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In situ cleaning of InGaAs surfaces prior to low contact resistance metallization

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ABSTRACT

In this work, we studied the pretreatment of InGaAs layers by employing Ar- and He-based direct plasmas and NH_3, H_2, NF_3/NH_3 remote plasmas. All the remote plasmas involved in this study were inadequate to remove the InGaAs native oxides. Moreover, for NF_3/NH_3 exposed samples, we noticed the addition of undesirable In–F and Ga–F bonds. Concerning Ar and He direct plasmas, investigations exhibited that both seem to be efficient for removing arsenic oxides whereas the elimination of indium oxides is more effective with Ar plasma. We also studied the addition of hydrogen into He direct plasma and we demonstrated that increasing the H2 content leads to decreasing the removal of arsenic oxides. The impact on indium oxides is also notable as we observed a reducing effect of hydrogen on indium and the emergence of In–In type bonds. Finally, whatever the plasma pretreatment, no degradation of surface morphology and roughness was observed by AFM. The RMS values obtained after surface treatments are similar with the ones acquired for reference samples.

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1. Introduction

The interest for contacting III-V materials has been growing since disruptive channel materials (including Ge and III-V materials) have been proposed for boosting the CMOS performance [1]. Studies are under progress in order to propose a contact science compatible with the Si CMOS technology. In this way, we observed a transition from non-self aligned technology to a self-aligned process [2,3]. Whatever the technology used (non-self aligned, self aligned, 3D…), cleaning technology is highly desirable for removing particles, organic materials, metallic impurities and native oxides. The classical salicide process (e.g. NiSi on Si or SiGe 30%) involves a two-step procedure where a wet HF treatment is coupled with an in situ plasma exposure [4]. Queue time related surface contamination and partial reoxidation caused by using only wet chemical cleaning is thus eliminated. For III-V contact technology, we assume that a similar strategy has to be developed. If wet chemical cleanings are generally proposed for realising InGaAs n-MOSFET, in situ cleanings (plasma treatments realised in the same equipment as the metal deposition) have not been extensively studied. For deeply scaled transistors, parasitic resistances between the source and drain (S/D) regions and the metal contact have to be reduced as much as possible. Then, a very cleaned and native oxide free surface must be provided prior to metal deposition.

In this work, we propose a study using a Si CMOS technology compatible equipment in order to investigate the in situ cleaning of InGaAs layers. We introduce results obtained for various types of plasma processes (e.g. direct versus remote plasmas).

2. Experimental details

150 nm thick InGaAs layers grown by MOCVD on InP substrates (or Si wafers for ATR characterisations only) were used in this study.

NH_3, H_2, NF_3/NH_3 remote plasma and argon and helium-based direct plasma in situ pretreatments described in this work were carried out in a 300 mm Applied Materials Endura platform usually dedicated to silicide process and fully compatible with the Si CMOS technology.

Before direct plasma treatments, a degas step was performed at 200 for 30 s under argon atmosphere. Then, samples were treated into a direct plasma chamber without air exposure. Argon and helium direct plasmas were carried out using RF1 power ranging from 20 to 130 W and RF2 power ranging from 150 to 750 W and the etching duration was varied from 10 to 150 s. No substrate heating was performed during the plasma treatment. During the etching step, the chamber pressure ranged from 0.15 to 3.8 mTorr. These processes were calibrated on thermal silicon oxide to obtain process time versus silicon oxide equivalent thickness tables. 2.5 to 9 nm of silicon oxide are etched by the Ar direct plasma employed in this study (depending on the etching duration) whereas the He plasma does not affect significantly the silicon oxide layer (e.g. the difference of thickness measured after plasma treatment is under the spectroscopic ellipsometer sensitivity).

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Concerning the remote plasma treatments, the samples were treated without previous degas step in a chamber maintained at 3 Torr during the etching step. The remote plasma power was set at 30 W and the process temperature was fixed at 65. The etching step duration was varied from 60 to 300 s. After the etching step, a sublimation step was performed in the same chamber at 180 for 90 s.

Because 300 mm III-V wafers are not available, we used small pieces of InGaAs/InP on dedicated holders in order to process the samples in the 300 mm equipment.

