison to that taken with 45 deg, indicating that the surface spectrum included a large amount of an oxide component. An asymmetric feature appeared in the Ga $2p$ core-level spectrum with 15 deg, as shown in Fig.1 (b). A shoulder at higher binding energies is attributed to the Ga oxide. From the XPS integrated intensity ratio taking account the sensitivity factors, the Ga/In atomic composition was determined to be 0.2, i.e., highly In-rich value. In the P $2p$ spectrum (Fig.1 (c)), an additional peak with the chemical shift of 4.9 eV against the pure InGaP bond was clearly seen. High intensity of the O $1s$ peak was also detected at a peak energy of 531.7 eV. All the results indicated that the air-exposed InGaP surface was covered with a natural oxide with highly In-rich phase.

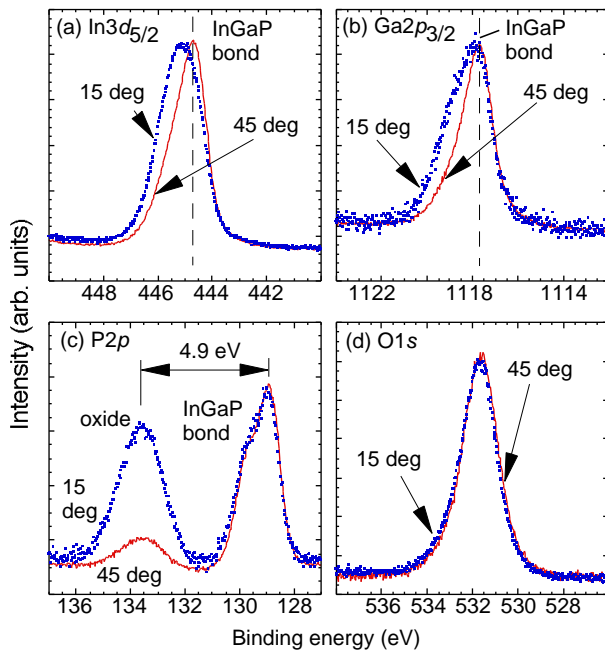


Fig.1 XPS core-level spectra of an air-exposed InGaP surface. The peak intensities were adjusted at each spectrum for comparison.

The measured valence-band spectra of the air-exposed InGaP surface are shown in **Fig.2**. The spectrum with the escape angle of 45 deg mainly originating from the bulk electronic band structure was similar to those of the base-binary materials, InP and GaP. On the other hand, the spectrum with the escape angle of 15 deg was very different from the bulk one, reflecting an electronic structure of the surface natural oxide. In comparison to the previous report [2], the spectrum is very similar to that of InPO_4 , one of the native oxides of InP. This is also confirmed by the O $1s$ peak energy, energy separations of oxide phases in main core levels and the chemical shifts in P $2p$ levels, as summarized in **Table I**. As seen, the position of the O $1s$ peak as well as the energy separations between the O $1s$ peak and In- and P-core level peaks are very

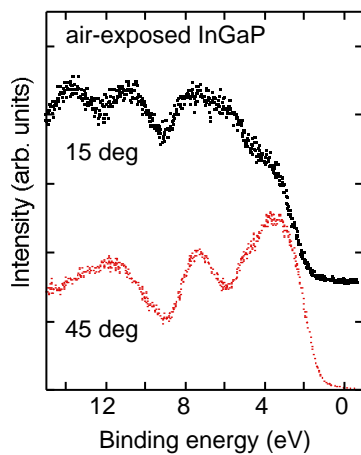


Fig.2 Valence-band spectra of an air-exposed InGaP surface.

TABLE I. The O $1s$ peak energies, energy separations and chemical shifts of oxide phases in P $2p$ spectra in the unit of eV.

oxides	O $1s$	O $1s$ -In $3d$	O $1s$ -P $2p$	O $1s$ -Ga $3d$	chemical shift in P $2p$
InPO_4 ^{a)}	531.8	86.1	397.7		5.3
InGaP oxide	531.7	86.3	397.9	511.3	4.9

a) Ref.3

close to those of InPO_4 [3]. In the P 2p level, in addition, the chemical shift of the oxide phase from the InGaP bond peak was found to be 4.9 eV, almost corresponding to the value of InPO_4 [3].

