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Anisotropic Etching of InP and InGaAs by Using an Inductively Coupled Plasma in Cl_2/N_2 and Cl_2/Ar Mixtures at Low Bias Power

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In order to obtain low-damage and vertical-etch profiles during etching of InP and $In_{0.53}Ga_{0.47}As$, we used inductively-coupled-plasma (ICP) etching with Cl_2/N_2 and Cl_2/Ar gas chemistries at bias powers below 25 W. Vertical etch features were obtained at a gas mixture of $Cl_2 : N_2 = 2 : 13$ and a bias power of 25 W for both materials. In the etch process for InP using Cl_2/N_2 gas chemistry, PN_x was formed on the sample surface. The vapor pressure of PN_x was significantly lower than that of PCl_x as revealed by X-ray photoelectron spectroscopy (XPS) results. Therefore, through the sidewall passivation by PN_x, the sidewall of InP was blocked from the etching species, and that resulted in a highly vertical profile at low bias power. On the other hand, in the etch process for InGaAs using Cl_2/N_2 gas chemistry, As-N bonds formed on the surface during the etching, and the sidewall passivation by As-N appeared to cause vertical etch profiles at low bias power.

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I. INTRODUCTION

The fabrication of III-V- or II-VI-based optoelectronic devices requires many etching steps using either wet or dry processing. Dry etching offers a number of advantages over wet etching these include the ability to perform *in-situ* processing and to consistently achieve highly anisotropic etching. The later is an important factor in controlling device dimensions. Several dry etching techniques, such as electron cyclotron resonance (ECR) plasma etching [1,2], inductively coupled plasma (ICP) etching [3–5], ion beam (IB) etching [6], *etc.* using high ion energies, have been used to realize highly anisotropic etch profiles. However, high-energy-ion-assisted etch techniques engender damage to the active layer and the contact layer. Therefore, a low-energy ion-bombardment etch process must be used to reduce damage during etching.

For the gas mixtures, hydrogen-based and chlorine-based gas mixtures have been widely used to etch InP and related compounds [5]. In the case of a hydrogen-based plasma for InP and InGaAs etching, the preferential losses of phosphorous and arsenic due to the formation of highly volatile H-related byproducts (PH_3 and AsH_3) cause undesirable surface properties. In-rich surfaces due to unbalance losses lead to serious current leakages between devices and increase the surface roughness after etching. Also the hydrogen atoms implanted in the active or the contact layers during etching cause the device to have poor electrical properties. Because of these problems mentioned above, most investigation on the dry etching of InP and related materials have been focused on chlorine-based etching without hydrogen (*e.g.*, Cl_2, BCl_3, CCl_4, $SiCl_4$, and CCl_3F) [4,7–9]. However, these gas chemistries require high-energy ions during etching to inhibit the undercut in the etch profiles. On the other hand, in low-energy ion bombardment, serious undercut can occur because chlorine-based etch products, such as PCl_x and $AsCl_x$, have very high volatilities in addition to the volatility of $InCl_x$.

In order to achieve highly anisotropic etch profiles of InP and InGaAs and low damage to the devices, a sidewall passivating additive gas needs to be introduced during etching by using a chlorine-based gas at a low bias power. In this work, Cl_2/Ar and Cl_2/N_2 gas mixtures were used for ICP etching of InP and InGaAs at low bias powers, and the effect of additive gases, such as Ar and N_2,on the etch characteristics were investigated to

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obtain vertical etch profiles at low bias powers.