The cleaning efficiency and impact on InGaAs surfaces have been studied on the CEA Minatec Nanocharacterisation Platform (PFNC) using surface analyses like X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and Fourier transform infrared (FTIR) spectroscopy in attenuated total reflection (ATR) mode. XPS spectra were collected in a PHI VersaProbe II Scanning XPS Microprobe system using a monochromatic Al K $_{\alpha}$ X-ray source. Ga 2p, Ga 3d, In 3d and As 3d spectra were collected with a constant pass energy of 23.5 eV leading to an overall energy resolution of 0.6 eV; curve fitting was done by CasaXPS 2.3.16 software. AFM measurements were performed in Tapping mode using a Bruker Dimension FastScan. For FTIR-ATR characterisations, the data were collected using a Ge prism pressed against the sample. A Bruker IFS 55 FTIR spectrometer probed the sample via a P polarized infrared beam through the prism at an incident angle of 65, ensuring total reflexion on the Ge prism dioptre.

3. Results and discussion

3.1. Comparison of remote plasmas versus Ar and He direct plasmas

The effects on InGaAs layers of various remote plasma exposures have been investigated. Normalized Fourier transform infrared spectroscopy spectra in attenuated total reflection mode (FTIR-ATR) for InGaAs layers treated with NF_3/NH_3, NH_3, H_2 remote plasmas and without pretreatment are depicted on Fig. 1.

Based on literature data [5,6], the absorption regions of InGaAs oxides are highlighted on Fig. 1. The bands observed in the 1100–1150 cm^{-1} and 1150–1200 cm^{-1} regions are not attributed to InGaAs oxides but might be related to carbonaceous pollution from Ge prism or samples.

No significant effect of the different remote plasmas can be observed. Indeed, the absorption band of AsO_X in the 850–950 cm^{-1} region does not seem to be impacted by the treatments. We can just notice that, for NF_3/NH_3 exposed samples, the AsO_X band seems to be narrowed or slightly shifted towards low wavenumbers. Whatever the nature of the remote plasma, no significant reduction of the absorbance intensity of the AsO_X band is observed. The same observation is drawn for InO_X and GaO_X bands.

From the Ga 2p, In 3d and As 3d fitted XPS spectra (not shown here) of the remote plasma treated samples and for the reference sample, the corresponding relative spectral weight of the different components were extracted and are depicted on Fig. 2. In 3d results are not shown here but the tendencies are similar to the gallium ones.

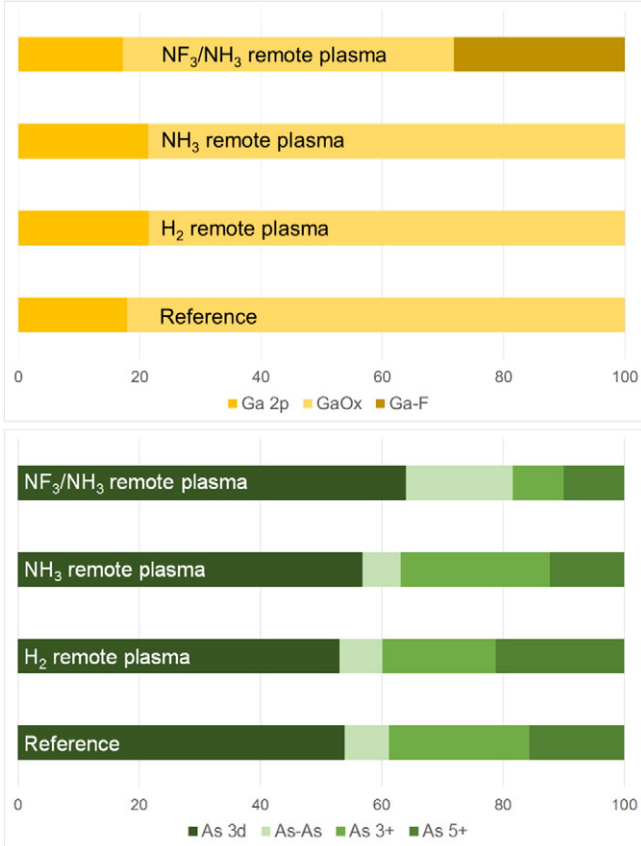

Fig. 2. Relative spectral weight of the components determined for the NF_3/NH_3, NH_3, H_2 remote plasma treated samples and for a reference sample for Ga 2p (top) and As 3d (bottom) regions.

