In situ x-ray photoelectron spectroscopy analysis of SiO$_x$F$_y$ passivation layer obtained in a SF$_6$/O$_2$ cryoetching process

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The oxyfluorinated silicon passivation layer created during various cryoetching processes is of interest in order to improve high aspect ratio profiles. In this work, the desorption of a SiO$_x$F$_y$ layer obtained in an overpassivating SF$_6$/O$_2$ regime was investigated during the wafer warm-up from the cryogenic temperature to room temperature. An *in situ* x-ray photoelectron spectroscopy (XPS) device is used in order to probe the top-surface layer and understand the desorption mechanism. A new mechanism can be proposed using the evolution of fluorine, oxygen, silicon, and carbon contributions evidenced by XPS. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3085957]

The so-called Bosch process is widely used in microelectronics and microelectromechanical systems (MEMS) industries in order to elaborate high aspect ratio structures [MEMS, microoptoelectromechanical systems (MOEMS), or integrated components].[1–3] Even if this process is robust, a polymerization effect during the deposition steps leads to an important coating on the reactor walls and on the trench sidewalls. This effect modifies the plasma parameters and frequent cleanings of reactor walls are necessary to maintain reproducible processes. To avoid this issue, other etching processes were investigated such as the standard cryogenic process,[4–6] which was first proposed by Tachi *et al.*[4] in 1988. It consists of etching a silicon wafer cooled at cryogenic temperature ($T \approx -100$ °C) by SF$_6$/O$_2$ gas mixture leading to a chemical etching of silicon with volatile SiF$_4$ as main etching product. Simultaneously, due to the low temperature and the addition of oxygen in the plasma, a SiO$_x$F$_y$ passivation layer forms on the sidewalls and inhibits lateral etching. Since ion bombardment prevents its formation at the bottom of the trench, anisotropic etching can be achieved. The cryoetching is a clean process without major process drift compared to the Bosch one because thin-film deposition is efficient only on cooled surfaces. In the other hand, standard cryoetching is very sensitive to the silicon temperature and oxygen flow. Hence it is less robust than the Bosch process.

To increase the robustness, other cryoetching processes were recently investigated, consisting of the alternation of isotropic (SF$_6$) or anisotropic (SF$_6$/O$_2$) etching steps and deposition steps in SiF$_4$/O$_2$ gas mixture (STiGer Iso and STiGer Aniso).[7] Again, this process only works at low temperature of the Si substrate. As for the standard cryoetching process, spectroscopic ellipsometry measurements evidenced the partial desorption of the passivation layer obtained in SiF$_4$/O$_2$ plasmas when the wafer is warmed-up to ambient temperature.[8] The formation of the passivation layer depends on various parameters (oxygen concentration, ion impact, local temperature, etc.).[9] An important O$_2$/SF$_6$ ratio can lead to an overpassivating regime. Without any energetic ion bombardment (no bias voltage), this regime allows the formation of an important SiO$_x$F$_y$ layer, whereas addition of bias volt-

age leads to the formation of columnar microstructures similar to silicon micrometric "grass" and often called black silicon.[10] In a previous work,[11] mass spectrometry was used in order to analyze the desorbed species from the passivation layer when the silicon wafer is warmed-up after a cryoetching process. Thus, we evidenced that a large amount of SiF$_4$ fragmentation products such as SiF$_3^+$ desorbs during the temperature increase in the wafer. At the same time, SiO$_x$F$_y$ fragmentation product intensities (SiOF$^+$, SiOF$_2^+$,...) very slightly increase. Even if SiF$_4$ is volatile in our pressure and temperature conditions, it may play a role in the passivation layer formation. Although silicon cryoetching was proposed 20 years ago,[4] mechanisms of the passivation layer formation which is stable only at low temperature, has never been explained. However, the SiO$_x$F$_y$ passivation layer is a key parameter to obtain high aspect ratio profiles. In this paper, we propose a qualitative interpretation of SiO$_x$F$_y$ layer formation and desorption in the cryoetching process of silicon. The desorption of SiO$_x$F$_y$ layer obtained in overpassivating SF$_6$/O$_2$ regime is studied using *in situ* x-ray photoelectron spectroscopy (XPS) during the wafer warm-up in order to better understand the passivation mechanisms.

