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LETTER TO THE EDITOR

In situ Raman spectroscopy of silicon surfaces during SF₆ plasma etching

Pascal Brault, Jacky Mathias, Claude Laure, Pierre Ranson and Olivier Texier
Groupe de Recherches sur l'Energétique des Milieux Ionisés, URA 831 du CNRS,
Département de Physique, Université d'Orléans BP6759, F-45067 Orleans Cédex 2, France

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Abstract. *In situ* Raman scattering spectroscopy is performed in order to probe the chemical dynamics and structure modifications at Ar and SF₆ low-pressure plasma-etched silicon surfaces. An Ar plasma induces relatively slight perturbation of the silicon surface, while a SF₆ plasma creates highly disordered overlayers induced by the fluorine atoms reacting at ion-induced defects. The overlayer structure is a mixing of an amorphous phase and 10 Å microcrystallites expected to be close to porous silicon structure.

Plasma etching of silicon is a major step in ultra-large-scale integrated circuits. Increasing miniaturization leads to the need for better understanding of surface reactions and induced damage. The problems for achieving ultimate miniaturization (for example, isolating trench width below 0.1 μm) will certainly be concerned with roughness and reactive atom diffusion in the bulk.

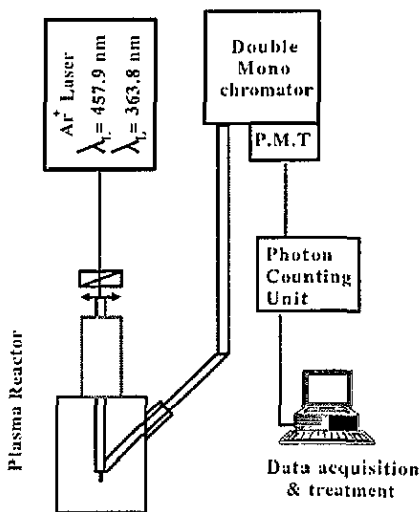


Figure 1. Schematic experimental set-up.

