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InGaAs Surface Pretreatment prior to Metal Solid-State Reactions for Low Resistance Contacts

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1. Introduction - Context

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 performances [1]. Studies are under progress in order to propose a contact technology compatible with the Si CMOS technology. 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 [2]. Queue time related surface contamination and partial reoxidation, in particular on patterned wafer, 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 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 before metal deposition.

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

2. Experimental details

All plasma treatments described in this work were carried out in a 300 mm Applied Materials Endura® platform usually dedicated to silicide process. Apart from the metal RF PVD chambers, this tool is equipped with various preclean chambers where one can make sample heatings, hot $NF_3/NH_3/H_2$ remote plasma exposure and argon- or helium-based direct plasmas. The aim of this work is to use the preclean chambers usually assigned to Si-based wafers and to adapt the plasma chemistries and process parameters for the cleaning of III-V surfaces. Because 300 mm III-V wafers are not available, we used small pieces of InGaAs layers grown on InP (or Si wafers for ATR characterisations only) on dedicated holders in order to process the samples in the 300 mm platform.

We employed Ar- or He-based direct plasmas with a previous degas treatment carried out at 200 °C for 30 s under argon. These processes were calibrated on thermal silicon oxide to obtain process time vs. 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). We also investigated the influence of remote plasmas of various nature (e.g. H_2, NH_3 and NF_3/NH_3).

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. 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. XPS spectra were collected in a PHI VersaProbe II Scanning XPS Microprobe system using a monochromatic Al K_α X-ray source. Ga 2p, 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®.

3. Results - Discussion

Impact of remote plasmas

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

Based on literature data [3], [4], the absorption regions of InGaAs oxides are highlighted on figure 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

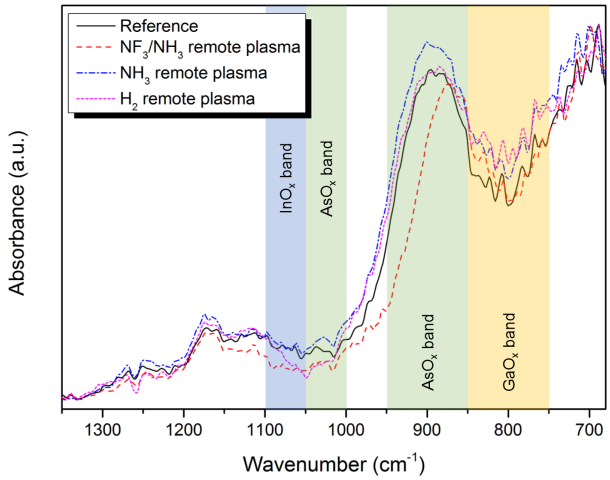


Fig. 1. Normalized FTIR-ATR spectra for InGaAs layers treated with NF_3/NH_3 (red line), NH_3 (blue line), H_2 (magenta line) remote plasmas and without pretreatment (black line).

the remote plasma, no significant reduction of the absorbance intensity of the AsO_x band is observed.

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 figure 2. In 3d results are not shown here but the tendencies are similar to the gallium ones.

XPS characterisations support the fact that remote plasma treatments involved in this study are not efficient 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 bonds (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.

Comparison of Ar and He direct plasmas

The figure 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 plasma processes.

We clearly observe differences between the spectrum obtained for an untreated sample and the spectra obtained for the plasma treated ones. In particular, 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

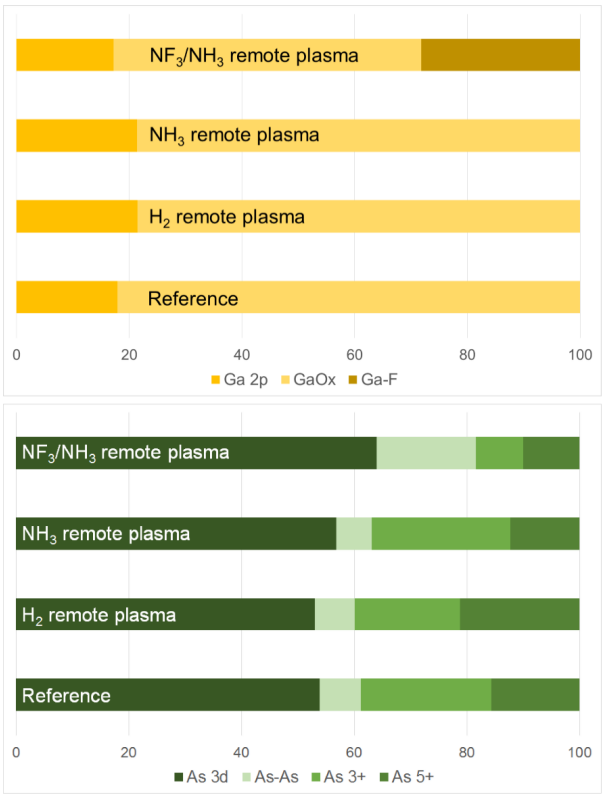


Fig. 2. Relative spectral weight of the components determined for the NF_3/NH_3, NH_3, H_2 remote plasma treated samples and for a reference sample for Ga 2p (top) and As 3d (bottom) regions.

