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LETTER TO THE EDITOR

Fluorine diffusion in silicon under plasma treatment

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Abstract. Plasma-etched silicon samples show deep in-diffusion of very different elements like H, F and Cl, as has been shown in our experiments and in the literature. Gathering all these available results, it is suggested that a plasma-induced porosity is responsible for the diffusion of the etching species in the substrate. It is shown that the in-diffusion occurs independently from steric properties of the diffusing particles and from plasma-ion energies. Results for fluorine–plasma interaction with silicon are more extensively discussed. On the other hand, the available models of plasma–surface interactions are examined and new approaches to theoretical understanding are described.

The manufacture of microelectronics materials, like integrated circuits, (IC: especially, very-large-scale integrated circuits (VLSI) and ultra-large-scale integrated circuits (ULSI)) is largely performed using plasma etching and deposition (cf d'Agostino 1989, for example).

Etch plasmas in use are mainly fluorine based: CF_4, SF_6, CHF_3 with some added gas like H_2 or O_2, depending on the properties of the wafers to be etched. Other halogen-containing plasmas are in use for plasma-assisted microelectronics technology. The understanding of such plasmas is relatively well established, even if numerous radicals resulting from the dissociation of the parent molecule complicate noticeably the chemical physics of the plasma phase. The state of the etched material is less evident: even if the behaviour of the outermost surface is well studied, mainly with the help of x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), the role of the subsurface (to a depth of several thousand Å) needs to be clarified. Indeed, the XPS probed depth is 100 Å maximum, depending on the electron escape depth of the probed atoms. Thus, if used alone, as it often appears, this technique cannot give information about the reactions taking place below the surface layers.

Nevertheless, in order to explain etching mechanisms theoretically, only kinetic models (Gerlach-Meyer 1989, Tachi 1986) or surface limited processes (Flamm and Donnely 1981, Winters *et al* 1983, Petit and Pelletier 1986, Pelletier *et al* 1987) (like adsorption–reaction–desorption, involving only the first atomic planes) are available. The main problem in the former lies in the absence of a description of the interaction of the plasma phase with the wafer. The knowledge of the volatilization products allows us to infer reaction mechanisms without their observation. The latter are built up by matching some assumptions: lateral diffusion, occupation of vacancy sites and formation

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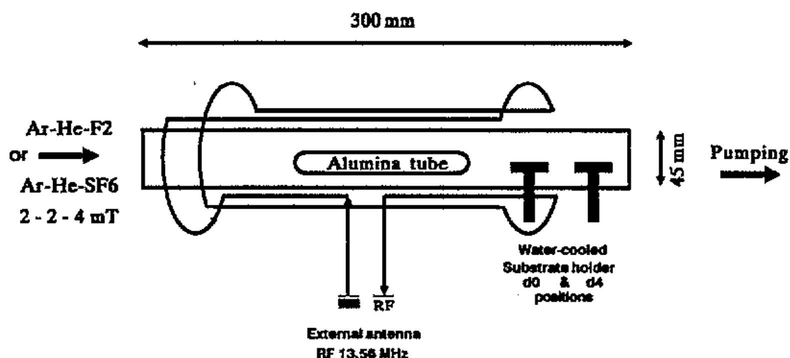

Figure 1. Schematic view of the plasma–surface interaction set-up.

of volatile compounds. However, no possible diffusion into the wafers of the reacting species is taken into account.

In order to clarify the existence or non-existence and the subsequent role of the incorporation of fluorine atoms in the subsurface, we performed plasma-etching experiments and analysis of the etched silicon crystals. Etching experiments were done using a continuous radiofrequency (RF, 13.56 MHz, $P = 160$ W) Ar–He–F_2 plasma (simple gas-phase chemistry) or Ar–He–SF_6 plasma (largely used for IC manufacturing) excited in an alumina cylinder of 4.5 cm inner diameter and 30 cm length (Brault *et al* 1990a, b), as shown in figure 1. Argon and helium are introduced for spectroscopic diagnosis of the plasma. Due to its low ionization potential, argon is the primary source of electrons ($\simeq 10^{11}$–10^{12} cm^{-3}, as measured with microwave interferometry, 2.45 GHz). It can dissociate F_2 or SF_6 molecules to produce F atoms ([F] $\simeq 10^{13}$–10^{14} cm^{-3}, as deduced from optical emission spectroscopy measurements) that are responsible for the etching, creating volatile SiF_4 molecules. F^+ ions are also produced, in the ratio $[Ar^+]/[F^+] \simeq 6$ (Ranson *et al* 1989).

The silicon (100) sample (0.6 cm^2; phosphorus N-doped) can be biased from 0 to -100 V, which allows variation, independently from the plasma potential, of the impinging ion (F^+ and Ar^+) kinetic energies 0 to 100 eV.

