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G. Bruno, M. Losurdo, P. Capezzuto. On the Use of H₂ Plasma for the Cleaning and Passivation of InP Substrates. Journal de Physique IV Proceedings, 1995, 05 (C5), pp.C5-663-C5-670. 10.1051/jphyscol:1995579 . jpa-00253941

HAL Id: jpa-00253941

<https://hal.science/jpa-00253941>

Submitted on 1 Jan 1995

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On the Use of H₂ Plasma for the Cleaning and Passivation of InP Substrates

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Abstract: The effectiveness of hydrogen plasma for the reduction process of surface native oxide on InP substrates is investigated by X-ray photoelectron spectroscopy (XPS) and by phase modulated spectroscopic ellipsometry (PMSE). H₂ plasmas, generated in a quartz tube by applying a r.f. field (13.56 MHz) to external electrodes, produce a very high H-atom flux ($5 \cdot 10^{20}$ atoms/cm²sec) in the downstream region. The ex-situ XPS and in-situ PMSE measurements indicate that the native oxide layer (25 Å) is completely removed. The end point of the cleaning process is well detected by kinetic ellipsometry. The plasma treated surface shows a higher stability to reoxidation than that observed for wet etches samples.

1. INTRODUCTION

Low pressure hydrogen plasmas (r.f., MW, ECR) are becoming increasingly important in the field of III-V semiconductors technology for: i) the removal of surface carbon contamination and native oxide [1, 2], ii) the etching process, when hydrocarbon (CH₄, C₂H₆...) are also added [3, 4], and iii) the hydrogen passivation of acceptors and defect saturation [5, 6].

Recently, much effort has been devoted to the development of H₂ plasma dry processes for the preparation of clean and well-ordered InP surfaces for epitaxial growth [7]. With respect to this, the major problems are the surface carbon contamination and the presence of native oxide overlayer. Adsorbed carbon is strongly bonded to the III-V surfaces where it still remains after annealing at high temperature, inducing a free-carrier depletion region at the epilayer-substrate interface. Native oxides on InP surface are detrimental to the formation of stable interfaces and can also induce defected epitaxial growth and, consequently, undesirable electrical characteristics of the devices. The standard cleaning procedures are, sometimes, not able to give reproducible cleaned surfaces. In particular, the "wet chemical etching" [8], by acid solution, is an *ex situ* procedure not able to remove the carbon contamination completely, the "thermal desorption" [9] requires high temperatures causing partial decomposition of InP substrates, and the "argon ion sputtering" [10] leads to lattice disruption. Alternative *in situ* H₂ plasma treatment, based on the interaction process of H-atoms with the InP surface, are presently under investigation. However, if the H-atoms flux impinging on the surface is not appropriately controlled, the InP substrates can lose their stoichiometry and mirror-like aspect as a consequence of the preferential etching of phosphorus [11,12,13]. Hence, in order to achieve high cleanliness and passivation while minimizing damage of the crystal structure, it is becoming important to utilize appropriate diagnostic methods to control the plasma, the H-atom flux onto the surface and the surface modifications.

In this study, results on the *in situ* cleaning and passivation of InP surfaces by a controlled atomic hydrogen flux present in the downstream region of a low pressure H₂ r.f. plasma are reported. The effect of the substrate temperature during plasma treatment has been investigated using *in situ* Phase Modulated Spectroscopic Ellipsometry (PMSE) and *ex situ* X-Ray Photoelectron Spectroscopy (XPS). The effectiveness of the remote H₂ plasma in the surface cleaning is compared to the conventional wet etching procedure.

2. EXPERIMENTAL

H₂ plasma treatments were performed in the home made "remote Plasma MOCVD" (RP-MOCVD) apparatus schematized in fig.1 (details can be found in ref.14).

Figure 1: Schematic representation of the RP-MOCVD apparatus.

The H₂ r.f. discharge was ignited between two semicircular external electrodes by applying a 13.56 MHz voltage in a 4 cm i.d. quartz tube. This plasma source is assembled on the stainless-steel MOCVD chamber. In this configuration it is assumed that the plasma region end coincides with the end of the quartz tube. Thus, effects related to plasma radiative damage of InP substrates can be minimized.