II. EXPERIMENT

Two-μm-thick Si-doped n-type InP and $In_{0.53}Ga_{0.47}As$ layers grown on semi-insulating InP substrates were used as the substrate in this experiment. Three-hundred (300)-nm-thick SiO_2 layers were deposited on the InP and the InGaAs layers by using plasma-enhanced chemical vapor deposition. The mask pattern definition on these samples was accomplished by using a lithographically patterned NiCr mask, and the etch patterns were finally transferred onto the SiO_2 layers by using CHF_3 reactive-ion-etching (RIE). InP and InGaAs were then etched using a PlasmaTherm SLR 770 ICP-RIE system. The inductive coil power (at 2 MHz) was fixed at 900 W. In order to investigate the effects of bias power and working pressure on the etch rates and profiles, we varied bias power at 13.56MHz supplied to the substrate during etching from 5 W to 25 W. The working pressure, which was controlled by a feedback-controlled throttle valve during the etching, was varied from 3 mTorr to 20 mTorr. The base chamber pressure was kept below 10^{-5} Torr. Separate mass flow controllers controlled the flow rates of the process gases (Cl_2, N_2, and Ar) while the total flow rate was kept constant at 30 sccm. The substrate temperature was also varied from room temperature to 300 °C.

Etch rates were determined from the depths of the etched features measured using a stylus profilometer before and after removing the SiO_2 mask layer in a buffered oxide etchant. The etch profiles were inspected using a scanning electron microscope (SEM) before removing the mask layer. X-ray photoelectron spectroscopy (XPS) was utilized to find the possible vertical etching mechanism.

III. RESULTS AND DISCUSSION

1. Etch Rate

In order to investigate the effects of Cl_2/N_2 and Cl_2/Ar gas chemistries on the etch rates of InP and InGaAs, 2-μm-thick Si-doped n-type InP and $In_{0.53}Ga_{0.47}As$ films were etched in the ICP etching system. Figure 1 shows the etch rates of InP and InGaAs as functions of the Cl_2 percentage in Cl_2/N_2 and Cl_2/Ar mixtures at a coil power of 900 W, a bias power of 25 W, a working pressure of 5 mTorr, and a substrate temperature of ∼25 °C. As expected, the etch rates of both InP and InGaAs increased with Cl_2 flow rates to Cl_2/N_2 and the etch rate of InGaAs was higher than that of InP. The etch rate of In-related materials using Cl-based gas chemistry is well known to depend on the formation

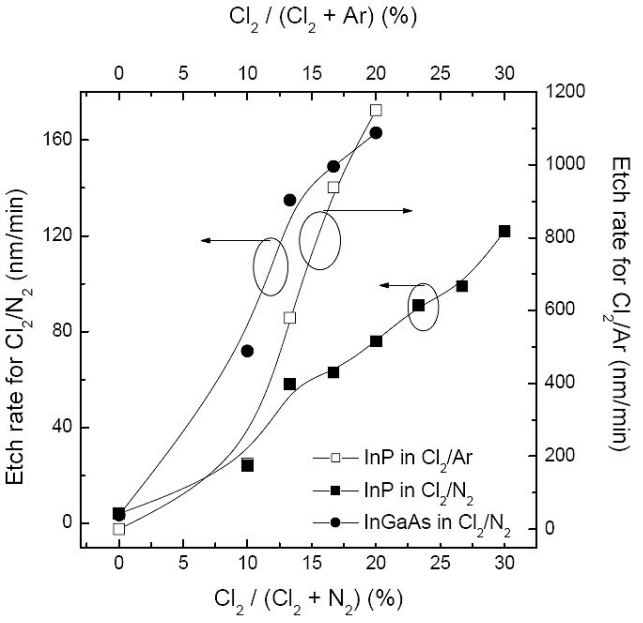

Fig. 1. Etch rates of InP and InGaAs as functions of chlorine flow rates to Cl_2/N_2 and Cl_2/Ar gas mixtures (coil power of 900 W, bias power of 25 W, working pressure of 5 mTorr, total flow rate of 30 sccm, and room temperature).

and removal rates of Cl-related byproducts. In the etch processes for InP and InGaAs using Cl-based chemistry, compounds such as InCl, $InCl_3$, $GaCl_3$, $AsCl_3$, and PCl_3 are produced, and their boiling points are 608, 586, 210, 130, and 76 °C, respectively. Therefore, the higher etch rate of InGaAs can be explained by the relatively high vapor pressures of the Cl-related byproducts.