The experimental apparatus consists of two high vacuum chambers: the inductively coupled plasma (ICP) reactor and the XPS analysis chamber. The ICP plasma is generated using a transformer-coupled plasma antenna connected to a 13.56 MHz power supply through a manual matching network. The residual pressure is about 3.10^{-4} Pa. SF$_6$/O$_2$ gas mixture in overpassivating regime (20 SCCM SF$_6$ and 13 SCCM O$_2$)[9,11] (SCCM denotes standard cubic centimeter per minute at STP) is injected through a gas inlet at a pressure of 3 Pa. rf power is set to 500 W during two minutes and substrate temperature is fixed to -100 °C. In order to minimize the ion bombardment of the surface, the sample is electrically connected to the ground ($V_{bias}=0$ V). Due to the plasma potential, the silicon substrate is still subjected to a 15–20 eV ion bombardment. Substrates are *p*-type boron doped silicon with a (100) orientation and a resistivity of 10–20 Ω cm. The sample (10×10 mm^2) is placed on the cryogenic holder. Low temperature of the sample is obtained by flowing liquid nitrogen through the sample holder and regulated by a heating resistance. Just after the plasma pro-
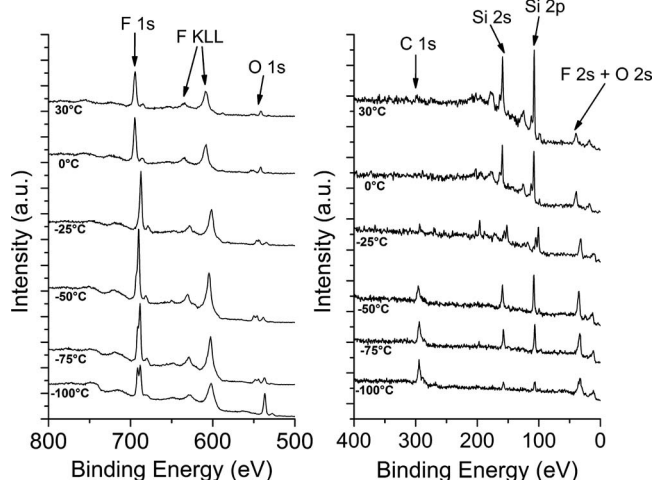
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FIG. 1. *In situ* XPS spectra of Si sample after an overpassivating SF_6/O_2 plasma from -100 °C to ambient temperature.

FIG. 2. Evidence of adsorbed CF_x groups at the top surface of the sample at $T=-100$ °C thanks to the deconvolution of C $1s$ and F $1s$ spectra.

cess, the sample is maintained at low temperature and is directly transferred to the XPS analysis chamber by translation of the rod for quasi *in situ* measurements. The XPS measurements are obtained using a Leybold AG LHS12 spectrometer and Mg $K\alpha$ radiation (1253.6 eV) at a pressure below 10^{-5} Pa.

The experimental procedure is as follows. We start to etch the silicon surface using a SF_6 plasma (20 SCCM, 500 W, 2.8 Pa) during 4 min at room temperature to remove the native oxide and to have an etched surface such as the one we have on the sidewalls where the passivation layer grows. Then, the sample is transferred into the XPS chamber in order to make a first reference analysis. XPS wide scan evidences the presence of fluorine corresponding to SiF_x sites incorporation within the silicon structure. Back to the ICP chamber, the sample is cooled down to -100 °C and exposed to a SF_6/O_2 plasma in overpassivating regime as described previously. The sample is again transferred into the XPS analysis chamber. The thermal stability of the deposited layer is then studied through successive warm-up steps followed by XPS analyses. To avoid significant pressure rises within the XPS chamber, the sample is transferred into the ICP reactor for the various sample warm-up steps.