2. Chemically treated InGaP surfaces

Figure 3 shows the In3d, Ga2p and P 2p core-level spectra of InGaP surfaces taken with an escape angle of 15 deg before and after the wet chemical treatments. As seen, all the treatments effectively decreased the intensity of the oxide phases in the core levels. For the In 3d and Ga 2p spectra, symmetric features with the narrowing of linewidths and noticeable peak shifts towards lower binding energies were observed after these treatments. In addition, the peak positions of In 3d and Ga 2p levels were very close to those of InGaP bonds. An HCl solution is known to act as an etchant for InP and InGaP, thereby reducing natural oxide of InGaP. Further reduction of the oxide intensity was realized by the HF treatment. It is also well known that natural oxides of InP mainly consisting of the InPO_4 component are effectively removed by the HF treatment [4]. After the treatments in HCl and HF solutions, the Ga/In composition values at the InGaP surfaces became 0.4 - 0.5 (the air-exposed surface has a value of 0.2). The reduction of In-rich natural oxide led to the recovery of surface stoichiometry.

Electrical properties of chemically-treated InGaP surfaces were investigated by an unique contactless technique, the UHV contactless C-V method. The basic set-up of the UHV contactless C-V system is schematically shown in **Fig.4**. An ultranarrow "UHV gap" (200-500 nm) is achieved and maintained between the upper plate and the sample surface, as shown in Fig.4 (b), using a piezo electric control based on the capacitance feedback from three parallelism electrodes. This UHV gap acts as an ideal insulating layer, realizing the C-V assessment on "free" semiconductor surfaces. The value of the UHV gap length was determined by an optical technique. When the UHV gap comes to the range of sub-micronmeter, the reflectivity of the laser light decreases due to the disturbance of evanescent wave. From the reflectivity change, the UHV gap length can easily be calculated. The area of measurement electrode is $7.5 \times 10^{-3} \text{ cm}^2$ and the measurement frequency is 500 kHz. The details of the UHV contactless C-V system are described elsewhere [5, 6].

Figure 5 shows the measured UHV contactless C-V curve of the InGaP surface after the HCl treatment. The result showed a large capacitance variation almost from the insulator capacitance, C_i , to the inversion capacitance, C_{inv} . This indicated that the surface potential of InGaP was fairly

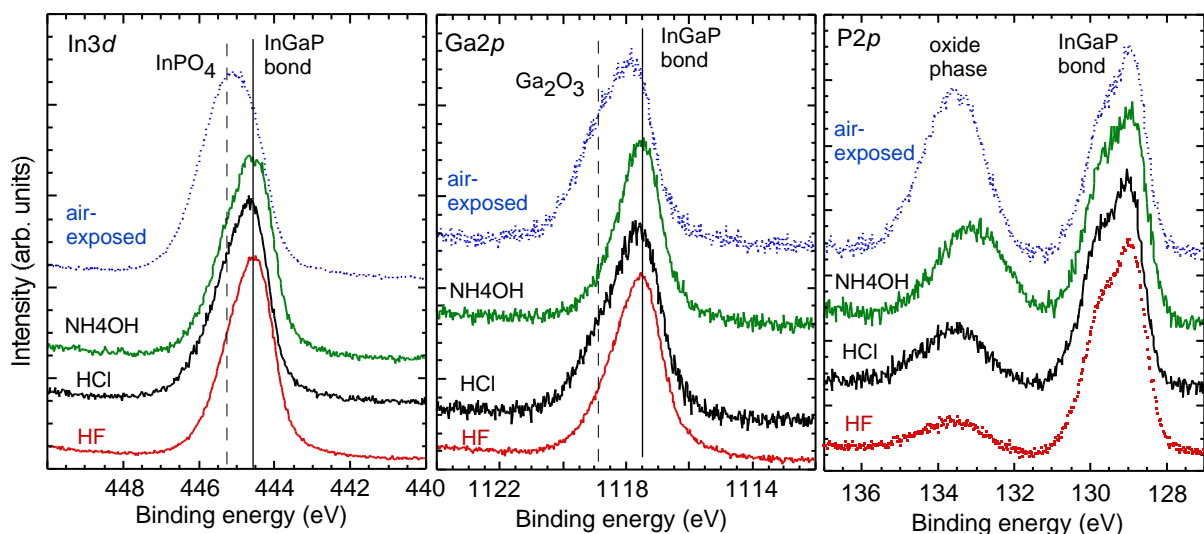


Fig.3 In3d, Ga2p and P 2p spectra with an escape angle of 15 deg before and after chemical surface treatments. The peak heights of the InGaP bond are adjusted for comparison.

controlled within the bandgap by the applied gate field, i.e., no pronounced Fermi-level pinning effect on the HCl-treated InGaP surface. As described above, the HCl treatment realized the reduction of natural oxide and the stoichiometry recovery, resulting in relatively well-ordered surface with lower density of surface state. This is not the case for GaAs.