To understand the effects of the bias power applied to the substrate on the etch rate, we etched InP and InGaAs at various bias powers from 5 W to 25 W while keeping the gas chemistry at Cl_2/N_2 = 4/26 sccm. Figure 2 shows the etch rates of InP and InGaAs as functions of the bias power for a coil power of 900W, and a working pressure of 5 mTorr at room temperature. As the figure shows, the etch rates of InP and InGaAs increased with the bias power. Furthermore, the increase in the bias power improved the etch profile, as shown in Figure 5. The increase in and improvement of the etch rate and the etch profile were dictated by the sputtering effect.

The effects of the working pressure and the substrate temperature on the etch rates were investigated by changing the pressure from 3 to 20 mTorr and the temperature from 25 to 300 °C, and the results are shown in Figures 3 and 4, respectively. Other conditions were kept the same; a coil power of 900 W, a bias power of 25 W, and a Cl_2/N_2 ratio of 4/26 sccm. As Figure 3 shows, the etch rates of InP and InGaAs increased with the working pressure. Due to an increase in the reactive species in the plasma as the working pressure increased at a fixed rf coil power of 900 W. Figure 4 shows that the etch rates of both InP and InGaAs increased with the substrate

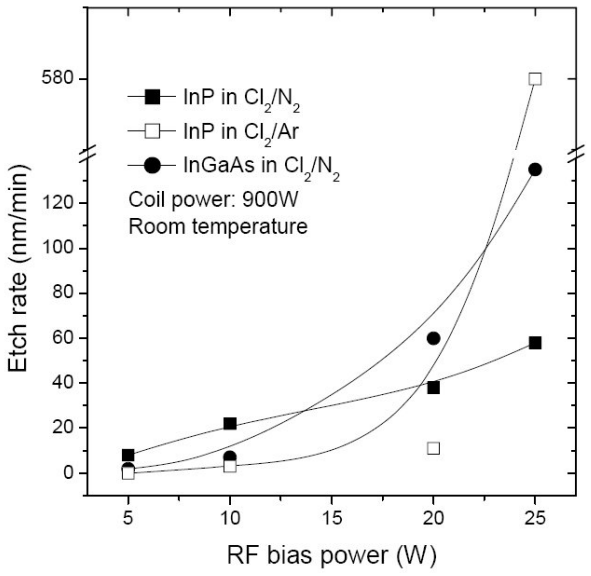

Fig. 2. Etch rates of InP and InGaAs as functions of the bias power applied to the substrate in Cl_2/N_2 and Cl_2/Ar plasmas (Cl_2/N_2 and Cl_2/Ar ratios of 4/26 sccm, coil power of 900 W, working pressure of 5 mTorr, total flow rate of 30 sccm, and room temperature).

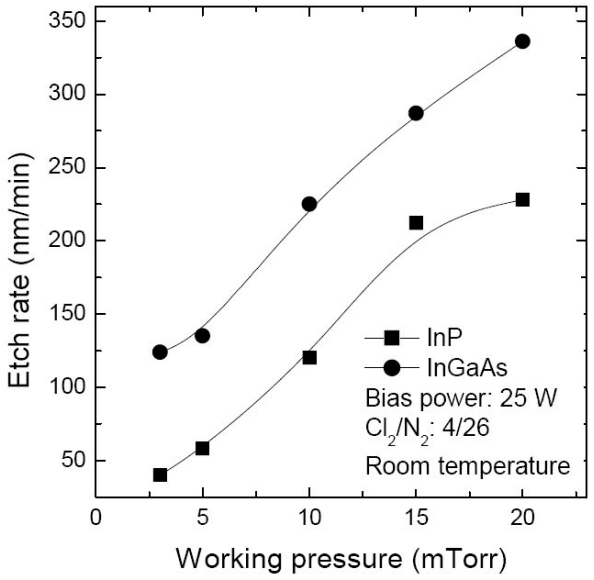

Fig. 3. Etch rates of InP and InGaAs as functions of the working pressure in a Cl_2/N_2 plasma (coil power of 900 W, bias power of 25 W, total flow rate of 30 sccm, and room temperature).

temperature over most of the range investigated when the etch products became more volatile. The etch rate, however, is nearly saturated at 250 °C for InGaAs and at 200 °C for InP. Several authors have reported an etch rate saturation or reduction at a relatively high temperature. Yoon *et al.* [10] reported a similar phenomenon while etching GaInP in a Cl_2/Ar plasma using ECR as