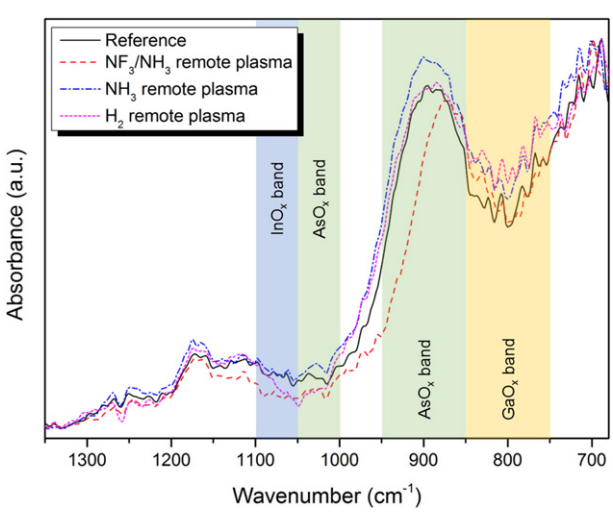

Fig. 1. Normalized FTIR-ATR spectra for InGaAs layers treated with NF_3/NH_3 (dash red line), NH_3 (dash dot blue line), H_2 (short dash magenta line) remote plasmas and without pretreatment (solid black line).

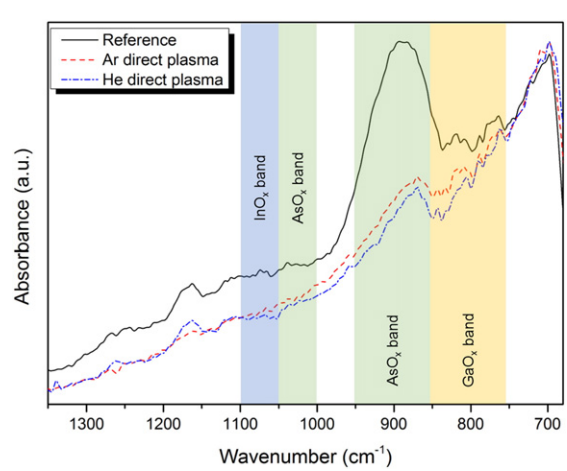

Fig. 3. Normalized FTIR-ATR spectra for InGaAs layers treated with Ar plasma (dash red line), He plasma (dash dot blue line) and without surface pretreatment (solid black line).