The H₂ plasma was generated at the pressure of 1 torr, at the r.f. power of 60 watt, and at the flow rate of 800 sccm. Before running the cleaning treatments, the inside wall of the plasma tube was covered with a thin film of phosphorus by operating a PH₃-H₂ plasma process. This assures the presence of few ppm of PH₃ during the cleaning. Few cleaning experiments were done by adding low amounts of PH₃ to H₂ plasma (PH₃/H₂ = 10⁻³ - 10⁻²).

InP plasma cleaning experiments were performed on SI (100) InP provided by Crismatec-InPact. The InP substrate was positioned 10 cm far from the plasma tube end. The H₂ plasma cleaning was performed for 1h on substrates at room temperature and at T = 130°C, while 7 min were enough for plasma cleaning at T = 270°C. The effectiveness of the H₂ plasma *in situ* dry cleaning was evaluated by a comparison with a wet etched sample obtained by isopropanol washes and DI rinse, followed by chemical etching in a H₂SO₄:H₂O₂:H₂O = (8:1:1) solution at room temperature.

For the process diagnostics, *in situ* ellipsometric spectra were taken using a Phase Modulated Spectroscopic Ellipsometer (PMSE) (Elli-UVISEL by ISA-JOBIN-YVON) operating in the range 200 - 800 nm [15]. Ellipsometric measurements at fixed wavelength (λ = 269 nm) were used for the kinetic study of the InP cleaning and for the end point detection of the native oxide reduction process.

Ex situ X-ray Photoelectron spectroscopy (XPS) data were collected using a PHI 5300 Perkin-Elmer spectrometer employing the Mg(1253.6 eV) K α X-ray source. The XPS analysis (smoothing, X-ray satellites subtraction and fitting) was performed on the high resolution In3d_{5/2}, P2p, O1s peaks by using the Perkin-Elmer software supplied with the system.

3. RESULTS AND DISCUSSION

3.1. H-atom plasma source

Low pressure hydrogen plasmas are good sources of H-atoms, whose density level results from the balance between the direct electron impact dissociation process:

and the recombination processes:

The extent of these processes is mainly determined, in the plasma volume, by r.f. power and pressure which directly affect the electron energy and density. However, in the plasma downstream (remote plasma conditions) the recombination processes only are effective and, hence, pressure and total flow rate determine the H-atom density decay profile.

Figure 2 shows the H-atom density, $[\text{H}]$, profile evaluated in the plasma downstream flow at different positions in the MOCVD chamber. The H-atom density was derived by the etching rate measurements of a phosphorus film, as the kinetic equation

$$[\text{H}] (\text{cm}^{-3}) = (2.1 \pm 0.4) 10^{15} r_E (\text{\AA}/\text{sec}) \quad (4)$$

was demonstrated to be valid [16]. Details on this method can be found in ref.[17]. Here it is important to underline that the H-atom density in the present system (see fig. 2) is much higher ($> 10^{15} \text{ cm}^{-3}$) than that reported by Tachibana [18], who found, in the afterglow region of a similar plasma system, $[\text{H}]$ values ranging between $10^{11} - 10^{13} \text{ cm}^{-3}$, depending on the r.f. power, pressure and gas flow. The high efficiency of our H-atom source is related to the high gas flow rate and, hence, to the low residence time ($< 1 \text{ sec}$) in the afterglow region, where the three-body recombination process (eq.2) controls the H-atom disappearance. Thus, the H_2 gas flow rate and the relative position of the InP substrate to be treated are crucial for determining the H-atom flux impinging on the surface.

Figure 2: Etching rate of phosphorus, r_E , vs axial position in the downstream flow of H_2 plasma at $P=1\text{ torr}$ and $P=1.5\text{ torr}$ (r.f. power = 60 watt, gas flow rate = 100 sccm). H-atom densities have been derived by eq. (4) (see text).

3.2. H₂ plasma cleaning experiments

Previous studies [12,13,17] demonstrate that a direct exposure of InP substrate to H-atom flux as high as $10^{17} - 10^{18}$ atoms/cm².sec induces, even at room temperature, a decomposition of the substrate forming metallic indium droplets. This is a direct consequence of phosphine formation. Here, it is important to underline that in the present remote plasma configuration, the H-atom flux impinging on the InP surface, at the axial position of 10 cm, is about $5 \cdot 10^{20}$ atoms/cm².sec.