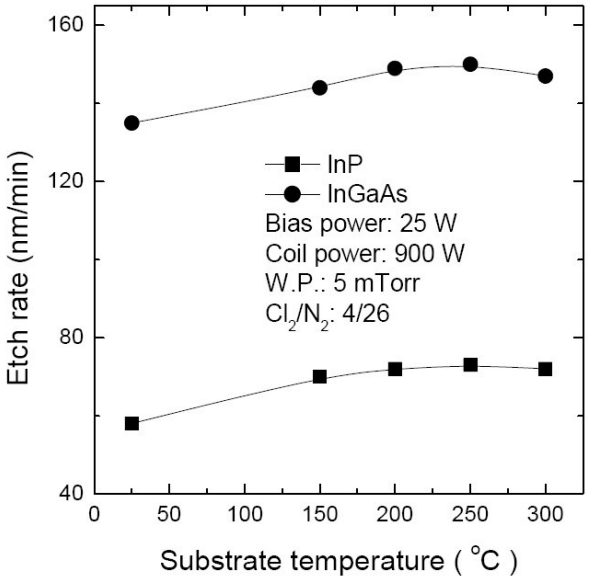

Fig. 4. Etch rates of InP and InGaAs as functions of the substrate temperature in a Cl_2/N_2 plasma (coil power of 900 W, bias power of 25 W, working pressure of 5 mTorr, total flow rate of 30 sccm).

the temperatures was changed from 55 °C to 110 °C. Ren *et al.* [11] also reported that the critical temperature, where the etch rate decreased, was 300 °C while etching GaInP in a BCl_3 plasma. Contolini [12] also presented a similar trend with Ren *et al.* under the same RIE condition for high temperature etching of GaAs. It is noteworthy that the etch rate decreases at a certain substrate temperature even though the saturation point seems to vary with the experimental conditions and the plasma system. The reason is desorption of the active species, the group of chlorine radicals, before it reach the material surface.

2. Etch Profiles and Surface Analysis

The degree of anisotropic etching here is defined as the vertical property (V = W/H), as shown in Figure 5, where H and W are the etch depth and the undercut depth, respectively. To compare the etch profile images of InP and InGaAs etched in Cl_2/N_2 and Cl_2/Ar plasmas, we utilized a SEM. All samples were etched using the same plasma conditions; a coil power of 900 W, a Cl_2/N_2 flow rate of 4/26 sccm, and a working pressure of 5 mTorr at room temperature. The value of vertical property (V) decreased to zero at a bias power of 25 W, which means that the profile at 25 W had a vertical feature. The figure also shows that the anisotropic feature of InGaAs is better than that of InP at low bias powers.

Figure 6 shows that etch profile images of (a) InP and (b) InGaAs etched in a Cl_2/N_2 plasma, and of (c) InP etched in a Cl_2/Ar plasma. In the case of the Cl_2/N_2

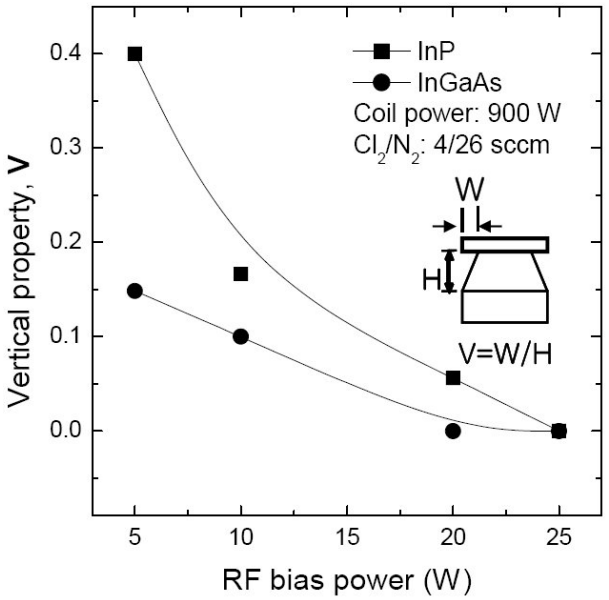

Fig. 5. Etch anisotropy of InP and InGaAs as functions of the bias power applied to the substrate in a Cl_2/N_2 plasma (coil power of 900 W, working pressure of 5 mTorr, total flow rate of 30 sccm, and room temperature).