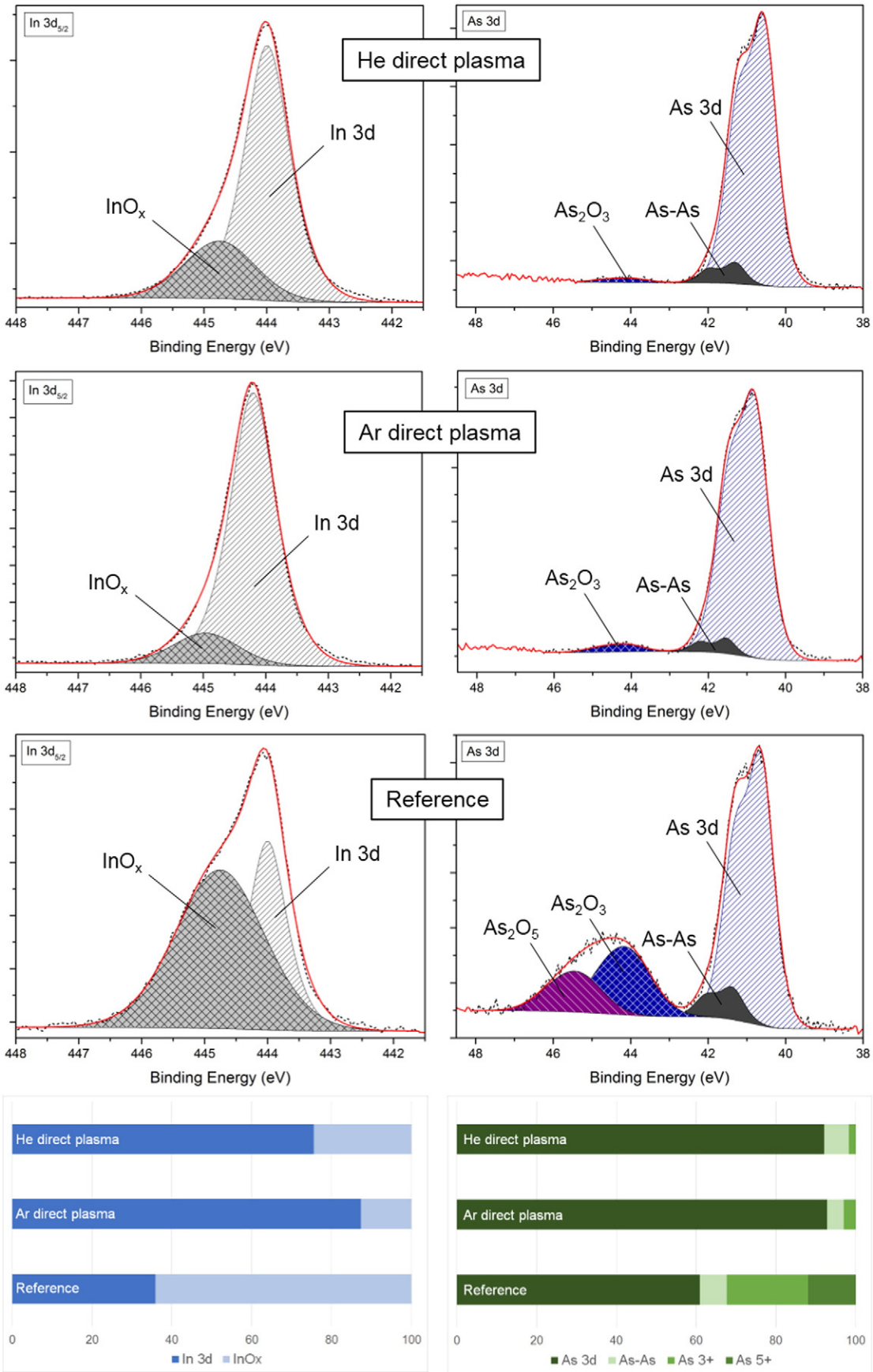

Fig. 4. XPS spectra peak fits of In 3d and As 3d regions for reference sample (bottom), Ar plasma treated sample (middle) and He plasma treated sample (top). The relative spectral weight of the components determined for the different samples is added.

XPS characterisations support the fact that remote plasma treatments involved in this study are not efficient at all for the removal of InGaAs oxides. The As^{5+} component is still detected whatever the treatment applied and the relative spectral weight of the bulk As 3d component of treated samples is similar to the reference sample one. Moreover, NF_3/NH_3 remote plasma seems to significantly increase the As–As bond (elemental arsenic) component to the detriment of As^{3+} component which might explain the slight shift observed for the corresponding FTIR-ATR spectrum. The analysis of the relative spectral weight of the components for the Ga 2p region confirms that the removal of InGaAs oxides is not achieved whatever the remote plasma treatment involved. Furthermore, for NF_3/NH_3 exposed samples a third component appeared in the XPS spectra of the Ga 2p and In 3d regions. These components are located at higher energies than oxide components and are attributed to undesirable Ga–F and In–F bonds.

Based on literature data [7,8,9], H_2 and NH_3 plasma treatments have the ability to remove, or at least reduce the proportion of InGaAs native oxides. In this study no such effects were evidenced by exposing InGaAs layers to H_2 and NH_3 remote plasma. This phenomenon could be explained by the fact that the experimental conditions involved in this work were dictated by the remote plasma chamber used (experimental parameters could only be varied in a narrow range) and were different from the ones described in the abovementioned references, especially concerning the process temperature and pressure. Indeed, our experiments were carried out at lower temperature and at higher pressure which is not favourable for the desorption of by-products.