In previous work, by means of x-ray photoelectron spectroscopy and nuclear reaction analysis [1–3], we found a strong incorporation of fluorine atoms in silicon during plasma etching and also induced roughness. These analysis tools needed to transfer etched samples and then dynamical information was lost. In order to obtain information simultaneously about fluorine chemical reactivity and structure modification in silicon, we have built an *in situ* Raman scattering (ISRS) experiment in a plasma reactor dedicated to a plasma etching of materials. Vibrational Raman spectroscopy is a powerful technique for investigating chemical and structural properties of materials [4,5], despite the low-level signal to be detected in our experimental conditions. As schematically drawn in figure 1, the ISRS experiment is a two-stage plasma reactor. The upper stage is an alumina cylindrical plasma source ($\phi = 70$ mm, $L = 250$ mm) surrounded by a four-wire antenna exciting continuous radio frequency low-pressure Ar and SF₆ plasmas. The excitation frequency is 13.56 MHz, the input RF power W_{rf} is in the range 100–1000 W and the pressure can be varied between 0.5 and 25 μ bar. This is the so-called helicon source, working here without axial static magnetic field [6]. The bottom stage is a stainless steel diffusion chamber ($\phi = 250$ mm, $L = 350$ mm, equipped with a multipolar magnetic confinement) in which the plasma can expand homogeneously. A 0.8 cm² boron p-doped silicon Si(100) sample, located in the bottom of the diffusion chamber, is exposed to the plasma at floating potential leading to an impinging ion energy of around 20 eV. Between successive plasma exposures, ISRS experiments are conducted without replacement of the wafer, allowing direct comparison of Raman intensities. The excitation light is provided by an Ar⁺ laser (Coherent Radiation Innova 20) operating at a wavelength of 457.9 nm (for which penetration depth is roughly 1000 Å for crystalline silicon in reflection geometry). The laser beam is focused perpendicular to the sample surface through a cylindrical lens, leading to a power density of 25 W cm⁻². The scattered light is collected at 60° with respect to the incident laser beam, within a very low collection angle of 4.6° (constraint due to the large chamber and *in situ* requirements in reactive environment), and is directed to an additive double monochromator (Jobin Yvon HRD2) followed by an Hamamatsu R2949 (–20 °C) photomultiplier (with a dark noise of 0.4 count per second), a photon counting unit (amplifier and discriminator) Hamamatsu C3855. Data acquisition is performed through an electronic card (EG&G ORTEC) fixed into a desk computer. The slit spectral width is 4 cm⁻¹ at 457.9 nm, when the slits are 100 μ m opened. Figure 2 displays wide spectra (40–540 cm⁻¹) of clean silicon, Ar and SF₆ (15 min, 1000 W) plasma treated silicon. Intense peaks below 400 cm⁻¹ Raman shifts are attributed to non-stimulated emission lines of the laser. The 520 cm⁻¹ sharp line is the Raman TO peak of crystalline silicon. We can observe that, after 15 min of Ar plasma exposure, no significant change occurs with respect to clean silicon, while after SF₆ plasma exposure, strong modifications have occurred. A growing shoulder appearing between 40 and 200 cm⁻¹ occurs on the off-specular reflection of the exciting laser line, indicating that strong roughness occurs. Detailed examination of the time evolution of the Si TO Raman peak region is illustrated in figure 3. For 1000 W plasma excitation, three peaks are growing. The first one, at 485 cm⁻¹, becomes slightly visible after 13 min and seems to be related to non-stimulated emission lines of the laser and will not be further discussed. At 17 min, two other lines appear at 465 and 510 cm⁻¹. The 465 cm⁻¹ line is attributed to a-Si:F growth during etching [7]. The 510 cm⁻¹ line originates from crystalline Si–Si TO vibration perturbed by F atoms [8]. The corresponding shift with respect to the unperturbed c-Si(TO) peak at 520 cm⁻¹ indicates the growth of 10 Å-sized microcrystals [7]. Due to the large penetration depth of the laser light, long exposure times were needed to observe such features. This also indicates that the damage induced by the plasma increases with time. It also means that fluorine has deeply incorporated silicon as already seen with XPS [1, 3].