plasma, both samples were vertically etched at a bias power of 25 W. N-related compounds formed during etching in a Cl_2/N_2 plasma are expected to suppress the fast removal of P and As atoms from the surfaces and to helps in inhibiting the undercut feature. On the other hand, the profiles of samples etched using Cl_2/Ar chemistry showed serious a undercut feature and rough etched surfaces at the same etch conditions. In the etch process using a Cl_2/Ar plasma, the volatilities of PCl_x and $AsCl_x$ are very high, in addition to the volatility of $InCl_x$; therefore, the undercut feature appears to be from the volatility of the etch products, and the rough etched surface appears to be from the differences in the volatilities of the etch products.

To find the etch mechanism and the byproducts formed on the etched surfaces, we utilized XPS. Figure 7 shows XPS core level spectra of In $3d_{5/2}$ and P $2p$ for InP samples etched in Cl_2/N_2 and Cl_2/Ar plasmas, respectively. The In $3d_{5/2}$ peaks for both samples can be deconvoluted into two peaks, one at 444.6 eV assigned to In in the In-P bond, and the other at 445.4 eV assigned to In in the In-Cl bond. On the other hand, the In $3d_{5/2}$ peak for the control sample has only one peak corresponding to the In-P bond. The P $2p$ peaks show two different kinds of $2p$ core level peaks; one at 133.4 eV corresponding to the P-N bond and the other corresponding to the P-In bond. From Figure 7, the peak intensity of the In-Cl bond for the sample etched in Cl_2/Ar is larger than that for Cl_2/N_2, whereas the peak intensity of the P-N bond for the Cl_2/N_2 plasma is much larger than that for Cl_2/Ar. The small peak of the P-N bond for the Cl_2/Ar plasma originates from the

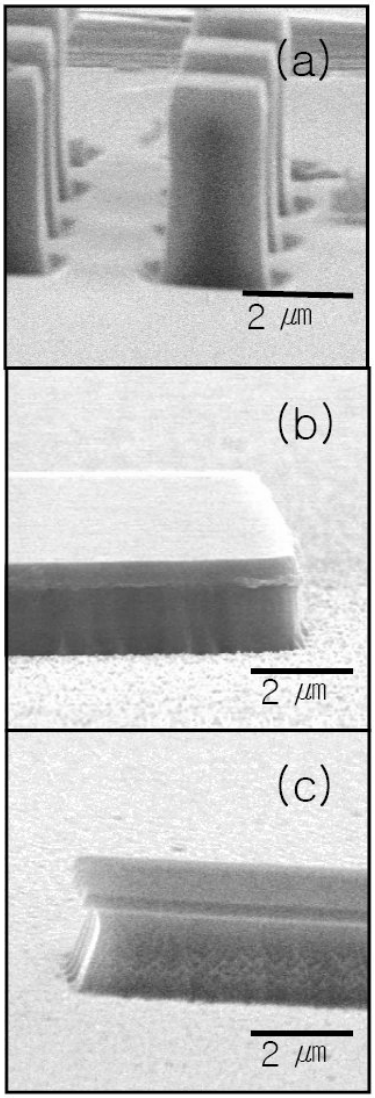

Fig. 6. Etch profile images of InP etched in (a) Cl_2/N_2 and (c) Cl_2/Ar plasmas and of InGaAs etched in a (b) Cl_2/N_2 plasma (Cl_2/N_2 and Cl_2/Ar ratios of 4/26 sccm, coil power of 900 W, bias power of 25 W, working pressure of 5 mTorr, total flow rate of 30 sccm, and room temperature).