By comparison with remote plasma exposure and in order to promote low temperature treatments, the impact of direct plasmas has been investigated. Fig. 3 exhibits the normalized FTIR-ATR spectra for an InGaAs reference layer (i.e. native oxides without any treatments) and for InGaAs layers after Ar and He direct plasma processes.

We clearly observe differences between the spectrum obtained for an untreated sample and the spectra obtained for the plasma treated ones. Especially, the large absorption band of AsO_x in the region of 850–950 cm^{-1} is drastically reduced after surface treatment. Both Ar and He direct plasma treatments seem to be efficient for eliminating the As oxides as indicated by the low absorbance intensity difference. While the impact of plasma treatment is less obvious on Ga and In oxides, it is also seen.

The corresponding In 3d and As 3d XPS spectra are shown on Fig. 4. From the fitted XPS spectra, we extracted the corresponding relative spectral weight of the different components. After direct plasma treatments, the fitting of Ga 2p XPS spectra were difficult to obtain with accuracy, moreover for Ga 3d region, the In 4d components tend to parasite the Ga ones. Thus, tendencies for Ga will not be discussed here.

The XPS studies clearly evidence that both direct plasma treatments were efficient for reducing the percentage of InGaAs oxides. It is obvious for As oxides where the As_2O_5 component is no more detected and the As_2O_3 is drastically reduced for treated samples. For In oxides, the proportion of oxide components are significantly reduced compared to the reference sample. Nevertheless, for these elements, the oxide component after treatment is still important. Various hypothesis are currently under investigation for explaining these observations: the efficiency of the cleaning processes might be improved or the plasma treatments investigated in this study may preferentially lead to indium terminated surfaces which are partially reoxidised during the queue time (30 to 45 min) between the sample preparation and its surface characterisation.

Nevertheless, XPS analyses tend to confirm the FTIR-ATR observations: both types of direct plasmas appear to be adequate for removing arsenic oxides. On the other hand, XPS investigations highlighted that Ar direct plasma is the most efficient for the removal of In oxides. Based on literature data [10], we believe that Ar plasma has an etching effect on InGaAs surface and that its native oxides are removed during this etching. Concerning the effect of He on InGaAs layers, we have exhibited a lack of literature data in order to elucidate the associated mechanisms. However, due to a lower kinetic energy, we believe that He ions have only an etching effect on InGaAs native oxide surfaces and that InGaAs layer is not etched during the process.