After plasma treatment, etched silicon samples were positioned in the analysis apparatus. Two kinds of characterization were performed. First, XPS measurements in order to determine chemical composition of the surface and depth profiles (between 4 and 75 Å) varying the detection angle. Secondly, nuclear reactions analysis, which provides elemental composition of the sample up to 1 μm, was used to probe F and O atoms, i.e. to see if they exist far from the surface.

The main result obtained using combined XPS and NRA (Brault *et al* 1990a), is the diffusion of fluorine atoms to a depth of 500 Å, at least, in the silicon and the location of oxygen in the outermost surface to a depth of less than 100 Å. A similar result has been reported with SF_6 and chlorine-based plasma by Oehrlein *et al* (1989, 1990). Note that chlorine is known to be a bad etchant because of its unfavourable steric properties (Seel and Bagus 1983, Bagus 1985, van den Hoek *et al* 1988, Weber and Sillinger 1990). Thus, in-diffusion of such species probably becomes an important process and its role in the formation of volatile etching products needs to be investigated. Up until now, only hydrogen diffusion in silicon has been established clearly and numerous works have

Table 1. Penetration depths and concentrations of fluorine and oxygen in silicon for some plasma parameters. These were calculated using the most simple XPS quantization model and NRA surface concentrations. The surface density of the native oxide was measured with NRA and was found to be 0.23×10^{16} at. cm^{-2} (Brault *et al* 1990a).

	NRA (10^{16} at. cm^{-2})	XPS (10^{22} at. cm^{-3})	Depth (Å)
$E_c = 0$ eV	[F] = 4.00	0.75	530
	[O] = 0.56	0.70	80
	[O]/[F] = 0.14	0.95	—
$E_c = -50$ eV	[F] = 2.70	0.85	320
	[O] = 0.45	1.45	30
	[O]/[F] = 0.17	1.70	—

been devoted to this topic (Oehrlein 1986, Corbett *et al* 1986, Noorbatcha *et al* 1985, Rice *et al* 1987, Seel and Bagus 1981) for various reasons.

Beside the diffusion of fluorine (or chlorine), it has been demonstrated (Brault *et al* 1990a, b) that the outermost surface layers are oxidized. Indeed, XPS measurements show clearly a mixing between oxygen and fluorine (both bound to silicon) over a thickness of 10 to roughly 100 Å. In fact, the high reactivity of fluorine with oxygen contained in the wall material (alumina) is responsible for the presence of oxygen impurities ($[O]/[F] \simeq 5\%$) in the gas phase, and consequently on the surface, but with a different concentration ratio: between 1 and 2 depending on the plasma parameters. Note that, when oxygen addition is controlled in fluorine plasma, the silicon etch rate is rapidly lowered to the silicon dioxide etch rate (Ninomiya *et al* 1987): less than 15% oxygen (with respect to fluorine) is sufficient to produce SiO_2-like surfaces. It becomes clear that etching mechanisms are rather complicated and are far from the idealized situations described by 'adsorption–reaction–desorption' models. Nevertheless, such models are successful when applied to SF_6 etching of silicon: it was demonstrated previously (Brault *et al* 1990a, b, Oehrlein *et al* 1989) that, even if fluorine is deeply incorporated, the composition of the surface is essentially made up of a thin 'oxy-fluorinated' overlayer ($\simeq$10 Å), which allows the use of a model involving the first atomic planes of the crystal.

One property of the plasma is to provide ion bombardment of the silicon surface. Increase of the ion energy, between 0 and 100 eV (biasing the substrate) reduces the thickness of the 'oxyfluorinated' overlayer from 80 Å to 15 Å. At the same time the fluorine diffusion is independent of the varying ion energies, as shown in table 1: this supports the effectiveness of the existence of a diffusion mechanism. In addition, the morphology of the surface is affected. At low ion energies (i.e. below the sputtering threshold: roughly 75 eV), some unreacted or re-deposited silicon islands are present. The islands disappear above this threshold leaving space for voids (Brault *et al* 1990a) (see figure 2). Such structural properties have been made evident for plasma deposition of amorphous Si:O:H:F films (Dias and Figueiredo 1989). Infrared absorption spectroscopy of these films showed formation of silicon clusters enbedded in the Si:O:H:F matrix. This formation seems to result from a segregation process of the fluorine and oxygen atoms in the amorphous Si:O:H:F matrix.

