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It is known, that Reactive Ion Etching (RIE) processes have various negative effects on the electronic performance of silicon devices. Detrimental RIE effects include lattice damage, diffusion of dopant ions and deposition of etching residues on the surface. Here the effect of plasma ashing and thermal treatment in an effort to remove these reactant residues from the surface of RIE processed silicon was studied by X-ray Photoelectron Spectroscopy (XPS) and Surface Enhanced Raman Spectroscopy (SERS).

RIE process

We used a SF6/O2 RIE process to fabricate silicon nanopillars. This structure is capable of being transformed into as a SERS substrate and therefore it is possible to verify the results with both XPS and SERS. After the RIE etch, the nanopillars were subsequently treated either/both with a standard O_2 plasma ash for 1 min and/or placed in a furnace at 800°C for 3 hours in a N_2 atmosphere.

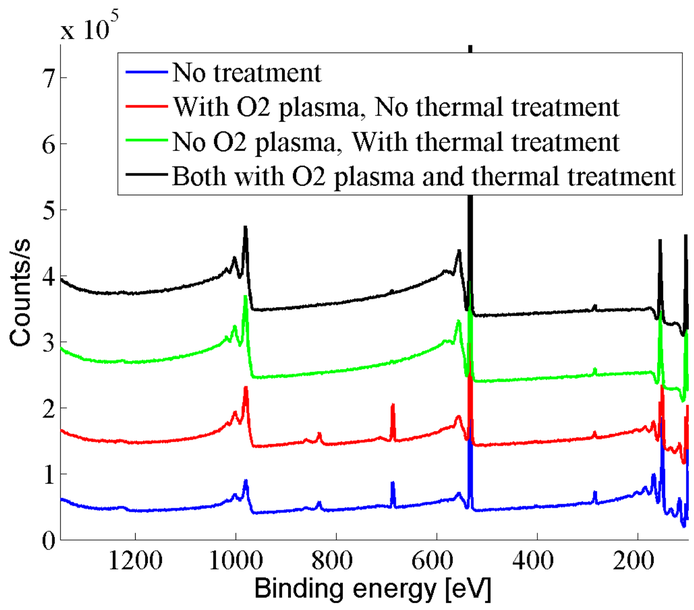

Figure 1. XPS results. The characteristic peak for fluorine is at 678 eV. The spectra are shifted for better visualization.

XPS results

The surface was characterized by XPS and the result is shown in Figure 1 and Table 1. XPS reveals that the surface contains a mixture of mostly silicon, carbon and oxygen and as expected, also fluorine as a residue from the RIE process. The surface is contaminated with approximately 5 atomic percent fluorine after the RIE process. This does not change upon O2 plasma ashing. However, the fluorine is practically removed after the thermal treatment.

SERS substrate

In order to perform SERS we create plasmonic structures by evaporating 225nm of silver onto the nanopillars after plasma/thermal treatment. Figure 2 shows that the pillars do not change shape or form after the thermal treatment, and that the coverage of the silver coating is similar in both cases, making it suitable to compare the SERS measurements. A significant part of the Raman signal originates from the silver cavity formed at the lower part of the silver cap on the silicon pillar. This plasmonic cavity mode gives a strong Raman response from the surface of the silicon pillar. Hence, this SERS substrate is sensitive enough to enhance the signal from any etch residues located on the surface of the silicon as well. This makes it excellent for analysis of the cleaning procedures.