The change in XPS spectra during the warm-up from the process temperature (-100 °C) to the ambient (30 °C) is shown in Fig. 1. Fluorine (F $1s$ core level in the range 685–700 eV) and oxygen (O $1s$ core level in the range 530–550 eV) peaks appear clearly on the spectra and come from the SF_6/O_2 plasma discharge. The two well-defined peaks at 150 and 100 eV are attributed to Si $2s$ and Si $2p$ core-level contributions, respectively. Their presence is associated to the detection of silicon coming from the Si(100) bulk substrate. The lack of sulfur core-level lines is a predictable result because of volatile SO_yF_x species formation.[12] We can also observe non-negligible amounts of carbon C $1s$ core level ($\sim$300 eV). The C atoms are contaminants resulting from residual gases in the chamber. Fluorine species are very reactive and can react with hydrocarbon compounds which are adsorbed on the inner walls of the ICP reactor.[13] The reaction products contaminate the cooled substrate surface and appear on the spectrum at $T=-100$ °C [significant contributions at 691.5 eV of the F $1s$ core-level peak, attributed to C–F bonds and numerous CF_x group contributions within the C $1s$ spectrum (Fig. 2)]. As it can be seen in Fig. 1, the C $1s$ core-level
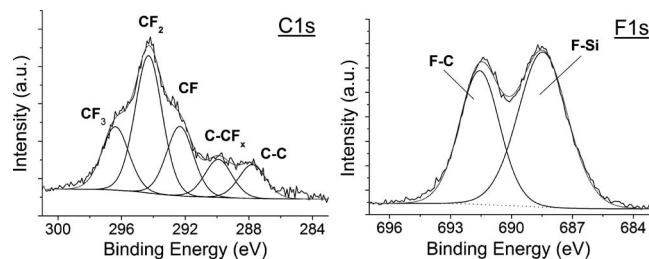
peak vanishes at around -25 °C, corresponding to a quite complete desorption of adsorbed CF_x groups. This result is confirmed in Fig. 3 by the regular decrease in the carbon atomic percentage during the sample warm-up.

Figure 3 summarizes the atomic fraction of the other elements constituting the top-surface layer (fluorine, silicon, and oxygen). First of all, we can observe the regular increase in silicon percentage from 4% at cryogenic temperature ($T=-100$ °C) to 40% at room temperature. This evolution shows the desorption of the top-surface layer during the sample warm-up, confirmed by the emergence of silicon coming from the silicon matrix (c-Si). For fluorine and oxygen, the atomic fraction evolution is less obvious. From -100 to -75 °C oxygen atom concentration seems to decrease at the top-surface, whereas fluorine one rises. This evolution can be associated to the desorption of oxygenated groups adsorbed and trapped at the cooled surface of the sample, such as CF_x groups. Then, above -75 °C, oxygen atomic fraction seems to be stable, whereas fluorine one begins to decrease, especially above -50 °C. These evolutions are associated to the desorption of the SiO_xF_y layer.

Thus, we can assume the presence of two distinct layers. A thin one, composed of physisorbed molecules such as CF_x and moieties groups, which is probably formed when we stop the plasma. This layer screens the underlying SiO_xF_y layer, explaining the very weak silicon atomic fraction obtained by XPS at -100 °C. A thicker one, below the adsorbed layer, corresponding to oxyfluorinated layer and resulting from the fluorine and oxygen incorporation within the silicon matrix.

The evolution of the Si $2p$ peak shape versus sample temperature clearly shows the desorption of the SiO_xF_y layer (Fig. 4). At -100 °C, the Si $2p$ peak is exclusively com-
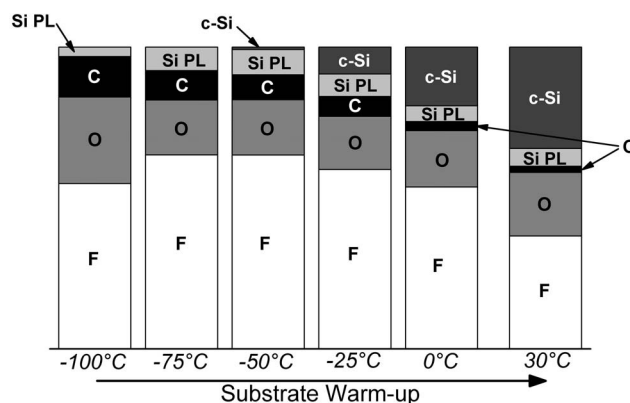

