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Passivation mechanisms involved in cryo-etching processes

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1. Introduction

Cryoetching of silicon was introduced about 35 years ago by a Japanese team. [1] Anisotropic etching was obtained using a plasma of SF₆ interacting with a masked silicon wafer cooled to a very low temperature (typically -100°C) in order to freeze chemical reactions on the trench sidewalls. But, a new interpretation of cryogenic etching mechanisms was proposed by Batha *et al.* in 1995 involving a passivation mechanism with an important role of oxygen. [2] Since this time, many in-situ experiments have been carried out to explain the formation of the SiO_xF_y passivation layer, which preferentially forms at low temperature. [3, 4] In particular, the role of SiF₄ molecules, which are the main by-products of silicon etching in fluorine based plasma was highlighted. [3] In this paper, we will describe the in-situ experiments using mass spectrometry, ellipsometry and XPS on ICP reactors in SF₆/O₂ and SiF₄/O₂ plasmas, that have been conducted to better understand the formation and the characteristics of the passivation layer.

2. Experiment

The cryoetching experiments were performed in 3 different Inductively Coupled Plasma (ICP) reactors: two industrial reactors installed at GREMI laboratory and one home made ICP reactor dedicated to in-situ XPS analyses installed at IMN laboratory. The reactors can operate in different gases such as Ar, SF₆, O₂, C₄F₈ and SiF₄. Industrial reactors are configured for 150 mm diameter wafers that are introduced from a load lock. The substrate is cooled with liquid nitrogen and its temperature is regulated with a distributed

thermal resistance to a set-point between +20 and -140°C. Helium gas is injected between the wafer and the substrate holder to enhance the thermal conductivity. For high aspect ratio etching experiments, a mask of SiO₂ was used. The industrial reactors are equipped with ellipsometry, mass spectrometry, Langmuir probe and OES diagnostics for in-situ measurements. Quasi in-situ XPS analysis was carried out on the OPTIMIST platform at IMN in Nantes where the home made reactor was installed. [5] 1 cm² samples are mounted on a rod and cooled at low temperature. They are first introduced in the ICP reactor for the plasma treatment and then directly transferred to the XPS chamber by keeping the temperature very low during the analysis.

3. Results

3.1 Composition of the passivation layer in SF₆/O₂ plasma

SF₆/O₂ plasma is usually used in deep etching of silicon at cryogenic temperature. SF₆ gas gives the best performances in terms of etch rate. The role of sulfur that acts as a catalyst was recently reported by Arora *et al.* [6] However, sulfur does not seem to play an important role on the formation of the passivation layer. In SF₆/O₂ plasma, SiF_x are formed on the trench sidewalls and react with oxygen to form a thin SiO_xF_y layer, which is stable at low temperature only. When the wafer is warmed back to room temperature, SiF₄ is formed and desorbs from the surface. It is worth to note that SiF₄ coming from the passivation layer is formed during the wafer warming, but not during the plasma at low

temperature. Indeed, SiF₄ is very volatile even at low temperature. We have shown that SiF₄ molecules do not physisorb in our etching conditions. But, SiF₄ gas can be used in the plasma in order to deposit SiF_x radicals on the sidewalls to reinforce the passivation.

3.2 Cryoetching using SiF₄/O₂ plasma to form the passivation layer

SiF₄/O₂ plasma can be used to create an SiO_xF_y layer that can be used to enhance the robustness of the passivation. This is the principle of the STiGer process. [7] In figure 1, we show the SiO_xF_y layer growth when 30s long SiF₄ plasma step is alternated with 30 s O₂ plasma step at 20°C and at -100°C. The growth occurs during the SiF₄ plasma. Without O₂ plasma, we obtain a growth as well, but the layer is less robust. The SiF_x growth is more efficient at low temperature. This result shows that the residence time of SiF_x species, which is longer at low temperature, has a key role to meet the reaction conditions between O atoms and SiF_x radicals to efficiently form the passivation layer.

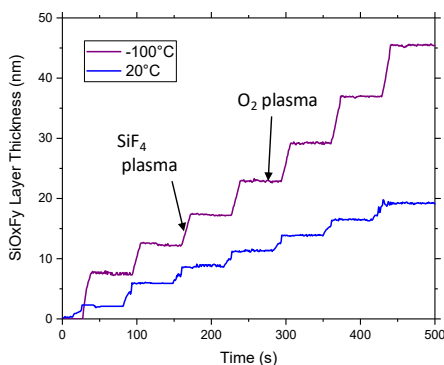


Figure 1: Passivation layer growth by alternating SiF₄ plasma with O₂ plasma at 20°C and -100°C.

The very low temperature (-100°C) is necessary to form the passivation layer. This was shown by in-situ XPS analysis. [8] In figure 2, the composition of the deposited layer that was obtained after 30 s of SiF₄/O₂ plasma on a silicon sample is reported for different temperatures. The “Ref” bar graph gives the surface composition before plasma. Then the surface composition after a process at low temperature and after heating the sample are provided. As observed, the most significant modification before and after heating is obtained at -100°C. It is clearly correlated to the SiF_x

molecule residence time that is increased by decreasing the temperature.

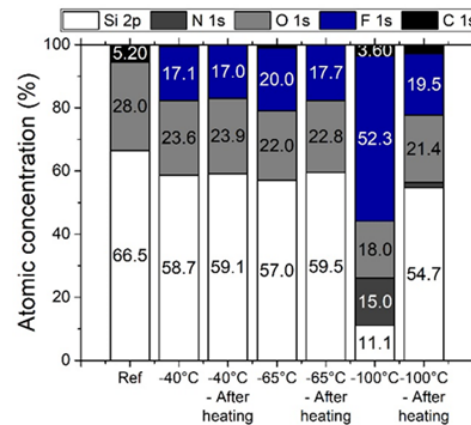


Figure 2: Surface composition of a silicon sample after a plasma of SiF₄/O₂ at different temperatures, before and after heating.

4. Conclusions

The chemistry at the silicon surface in Si₄/O₂ plasma is significantly modified at very low temperature. This property is attributed to the longer residence time of SiF_x radicals at the surface at low temperature.

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