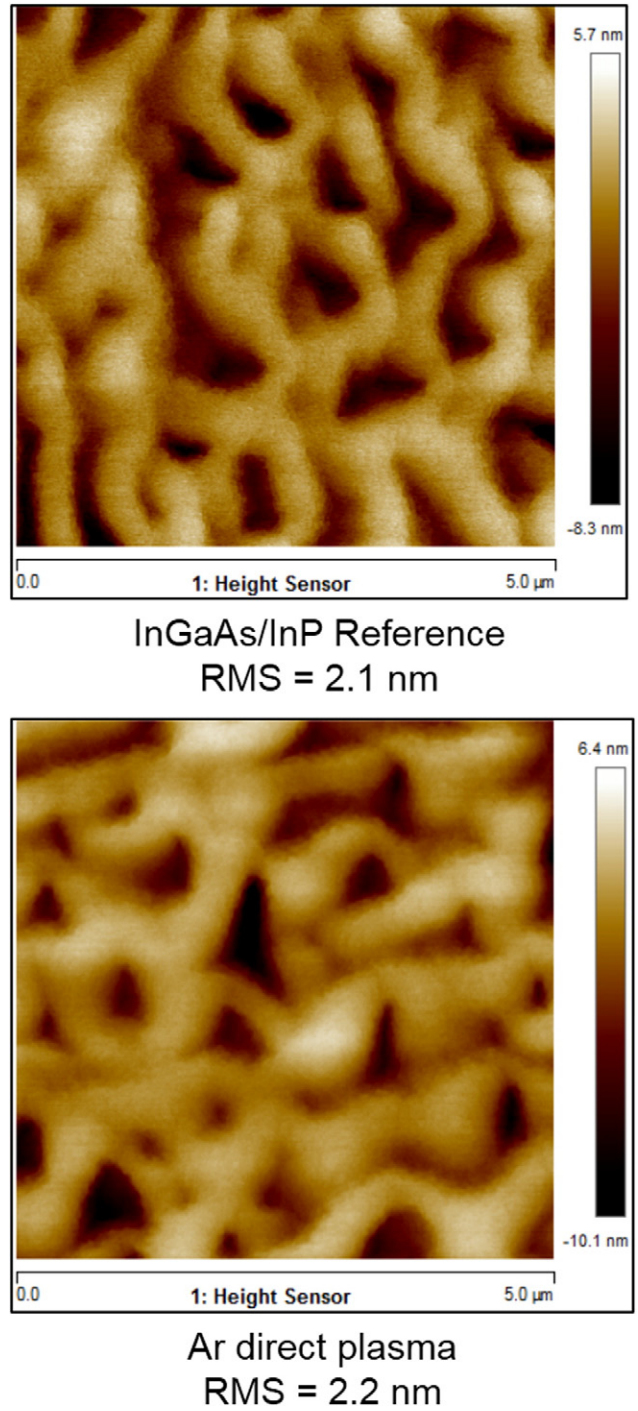

Fig. 5. AFM images for reference sample (top) and Ar direct plasma treated sample (bottom). The image space is 5 m × 5 m.

The impact of direct plasma treatments have been explored by AFM. Fig. 5 shows the AFM images obtained for the InGaAs/InP surface without any pretreatment (Reference) and the InGaAs surface after Ar treatment (the AFM image of sample after He plasma treatment is not shown here). AFM experiments have evidenced that, whatever the nature of the pretreatment, the surface morphology and roughness of InGaAs layers were not significantly impacted. RMS values are similar before (2.1 nm) and after plasma processing (2.2 nm for Ar and He direct plasma treated samples). Thus, for InGaAs surfaces with an initial roughness

around 2 nm, no significant impact of plasma treatments has been highlighted.

3.2. Effect of hydrogen addition in He-based plasmas

Fig. 6 shows the normalized FTIR-ATR spectra for InGaAs layers treated with He, He/H_2 20/1, He/H_2 10/1 plasmas and without pretreatment.

From the results depicted on Fig. 6, some tendencies can be drawn. First, the introduction of a slight percent of hydrogen in He-based plasma appears to modify the removal efficiency of the InGaAs oxides. The effect of hydrogen is visible not only for the large absorption band of AsO_x in the 850–950 cm^{-1} region but also for the narrower band in the 1000–1050 cm^{-1} region. Regarding the shape and the intensity of the corresponding bands, AsO_x removal seems to be inversely proportional to the H_2 plasma content. By only using FTIR-ATR analyses, the effect of hydrogen addition in He-based plasma on indium and gallium oxide removal is less obvious.

From the In 3d and As 3d fitted XPS spectra (not shown here) of the He-based plasma treated samples with or without addition of hydrogen and for a reference sample, the corresponding relative spectral weight of the different components were extracted and are depicted on Fig. 7. It should be noted that the addition of hydrogen into He plasma increases the pressure into the reactor during the sample pretreatment. As a result we also prepared additional samples treated with He direct plasma without addition of hydrogen but at higher pressure in order to evaluate the impact of this latter parameter.

The analysis of XPS results comforts the trends outlined by FTIR-ATR analyses. Addition of hydrogen clearly impacts the removal efficiency of InGaAs oxides. Indeed, increasing hydrogen content into He plasma leads to decrease the removal of arsenic oxides. As evidenced by comparing the samples treated with He plasma at 2.9 mTorr and at 3.8 mTorr, this trend might not only be attributed to hydrogen addition but could be related to the increase of pressure. Indeed, increasing the operating pressure is known to increase the ion scattering in the sheath and then to decrease the plasma efficieny [11]. On the other hand, if the increase of the pressure is clearly unfavourable for In oxides removal (compare the He plasma treated samples at 2.9 mTorr and at 3.8 mTorr), the addition of hydrogen seems to significantly impact the oxide removal. Indeed, compared to the reference sample, the relative spectral weight of the InO_x component appears to be reduced for the samples treated with hydrogen. Moreover, hydrogen addition leads to the apparition of a third component in the XPS spectra of the In 3d region. This component is located at approximately −0.8 eV from the bulk peak and is attributed to under coordinated indium at the surface or possibly indium dimers [12]. Thus, hydrogen addition might have a reducing effect on indium atoms. No such effect was observed on Ga XPS spectra.