A preliminar angle-resolved XPS characterization of the InP native oxide layer shows a layered structure, i.e. the topmost layer mainly includes phosphorus-rich indium phosphates, and the sublayer, at the interface with InP substrate, is rich in indium oxide, In₂O₃. Spectroscopic ellipsometric measurements indicate a native oxide thickness of about 25Å.

Fig. 3 shows the In3d_{5/2} and O1s core level spectra for the H₂ plasma treated and the wet etched substrates. The spectra are acquired at the take-off angle $\Theta = 15^\circ$, which means that the first 20 Å are sampled. For a comparison, the XPS spectra of the InP untreated substrate are also reported.

Figure 3: XPS high resolution spectra of In3d_{5/2} and O1s photoelectron peaks of (a) untreated InP substrate, and H₂ plasma treated InP substrates at (b) T=25°C for 1h (c) T=130°C for 1h (d) T=250°C for 15min, and of (d) wet etched sample.

In order to evaluate the effectiveness of H₂ plasma cleaning, the ex-situ XPS analysis is simplified as follow:

(a) the In3d_{5/2} peak is fitted by the component at 444.4 eV due to In-P bond and by a second component, at higher energy, ascribed to oxidized-indium compounds (In-oxide) whose B.E. value depends on their oxidation degree;

(b) the O1s peak is deconvoluted to evidence the presence of phosphorus oxide P₂O₅ (peak at 534.1 eV), and indium oxide, In₂O₃ (peak at 530.2 eV), in addition to phosphates InP_xO_y (peaks at 531.87 eV and 532.7 eV).

From core level intensities and by using sensitivity factors, oxygen and carbon contaminations and the overall stoichiometry, In/P, are estimated and reported in Tab.I.

Table I: Compositional ratio, as derived by XPS analysis, for different InP samples.

SAMPLE	In/P	C/(In+P)	O/(In+P)
<i>untreated InP</i>	0.8	8.3	1.7
<i>H₂ plasma 1h - 25°C treated InP</i>	0.6	5.5	2.5
<i>H₂ plasma 1h - 130°C treated InP</i>	0.7	5.9	1.5
<i>H₂ plasma 15min - 270°C treated InP</i>	1.0	3.3	1.3
<i>wet etched InP</i>	1.0	12	3.3

The results of fig. 3 and Tab.I suggest that the higher the substrate temperature during plasma exposure, the higher the effectiveness of carbon and oxide reduction process. In particular, the H₂ plasma cleaning treatment at T = 270°C exhibits InP surface with lower oxygen and carbon contamination than any other treated sample.

The effectiveness of the plasma treatment at T = 270°C is also evidenced by the detailed analysis of the O1s spectra. In fact, the In₂O₃ oxide component is completely removed, whereas it is still present on the wet etched sample. In addition, the surface analysis of the plasma treated substrates at T < 130°C reveals the presence of P₂O₅. The origin of P₂O₅ is related to the fact that the PH₃/H₂ plasma gives, on the InP surface, deposition of a very thin phosphorus layer, which oxidizes to P₂O₅ after air exposure. This phenomenon does not occur at high temperature (270°C) because of the high phosphorus (P₂) desorption rate. In addition, at temperature as high as 270°C, the phosphorus atoms can diffuse into the InP bulk, so eliminating possible defect associated to P-vacancies [18]. In fact, no trace of metallic indium (B.E. = 440.0 eV) is revealed by the analysis of In3d_{5/2} peak.

Fig. 4 shows the SE spectra (imaginary part, ϵ_1 , of the pseudodielectric function χ_s energy) recorded, in-situ, for the H₂ plasma cleaned sample at T = 270°C and ex-situ for the wet etched substrate; in the same figure the SE spectrum of the untreated substrate is also shown. Using a three-layer (substrate-film-ambient) optical model based on the Bruggeman effective medium approximation (BEMA) [19] it is possible to evaluate thickness and composition of the overlayer on the InP substrate. The presence of an oxide layer induces a decrease of the ϵ_1 value at the E₂ critical point (4.7 eV) and an increase in the region below 3 eV. From figure 4, it is evident the large difference of the pseudodielectric function which occurs between H₂ plasma treated surface and the wet etched surface. This is indicative of a very different chemical and morphological nature of the InP surface. In fact, the BEMA model gives (see inset