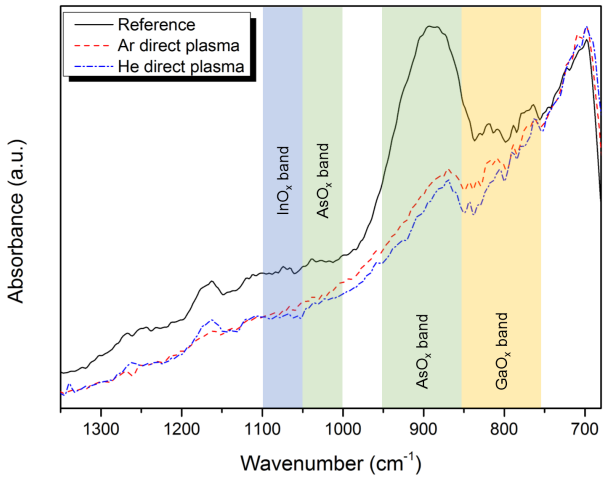


Fig. 3. Normalized FTIR-ATR spectra for InGaAs layers treated with Ar plasma (red line), He plasma (blue line) and without surface pretreatment (black line).

the impact of plasma treatment is less obvious on Ga and In oxides, it is also seen.

From the In 3d and As 3d fitted XPS spectra (not shown here) of the He- and Ar-based plasma treated samples and for a reference sample, the corresponding relative spectral weight of the different components were extracted and are depicted on figure 4. After direct plasma treatments, the fitting of Ga 2p spectra were difficult to obtain with accuracy, moreover the

In 4d spectra tend to parasite the Ga 3d ones. Thus, tendencies for Ga will not be discussed here.

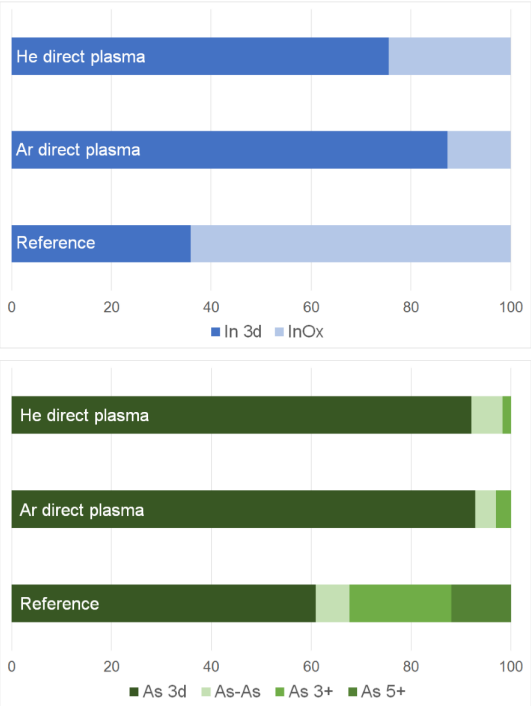


Fig. 4. Relative spectral weight of the components determined for the He- and Ar-based plasma treated samples and for a reference sample for In 3d (top) and As 3d (bottom) regions.

The XPS investigations clearly evidence that 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 this element, 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 re-oxidised 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 plasmas appear to be adequate for removing arsenic oxides. On the other hand, XPS investigations highlighted that Ar-based direct plasma is the most efficient for the removal of In oxides.

The impact of direct plasma treatments have been explored by AFM. The figure 5 shows the AFM images obtained for the InGaAs 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).