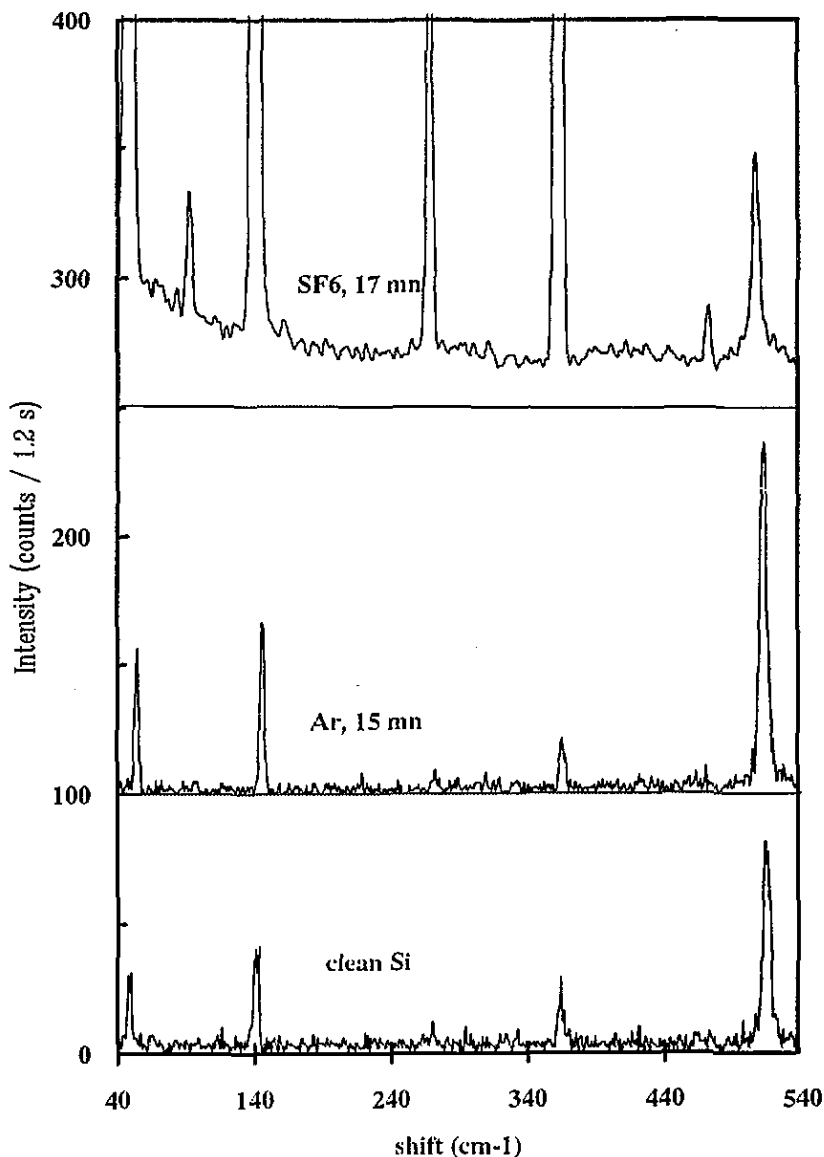


Figure 2. Comparison of Raman spectra of clean silicon, Ar and SF_6 plasma-treated (1000 W and $p = 1.2 \mu\text{bar}$) silicon. Horizontal straight lines give the zero intensity of the corresponding upward shifted spectra.

In figure 4, we plot the time evolution of the 145 cm^{-1} non-stimulated emission line of the laser during SF_6 plasma exposure. Because the roughness allows light to reflect in all directions, the exponential increase of such a line describes a diverging roughness growth. At the same time, an Ar plasma does not roughen the surface as much, even after long exposure times (cf. figure 2). Such evolution of plasma-induced roughness is far from the etching rate (which is identical to the removal rate of matter) evolution. Indeed, after a few seconds, etching rates reach a time-independent regime [6,9]. Thus, contrary to the

