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# An insight on plasma-surface interaction mechanisms during cryoetching in SiF<sub>4</sub>-O<sub>2</sub>, using *in situ* XPS

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Since about 5 years, cryogenic etching processes have been generating more and more interest in the semiconductor industry (equipment suppliers, foundries) and among the plasma etching research community for new nanoscale device applications [1,2]. However, even if the understanding and control of cryoetching have been improved over the years, questions about the fundamental mechanisms involved in this process remain.

Recently we reported on the surface chemistry of a-Si after exposure to a SiF<sub>4</sub>-O<sub>2</sub> inductively coupled plasma at sample temperatures of 20, -40 and -100°C, and its evolution upon warm-up at 20°C [3]. At -100°C a “thick” SiO<sub>x</sub>F<sub>y</sub> layer is masking the a-Si surface (Fig 1b) and after warm-up the surface chemistry appears quite identical to that obtained when operating the process at -40°C (Fig 1c and Fig 2c). Yet this study and a similar one carried out on Si<sub>3</sub>N<sub>4</sub> does not allow to characterize the individual role of SiF<sub>x</sub> and O plasma species at the surface nor if and how the sample species (Si) contribute to the formation of the SiO<sub>x</sub>F<sub>y</sub> layer.

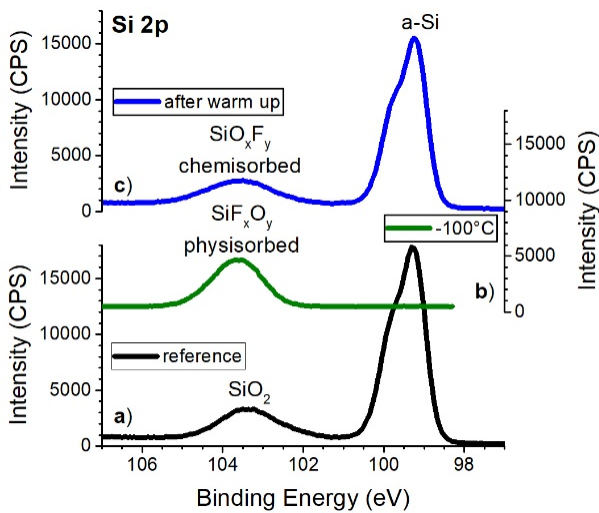
The set-up is the same as in [3]. The particularity of this plasma system is its sample holder, controllable in temperature from -180°C to +1100°C, and the availability to transfer the sample under UHV to the XPS at any temperature between -180°C and +150°C [4]. This enables us to compare the surface chemistry at the temperature of the plasma treatment and after warming up the sample to 20°C. Experiments are carried out in two directions. 100% O<sub>2</sub> plasma are used to evaluate both the impact of oxygen on the surfaces and that of fluorine contamination released from the reactor walls during the process. Samples not containing Si are used to discriminate the role of the SiF<sub>x</sub> plasma species and the etched sample species in the formation of the passivation layer.

Exposing the a-Si sample to O<sub>2</sub> plasma at -40 or -100°C does not bring any strong changes to the surface chemistry, the only significant observation being a very slight shift (+0.15eV) of the SiO<sub>2</sub> component in reason of some fluorine contamination (Fig 3), but no increase in the oxide layer thickness is observed. On InP, after exposure at 20°C and -100°C, one observes an increase of the surface oxide, highlighted both on the In (Fig 4) and the P core levels spectra. Interpretation is that, in this temperature range and in absence of sample bias, the native oxide on a-Si protects the material from further oxidation, whereas it is not the case for InP.

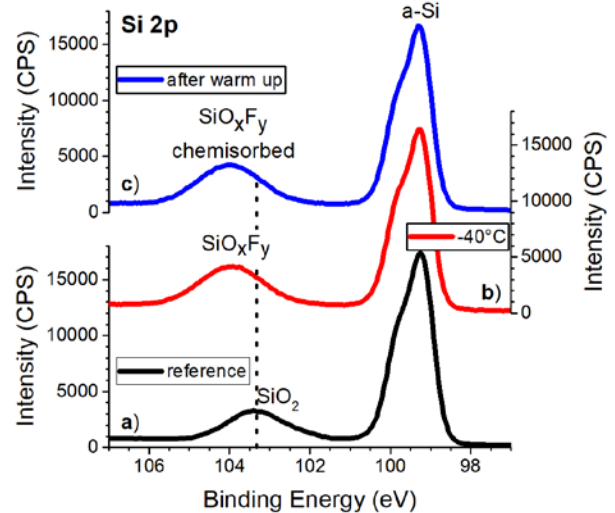
After processing the InP sample in SiF<sub>4</sub>-O<sub>2</sub>, either at -40°C and -100°C, and warm-up to 20°C, the In (Fig 5) and P core levels spectra reveal the presence of some InO<sub>x</sub>F<sub>y</sub> and PO<sub>x</sub>F<sub>y</sub> species. Moreover, analysis after exposure at -40°C reveals a surface chemistry similar to that after warm-up. For these three situations, no trace of Si is detected on the surface, as shown for the latter (Fig 6b). As already encountered in the case of a-Si, the situation is very different when exposure is done at -100°C; in this case the sample surface is covered by a “thick” SiO<sub>x</sub>F<sub>y</sub> layer that masks the XPS signal from the InP material (Fig 6c). These results, together with others, will be presented and discussed in detail.