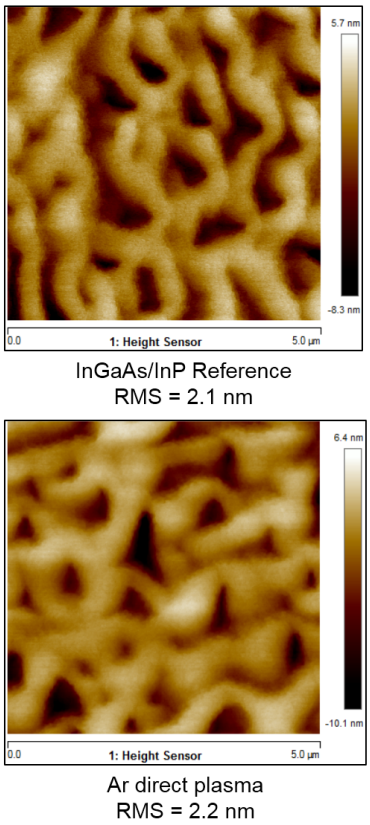


Fig. 5. AFM images for reference sample (top) and Ar direct plasma treated sample (bottom). The image space is 5 µm × 5 µm.

Effect of H_2 addition in He-based plasmas

The figure 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.

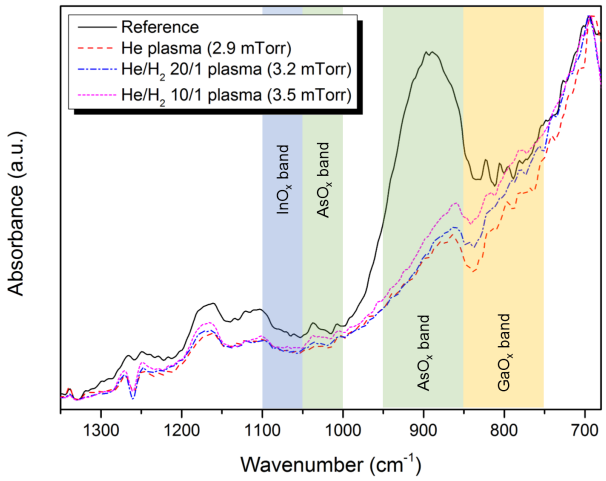


Fig. 6. Normalized FTIR-ATR spectra for InGaAs layers treated with He (red line), He/H_2 20/1 (blue line), He/H_2 10/1 (magenta line) plasmas and without pretreatment (black line).

From the results depicted on figure 6, some tendencies can be drawn. First, the introduction of a slight percent of hydrogen in He-based plasma appears to modify the cleaning

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 using only FTIR-ATR analyses, the effect of hydrogen addition in He-based plasma on indium and gallium oxides removal is not 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 figure 7. It should be noted that 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-based direct plasma without addition of hydrogen but at higher pressure in order to evaluate the impact of this latter parameter.

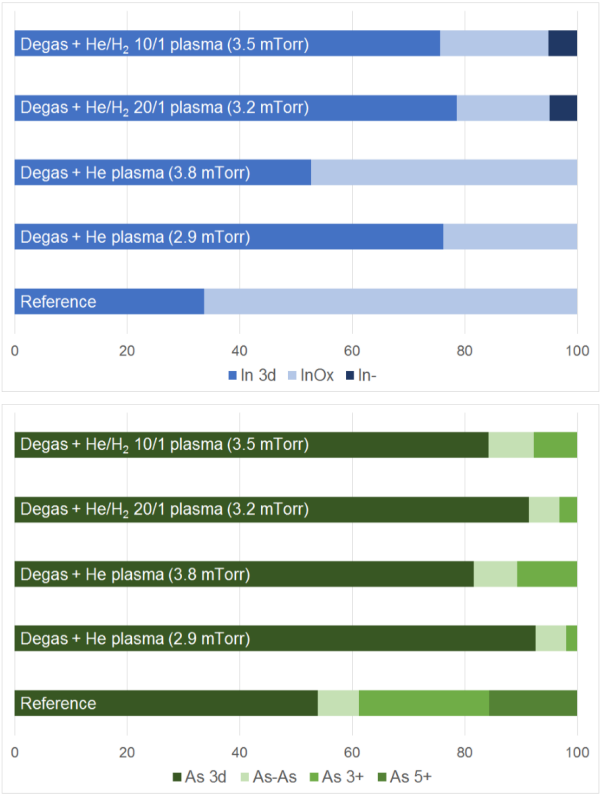


Fig. 7. Relative spectral weight of the components determined for the He-based plasma treated samples with or without addition of hydrogen and for a reference sample for In 3d (top) and As 3d (bottom) regions.

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 decreases 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 [5]. 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 approximatively -0.8 eV from the bulk peak and is attributed to under coordinated indium at the surface or possibly indium dimers [6]. Thus, hydrogen addition might have a reducing effect on indium atoms. No such effect was observed on Ga XPS spectra.

4. Conclusion - Perspectives

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 oxides 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. Whatever the nature of the pretreatment, the surface morphology and roughness of InGaAs layers were not significantly impacted.

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