FIG. 3. XPS atomic quantification vs sample temperature (°C) of fluorine (F), oxygen (O), carbon (c), silicon of the SiO_xF_y "passivation layer" (PL) compound (Si PL), and silicon coming from the substrate (c-Si).
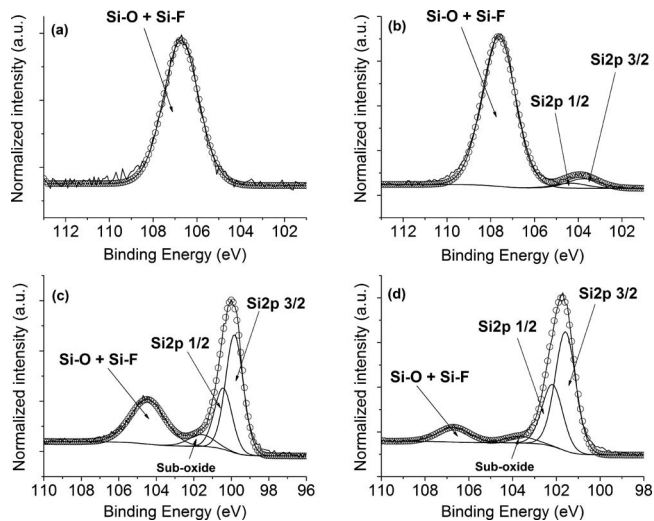
FIG. 4. Evolution of Si 2*p* peak shape during the sample warm-up. (a) $T=-100\ °C$, (b) $T=-50\ °C$, (c) $-25\ °C$, and (d) 30 °C.

posed of Si–O and Si–F bonds, indicating the presence of SiO_xF_{4-x} compounds ($x < 4$) [Fig. 4(a)]. It seems to be quite difficult to distinguish Si–O and Si–F contributions because the induced chemical shifts are quite close to each other. Since no indication of Si–Si$_4$ bonds appears around 100 eV, we assume that the oxyfluorinated layer screens the silicon substrate. A regular increase in temperature leads to the regular decrease in SiO_xF_{4-x} contribution corresponding to the desorption of the oxyfluorinated layer. At the same time, we can observe the emergence of Si–Si contributions (Si $2p_{1/2}$ and Si $2p_{3/2}$) associated to the silicon matrix. We also distinguish the appearance of various suboxides such as Si–SiO_xF_{3-x} ($x \leq 3$), Si–$Si_2O_xF_{2-x}$ ($x \leq 2$) and Si–$Si_3O_xF_{1-x}$ ($x \leq 1$) with chemical shifts of +3, +2, and +1 eV, respectively. At room temperature (30 °C), the Si $2p$ peak is almost exclusively composed of Si–Si$_4$ components, corresponding to silicon matrix [Fig. 4(d)].

These results provide a better understanding of the passivation mechanisms which occur only at cryogenic temperatures. It is well known that the mechanism for the etching of silicon by fluorine radicals only leads to a fluorine incorporation into 2–5 monolayers of silicon matrix through the formation of a SiF$_x$ layer ($x < 4$).[14] The fluorine to silicon ratio obviously depends on the layer depth. For example, at the top of this layer, SiF$_x$ are mainly SiF$_3$ groups, whereas the F/Si ratio falls to zero at the SiF$_x$/Si interface. In SF$_6$/O$_2$ discharges, we can assume that oxygen atoms, quite similarly to fluorine, are also incorporated within the silicon matrix. There is formation of nonvolatile SiO_xF_y sites on a few silicon monolayers. In a "real" etching process, SiF$_x$ reaction products coming from the reaction of SF$_6$ plasma on the silicon matrix can also participate to the formation of the SiO_xF_y passivation layer through redeposition and oxidation mechanisms.[11] Actually, in our conditions, the silicon surface exposed to the plasma is small enough to assume that the SiF$_x$ density in the plasma is negligible. In these conditions, fluorination and oxidation of the silicon lattice must be predominant. Moreover, due to the plasma potential, a weak ion bombardment can enhance the diffusion of fluorine and oxygen within the silicon matrix, contrary to what happens on the vertical sidewalls of trenches. Nevertheless, the desorption mechanisms must be similar.