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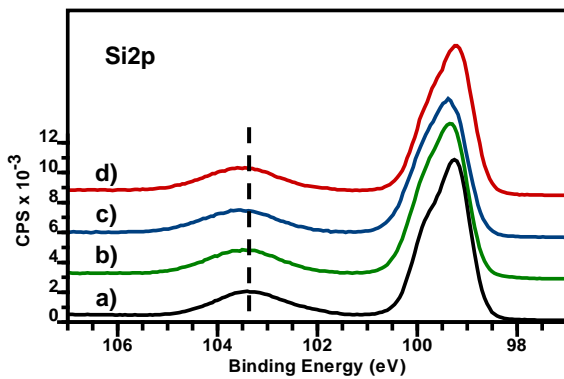
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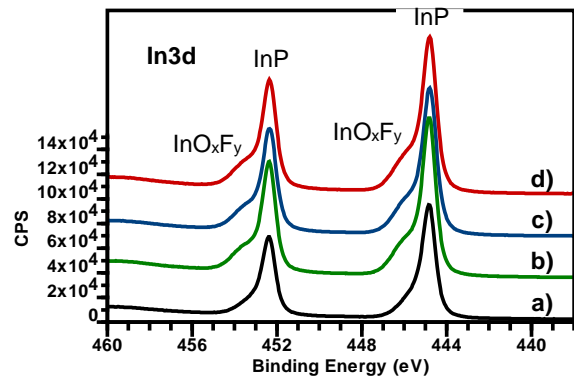
**Figure 1.** Si2p spectra of a-Si sample before (a), after (b) exposure to SiF<sub>4</sub>-O<sub>2</sub> plasma at -100°C, and (c) after warm-up to 20°C [3].



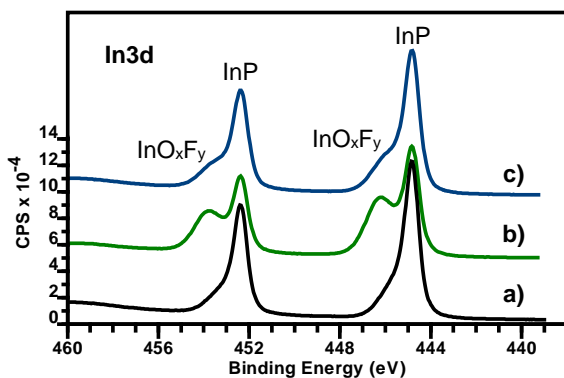
**Figure 2.** Si2p spectra of a-Si sample before (a), after (b) exposure to SiF<sub>4</sub>-O<sub>2</sub> plasma at -40°C, and (c) after warm-up to 20°C [3].



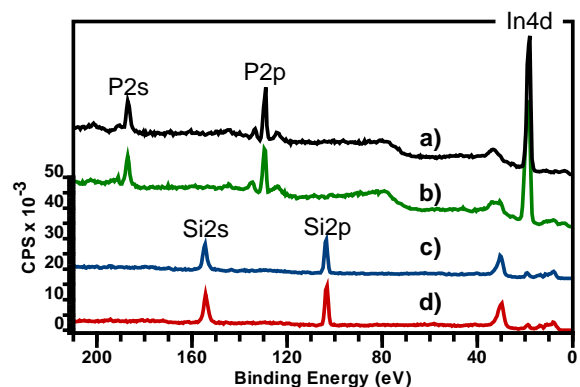
**Figure 3.** Si2p spectra of a-Si sample before (a), after exposure to O<sub>2</sub> plasma at 20°C (b) and -100°C (c), and (d) after warm-up to 20°C.



**Figure 4.** In3d spectra of InP sample before (a), after exposure to O<sub>2</sub> plasma at 20°C (b) and -100°C (c), and (d) after warm-up to 20°C.



**Figure 5.** In3d spectra of InP sample before (a), and after exposure to SiF<sub>4</sub>-O<sub>2</sub> plasma + warm-up; plasma at -40°C (b), plasma at -100°C (c).



**Figure 6.** P-Si-In4d spectral region for the InP sample before (a), after exposure to SiF<sub>4</sub>-O<sub>2</sub> plasma at -40°C (b) and -100°C (c); comparison with the a-Si sample exposed at -100°C (d).