residual nitrogen in the chamber. In the In $3d_{5/2}$ and the P $2p$ core level XPS spectra shown in Figure 7 the predominant byproduct remaining on the etched surfaces is an In-Cl compound for the Cl_2/Ar plasma and, a P-N compound for the Cl_2/N_2 plasma. Figure 8 shows As $3d$, Ga $3d$, and In $3d$ XPS spectra obtained from the InGaAs surface etched in Cl_2/Ar and Cl_2/N_2 plasmas and from the control sample. All of the peaks can be deconvoluted into a few peaks, the one on the lower binding energy side corresponding to the In-Ga-As bonds, and the others on the higher binding energy side corresponding to the O- or N-related bonds. Furthermore, from the As $3d$ XPS core level peak for the samples etched in a Cl_2/N_2 plasma, a new peak on the lower binding side of the As-O bond, besides the In-Ga-As and As-O bonds,

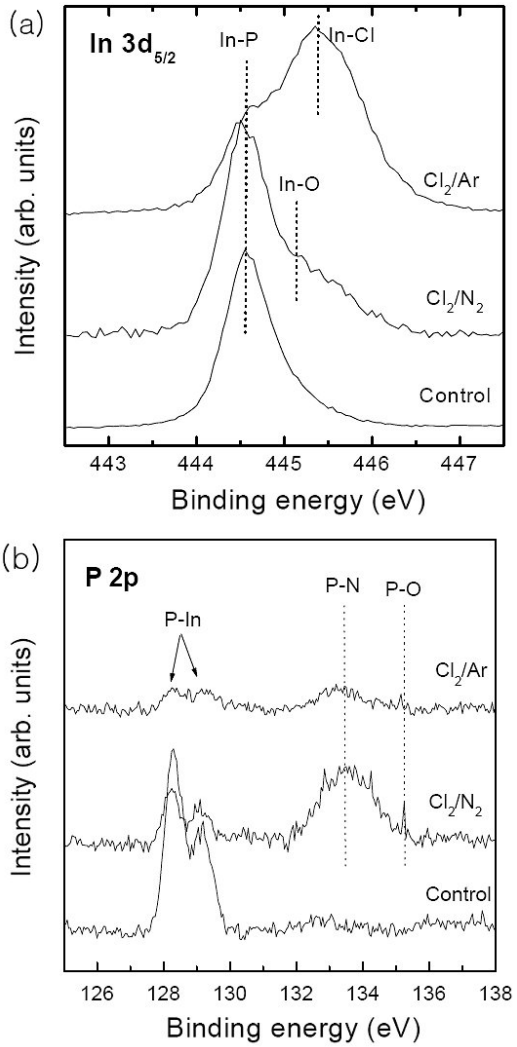

Fig. 7. (a) In $3d_{5/2}$ and (b) P $2p$ XPS core level spectra for InP etched in Cl_2/N_2 and Cl_2/Ar plasmas, and for a control sample. (Cl_2/N_2 and Cl_2/Ar ratios of 4/26 sccm, coil power of 900 W, bias power of 25 W, working pressure of 5 mTorr, total flow rate of 30 sccm, and room temperature).

appears. Although the binding energy of the As-N bond is not well known, from the chemical shift of this additional peak, we assigned this peak to the As-N bond. This is consistent with the result reported by Berkovits *et al.* [13]. The formations of As-N bonds on sidewall may suppress the preferential loss of As atom from the etched surface and help in improving the vertical etch property.

IV. CONCLUSIONS

In this study, dry etching of InP and InGaAs under low bias voltage was investigated in an ICP etching system using both Cl_2/N_2 and Cl_2/Ar chemistries. In