Finally we investigated Schottky interface properties. **Figure 6** compares I-V characteristics of the Cr/n-InGaP Schottky contacts with and without the HCl treatment. The contact without the HCl treatment showed relatively high ideality factor, n , of 1.20, while it lowered to 1.06 for the diode with the surface treatment, as shown in the inset of Fig. 6. In the reverse bias region, a stronger dependence of the leakage current on the bias voltage appeared for the diode without the HCl treatment. The InPO_4 -dominant native oxide inhomogeneously formed on the air-exposed InGaP could degrade the interface electric properties, similar to the InP surface [7]. Significant reduction of reverse leakage current was obtained in the contact with the HCl treatment, consistent with the UHV contactless C-V result.

SUMMARY

Chemical and electrical properties of n-InGaP surfaces grown by MOVPE were systematically investigated using XPS, UHV contactless C-V and I-V techniques. An air-exposed surface possessed large amounts of InPO_4 -like natural oxide. Poor I-V behavior appeared in the Schottky contacts fabricated on the air-exposed surfaces. Chemical treatments in HCl and HF solutions were found to be effective in reducing natural oxide and in recovering the surface stoichiometry. The UHV contactless C-V results indicated no pronounced Fermi level pinning at the chemically treated InGaP surfaces. Furthermore, such treatments improved Schottky interface properties.

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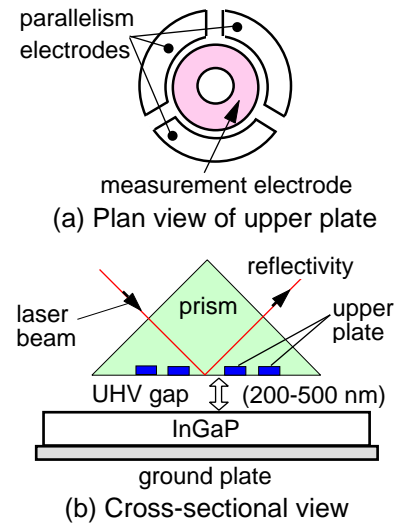


Fig.4 Basic set-up of the UHV contactless C-V system.

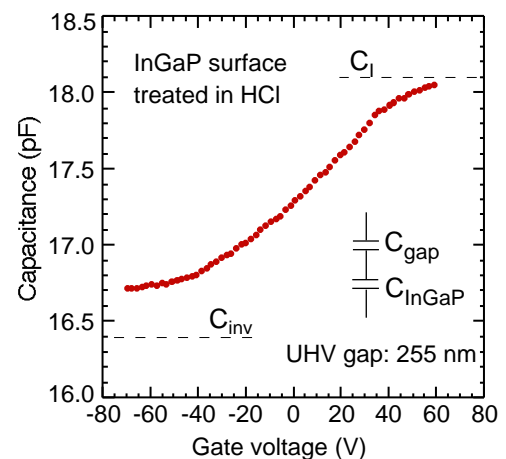


Fig. 5 UHV contactless C-V curve of a free InGaP surface after the HCl treatment.

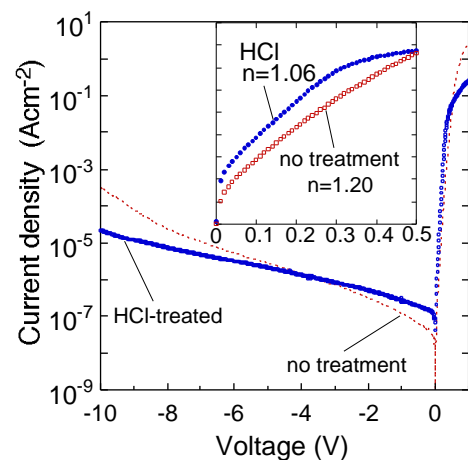


Fig. 6 I-V characteristics of the Cr/n-InGaP Schottky contacts with and without the HCl treatment.