Following the Arrhenius model, the oxygen and fluorine thermal diffusion coefficients increase versus temperature. Hence, the sample warm-up from −100 °C to the ambient temperature enhances the diffusion of fluorine and oxygen within the SiO_xF_y structure. XPS atomic quantification reveals that fluorine incorporation is three times higher than oxygen one. We can assume that SiOF$_3$ is the main molecule of the SiO_xF_y top surface. The migration of fluorine atom replacing oxygen sites leads to the formation of volatile SiF$_4$ groups which are volatile and desorbs from the surface. This interpretation is consistent with several results obtained in this paper and in our previous works. First, we observed a decrease in the SiO_xF_y layer thickness by ellipsometry after a SiF$_4$/O$_2$ plasma at low temperature of the substrate during the warming up.[8] Then, a strong increase in the SiF$_4$ fragmentation products (mainly SiF$_3^+$) was detected by mass spectrometry between −70 and 30 °C during the warm-up of the sample after a SF$_6$/O$_2$ plasma at low temperature of the substrate,[9] whereas SiF$_4$ is volatile in the plasma pressure and temperature conditions. Indeed, SiF$_4$ formation occurs during this warming step and immediately desorbs.

In situ XPS measurements and previous results permit to propose an other mechanism for the formation of the SiO_xF_y passivation layer at cryogenic temperature and its desorption. Its formation corresponds to fluorine and oxygen incorporation within the silicon matrix leading to the formation of nonvolatile SiO_xF_y structures. During the sample warm-up, the diffusion of oxygen and fluorine leads to the formation of SiF$_4$ volatile compounds, correlated with the desorption of the passivation layer. This mechanism seems to be similar in SiF$_4$/O$_2$ even if the thickness of the passivation layer is increased due to the silicon contribution within the gas mixture.

[1] C. Cardinaud, M. C. Peignon, and P. Y. Tessier, Appl. Surf. Sci. **164**, 72 (2000).
[2] F. Lärmer and A. Schilp, German Patent No. DE4241045 (23 June 1994).
[3] M. J. de Boer, J. E. Gardeniers, H. Jansen, E. Smulders, M. J. Gilde, G. Roelofs, J. N. Sasserath, and M. Elwenspoek, J. Microelectromech. Syst. **11**, 385 (2002).
[4] S. Tachi, K. Tsujimoto, and S. Okudaira, Appl. Phys. Lett. **52**, 616 (1988).
[5] T. Chevolleau, P. Y. Tessier, C. Cardinaud, and G. Turban, J. Vac. Sci. Technol. A **15**, 2661 (1997).
[6] R. Dussart, M. Boufnichel, G. Marcos, P. Lefaucheux, A. Basillais, R. Benoit, T. Tillocher, X. Mellhaoui, H. Estrade-Szwarckopf, and P. Ranson, J. Micromech. Microeng. **14**, 190 (2004).
[7] T. Tillocher, R. Dussart, L. J. Overzet, X. Mellhaoui, P. Lefaucheux, M. Boufnichel, and P. Ranson, J. Electrochem. Soc. **155**, D187 (2008).
[8] R. Dussart, X. Mellhaoui, T. Tillocher, P. Lefaucheux, M. Boufnichel, and P. Ranson, Microelectron. Eng. **84**, 1128 (2007).
[9] T. Tillocher, R. Dussart, X. Mellhaoui, P. Lefaucheux, N. Mekkakia Maaza, P. Ranson, M. Boufnichel, and L. J. Overzet, J. Vac. Sci. Technol. A **24**, 1073 (2006).
[10] R. Dussart, X. Mellhaoui, T. Tillocher, P. Lefaucheux, M. Volatier, C. Socquet-Clerc, P. Brault, and P. Ranson, J. Phys. D **38**, 3395 (2005).
[11] X. Mellhaoui, R. Dussart, T. Tillocher, P. Lefaucheux, P. Ranson, M. Boufnichel, and L. J. Overzet, J. Appl. Phys. **98**, 104901 (2005).
[12] K. Ninomiya, K. Suzuki, S. Nishimatsu, and O. Okada, J. Appl. Phys. **63**, 1468 (1987).
[13] K. Ninomiya, K. Suzuki, S. Nishimatsu, and O. Okada, J. Appl. Phys. **58**, 1177 (1985).
[14] M. A. Lieberman and A. J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing* (Wiley, New York, 1995).