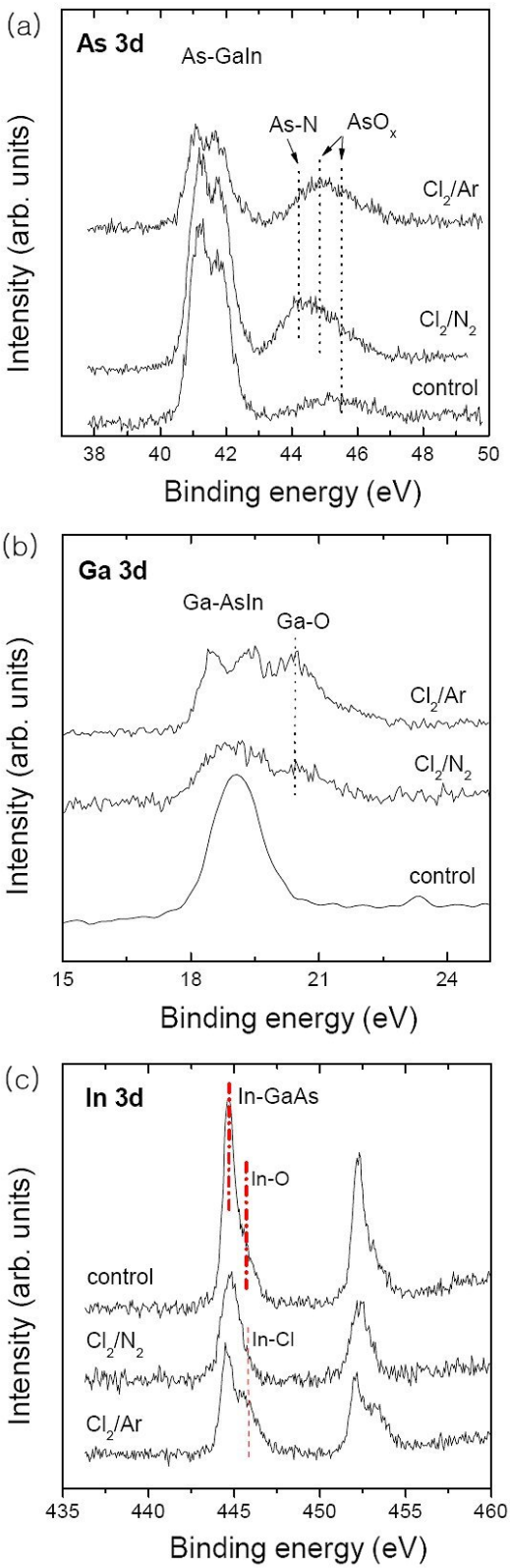

Fig. 8. (a) As $3d$, (b) Ga $3d$, and (c) In $3d$ XPS core level spectra for InGaAs etched in Cl_2/N_2 and Cl_2/Ar plasmas and for a control sample (Cl_2/N_2 and Cl_2/Ar ratios of 4/26 sccm, coil power of 900 W, bias power of 25 W, working pressure of 5 mTorr, total flow rate of 30 sccm, and room temperature).

the etch process using Cl_2/N_2 gas chemistry, nitrogen-related byproducts were formed on both samples' surfaces during the etching. XPS data for the Cl_2/N_2 gas chemistry show that the peak intensity of the P-Cl bond is much smaller than that of the P-N bond. Although the vapor pressure of PN_x is not well known, it is supposed to be much higher than that of PCl_x. Therefore, the formation of low-pressure etch products on the etched sidewall surface suppresses the etching of the sidewall, resulting in a vertical profile for InP etched at low bias power. On the other hand, the preferential loss of P atoms from the InP surface during etching with the Cl_2/Ar gas chemistry causes a serious undercut profile and is responsible for the rough etched surface due to the remaining In-droplets seen in the SEM image of Figure 6(c). According to the As 3*d* XPS data obtained from the InGaAs sample etched using the Cl_2/N_2 gas chemistry, the peak due to the As-N bond appeared on the lower binding energy side of that due to the As-O bond. The formation of As-Ns bond on the etched surface may reduce the fast etching of InGaAs, resulting in a vertical profile of InGaAs etched by using a N_2 added to Cl_2 gas mixture. In the nitrogen containing-plasma, N_2 should dissociate into several kinds of atoms such as neutral N atoms, N^+ ions or N^* radicals. Among these three different species, ions and radicals can combine with exposed surface materials such as In, P, and As to form InN, PN, and AsN compounds, respectively. In general, the ions and the radicals formed in the plasma become energetically active enough to react with the other materials. The vertical etch profiles of both InP and InGaAs etched using ICP were attained at a gas chemistry of $Cl_2 : N_2 = 2 : 13$ and at low bias powers below 25 W.

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