of fig. 4), for the H₂ plasma cleaned sample, a substrate covered by a $\sim 20\text{\AA}$ thick layer of c-InP which includes 15% of voids. These voids are the consequence of the O-atoms removal process:

in which H-atoms impinging on the surface can diffuse in the material and react with oxygen to produce H₂O. The subsequent diffusion-desorption of H₂O is, probably, the rate limiting step controlling the overall kinetics. On this last aspect more investigation are needed, especially on the substrate temperature effect.

Figure 4: Ellipsometric spectra of the imaginary part, ϵ_i , of the pseudodielectric function, for (a) the plasma treated InP surface, (b) wet cleaned InP surface, and (c) for the "as received" InP substrate. The inset shows the correspondent film structures as derived by BEMA model [19].

For the wet etched sample (see curve b of fig. 4) a residual oxide layer of $16\text{\AA}$ is still present on the InP substrate, though the SE spectrum is recorded soon after the cleaning.

These results clearly indicate that no plasma induced structural damage and no preferential phosphorus etching was observed even at temperature as high as 270°C and at H-atom flux as high as $5 \cdot 10^{20}$ atoms/cm²sec. The preservation of the good surface morphology is due to the fact that, in the present plasma configuration, the InP substrate is not directly exposed to ion bombardment. Also, the presence of few ppm of PH₃ in the H₂ gas feed is sufficient to preserve InP stoichiometry.

Furtherly, plasma treated InP substrates exhibit a higher stability to reoxidation. This is well evidenced by the lowering of both the oxide thickness measured by SE and the oxide component in the In3d_{5/2} XPS spectra as recorded after two months of air exposure. In addition, the analysis of the O1s core level demonstrates that, during the reoxidation, the In₂O₃ formation on the InP surface treated with H₂ plasma at $T = 270^\circ\text{C}$, is suppressed. These last phenomena seems to indicate a sort of stabilizing effect of the InP surface, i.e. H-atoms act for the indium-defect saturation and passivation.

3.3. End point detection of the plasma cleaning process

Real time in-situ ellipsometric measurements at the fixed wavelength of 270 nm (4.6 eV) are well adapt to follow the kinetics of the plasma cleaning process. SE measurement at 4.6 eV is very sensitive to surface modification, since the optical penetration depth is about 20Å.

Fig. 5 shows the time dependence of ϵ_i (4.6 eV) during the plasma treatment with PH_3/H_2 mixtures at different PH_3 amount: $\text{PH}_3/\text{H}_2 = 0.2\%$ (BC curve), $\text{PH}_3/\text{H}_2 = 1\%$ (CD curve) and $\text{PH}_3/\text{H}_2 = 50\text{ppm}$ (DE curve).

Figure 5: Time evolution of ϵ_i (4.6 eV) during PH_3/H_2 plasma treatment of InP substrate at $T=270^\circ\text{C}$, r.f power = 60 watt, gas flow rate = 800 sccm, and at different PH_3/H_2 ratio: (a) $\text{PH}_3/\text{H}_2=0.2\%$ (BC curve), $\text{PH}_3/\text{H}_2=1\%$ (CD curve) and $\text{PH}_3/\text{H}_2=50\text{ppm}$ (DE curve).

The observed ϵ_i decrease, at PH_3 percentage higher than hundreds of ppm, indicates that phosphorus deposition occurs on the InP substrate. On the contrary, the ϵ_i value starts to increase (D point in fig. 5) when the PH_3 amount in the feed is reduced to 50ppm. Under this last condition, the H-atoms predominate on the PH_x radicals (building block for phosphorus deposition) and, hence, the reduction process overcomes the phosphorus deposition. As soon as the oxide layer is completely removed, the H-atoms induce roughness of InP surface so causing a decrease of the ϵ_i value (EF curve). Thus, point E represents the end point detection of the cleaning process.

In concluding this section, it is important to underline that the native oxide reduction process by H-atoms is very effective but needs to be appropriately controlled to avoid film deposition and/or surface roughening.

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