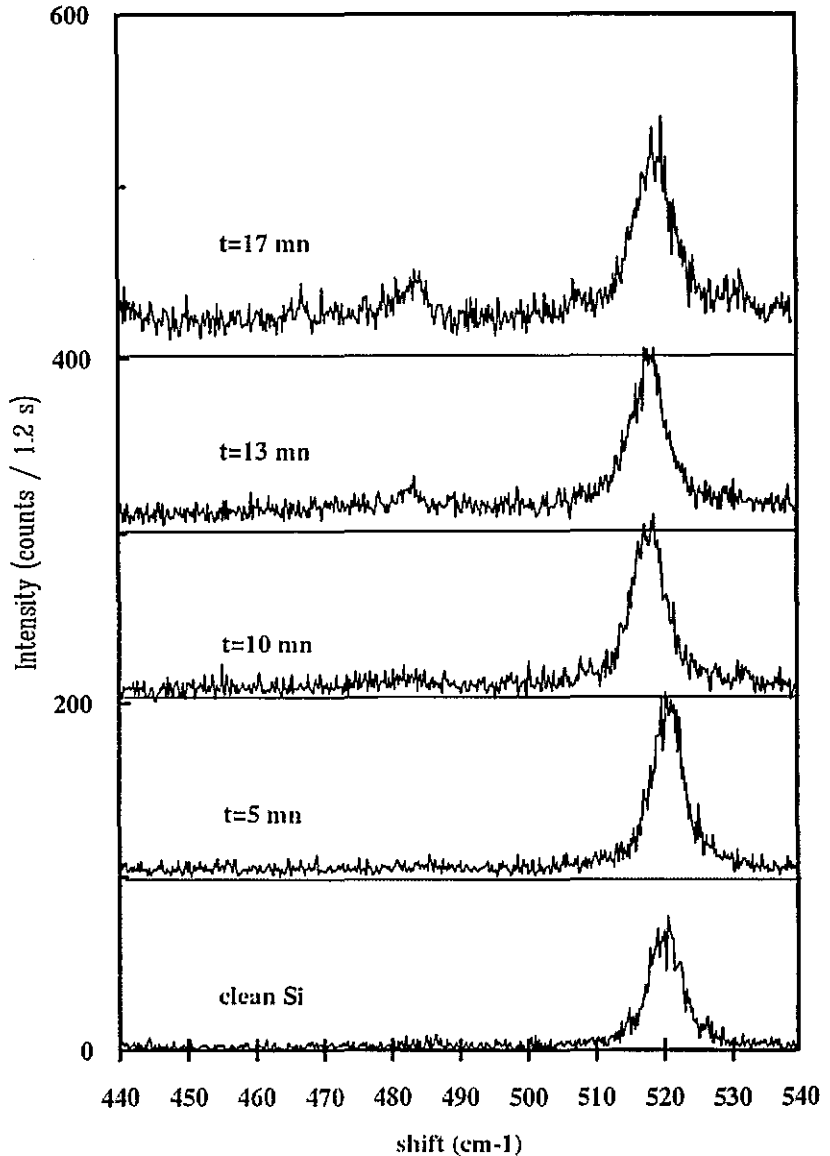


Figure 3. Time evolution of the TO Raman region after SF_6 etching ($W_H = 1000 \text{ W}$, $p = 1.2 \mu\text{bar}$).

common idea that residual damage is largely due to etch rates, the roughness grows in an independent way. We predict that roughness correlates with reaction kinetics rather than the removal of matter. Because the density ratio of ions to reactive F neutral atoms is in the range 10^{-3} to 10^{-2} , and because unreactive ions like Ar^+ do not induce a significantly higher roughness than clean silicon, we conclude that the present roughness is largely due to the effects of F atoms: statistically, a large amount of reactive F atoms enhance local disorder at a defect induced by an ion. Such a mechanism of etching is of the same kind as those involved in HF electrochemical dissolution of silicon leading to porous silicon growth

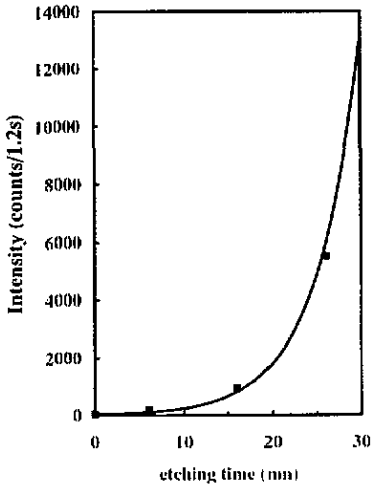


Figure 4. Time evolution of reflected laser light after SF_6 etching ($W_{\text{rf}} = 1000 \text{ W}$, $p = 1.2 \mu\text{bar}$): ♦ experimental points taken at 145 cm^{-1} , solid curve: best exponential fit.

[10]. We are expecting that the disordered overlayers are some kind of porous silicon thin film. These results are consistent with previous works using XPS and NRA [1, 3], concerning the induced damage (presence of voids) and fluorine diffusion in the bulk. Very recently, atomic force microscopy studies, in displaying in growth of columnar structures, confirm such interpretation of the basic mechanisms of plasma etching [11], as well as molecular dynamics calculations [12] and molecular beam experiments [13].

In conclusion, examination of Raman spectra and off-specular elastic laser light scattering of SF_6 plasma etched crystalline silicon, gives evidence that F atoms generate enhanced roughness when reacting at plasma ion induced defects. Moreover, the roughness is probably of the same kind as porous silicon and it is in the form of a thin film. As a general consequence, further scaling down of integrated circuits will certainly suffer from such a roughening effect.

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