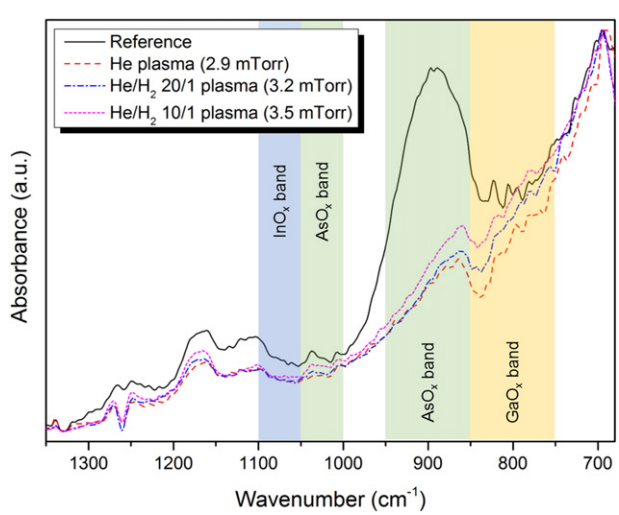

Fig. 6. Normalized FTIR-ATR spectra for InGaAs layers treated with He (dash red line), He/H_2 20/1 (dash dot blue line), He/H_2 10/1 (short dash magenta line) plasmas and without pretreatment (solid black line).

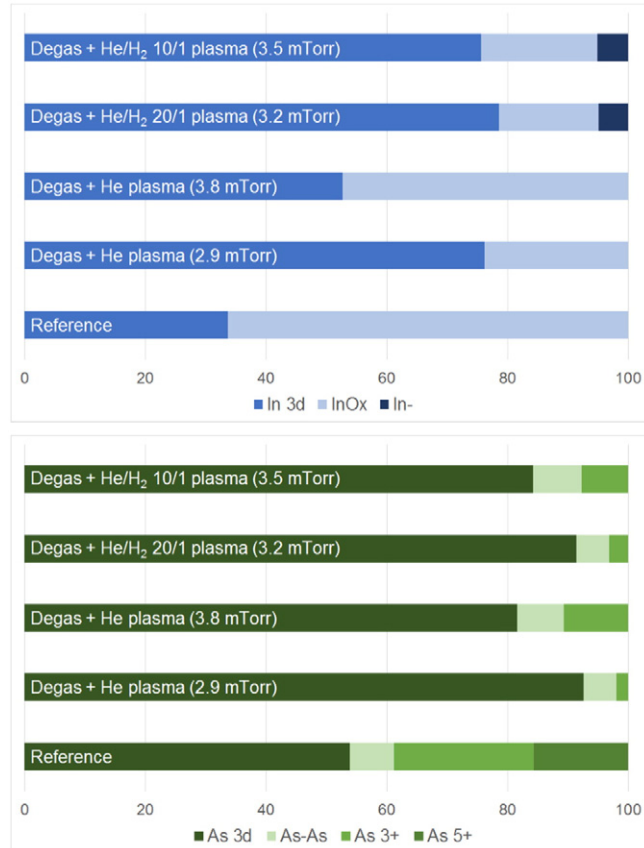

Fig. 7. Relative spectral weight of the components determined for the He-based plasma treated samples with or without addition of hydrogen and for a reference sample for In 3d (top) and As 3d (bottom) regions.

4. Conclusion

We have investigated the impact of various plasma treatments on InGaAs layers. Argon- and helium-based direct plasmas are more efficient than remote plasmas for the removal of InGaAs native oxides. We have demonstrated that the nature of direct plasma influences the InGaAs oxide removal efficiency. Indeed, both types of plasma seem to be efficient for removing arsenic oxides whereas the elimination of In oxides is more effective with Ar plasma. Hydrogen addition in He plasma impacts the removal of InGaAs oxides and appears to have a reducing effect on indium atoms. Finally, whatever the nature of the pretreatment, the surface morphology and roughness of InGaAs layers were not significantly impacted.

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