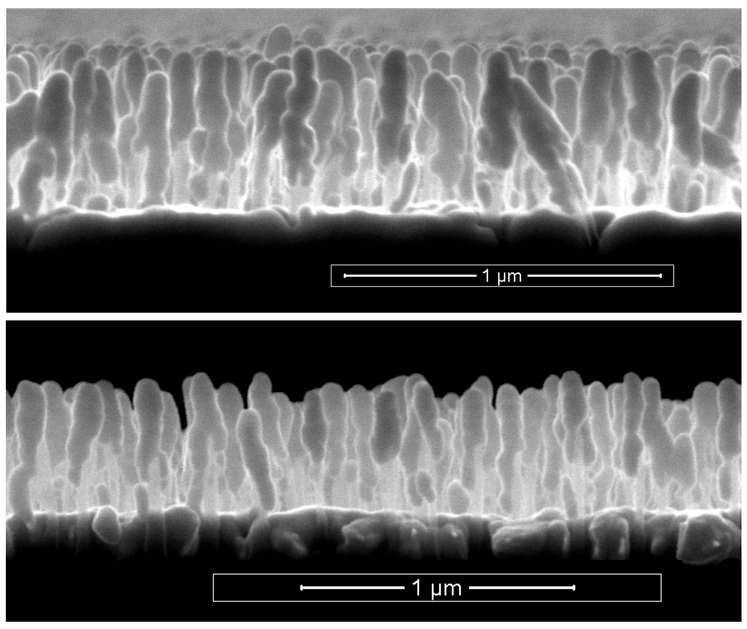

Figure 2. Sem image of silicon nanopillars with silver coating. The top image show silicon nanopillars which were not heated, while the pillars on the lower figure has been heated to 800 C before silver coating.

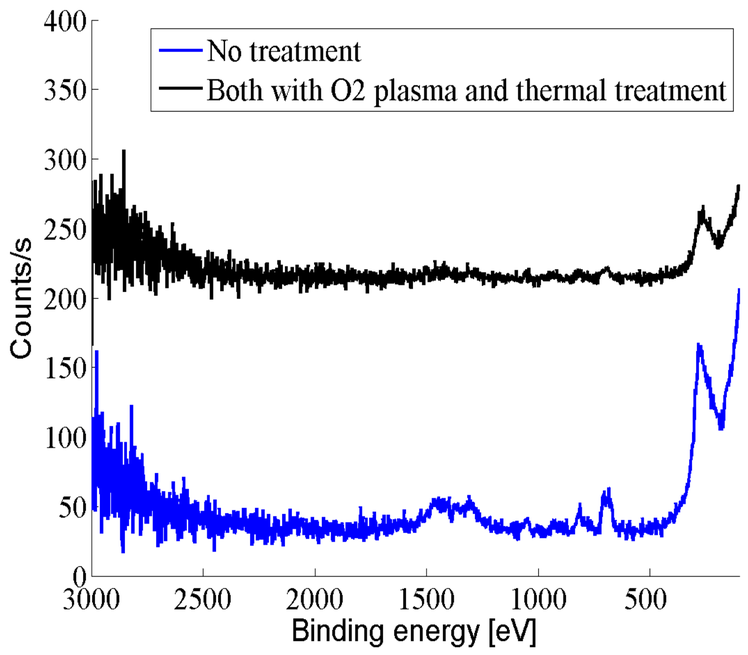

Figure 3. SERS results. The spectra are shifted for better visualization.

SERS results

A 1µl drop of H2O is positioned on the SERS substrate. H2O does not give rise to a significant Raman shift with our measurement conditions. As the drop evaporates, the surface forces pull the pillars together forming clusters creating electromagnetic “hot spots” which greatly enhance the SERS signal. The signal is measured at 780nm with 0.5mW and 50X for 3x1sec. The results shown in Figure 3 indicate that significant levels of etchant residues are removed from the silicon surface at 800°C.

Table 1. Results of the XPS analyzed by Thermo Advantage v4.88. The thermal treatment removes the fluorine from the surface of the sample.

At%	No O_2 plasma ashing No thermal treatment	O_2 plasma ashing No thermal treatment	No O_2 plasma ashing Thermal treatment	O_2 plasma ashing Thermal treatment
Oxygen	30.67	45.01	57.13	58.53
Silicon	54.67	44.72	38.95	37.90
Carbon	8.73	4.86	3.92	3.17
Fluorine	4.72	5.42	-	0.40
Nitrogen	1.22	-	-	-

The standard plasma ashing procedure has no effect on the cleanness of the silicon substrate after the RIE process. However, the thermal treatment of 800°C seems to remove the unwanted fluorine from the surface. These findings can be utilized in applications where the surface of the silicon is important, e.g. in the solar cell and chemical sensing industries.

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