In other respects, fabrication of microporous silicon has been performed using anodic oxidization (Goudeau *et al* 1989) in ethanol electrolytes composed of 50% ethanol and

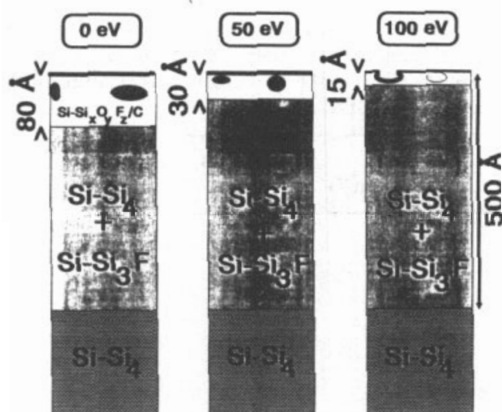

Figure 2. Cross sectional view of the fluorine etched silicon samples for different ion energies as deduced from XPS and NRA measurements.

Table 2. Relevant data for porous silicon as observed by small-angle scattering of x-rays (from Goudeau *et al* 1989).

Dopant type	n	p	p^+
Pore radii (nm)	≃50	≤2	1.8–2.8
Porous layer thickness (μm)	7	5	5
Forming current density (mA cm^{-2})	5	10	10

different concentrations of hydrofluoric acid (15% to 35%). Depending on the silicon doping (n, p, p$^+$), various pore structures were observed: anisotropic columnar structures perpendicular to the surface, isotropic networks of small pores, and anisotropic branched networks of pores perpendicular to the surface, respectively. The dimensions of such structures are given in table 2 with the operating conditions of the oxidization. What is of interest here is the similar current density: in our etching experiments the ions induced a current density in the substrate. We used an n-type silicon identical to the one described in these oxidization experiments and we can assume it will behave similarly under plasma exposition, provided that the electrical parameters (i.e. current density etc) are nearly identical.

If this assumption is shown to be true, it will explain the diffusion behaviour. Above it has been mentioned that the diffusion is independent of steric factors, i.e., that it acts similarly for H, F and Cl. If such porosity occurs during plasma treatment, as it does under anodic oxidization, it will explain this surprising diffusion and the relatively large radii of the columnar structure will ensure the diffusion of any elements independently of their size. In addition it can explain the XPS measurements that we performed on fluorine-plasma-exposed silicon samples (Brault *et al* 1990a, b). Knowing that another effect of the ions is surface amorphization, some additional voids or silicon clusters can be formed, as mentioned previously, depending on the ion energies compared with the sputtering threshold. An important effect is the enhancement of etch rates under plasma treatment. To be precise, under these circumstances, the etch rates are greater than the sum of pure gas-phase and pure ion-bombardment etch rates (Winters *et al* 1983). If porosities occur during plasma treatment the enhancement could be explained in the following way: because porosities induce a high specific area of the surface, chemical

reactions occur with more solid surface atoms, which are available for creating volatile species (SiF_4, $SiCl_4$, . . .), than occur on atomically flat surfaces.

Moreover, when the etched materials are exposed to air after XPS and NRA analysis, and re-examined a few weeks later with NRA, we have shown that there is a disappearance of all fluorine and a substitution of this by deeply incorporated nitrogen. The nitrogen concentration was greater than 10^{16} atoms cm^{-2} (compare with O and F values of table 1); this nitrogen originates in air and has been reacted with the deep fluorinated silicon. This process is only possible if we also invoke diffusion of nitrogen into the silicon (at ambient temperature and atmospheric pressure). This observation re-enforces the possible existence of the plasma-induced porosity of silicon, which has become a sponge for fluorine and, when exposed to air, a sponge for nitrogen (Brault *et al* 1990a).

Because etch plasmas are a source of additional heating (from UV radiation for example), it could be inferred that heating may play a role in the diffusion of fluorine. In our experiments, power density is 0.6 W cm^{-2} maximum (assuming isotropic and complete coupling of the electrical power to the plasma), which gives a sample power of 0.35 W. This is insufficient to explain a diffusion over such a depth as is observed. The diffusion of H, F and Cl has been observed under very different plasma conditions and the same behaviour has always been recorded: in-diffusion over a few hundred Å with oxidization of the outermost surface.

Two simple mechanisms: the Cabrera–Mott mechanism (Cabrera and Mott 1949, Babanov *et al* 1989) (local electric fields assisted diffusion) and the Brunauer–Emmett–Teller multilayer adsorption (Brunauer *et al* 1938, Petit and Pelletier 1986) may be invoked to explain the deep penetration of fluorine on condition that the surface under consideration is not taken to be limited to the classical external one for which these models are applied. If porosity is present, diffusion along it following such mechanisms and consequently enhancement of chemical reactions, takes place efficiently. Indeed, multilayer-adsorption-on-rough-surface theories (Thurtell and Thurtell 1988, Pfeifer *et al* 1989, Levitz *et al* 1986) applied to diffusion through porosities can be a good tool to investigate such a mechanism, especially those involving fractally rough surfaces (Pfeifer *et al* 1989, Levitz *et al* 1986). The use of scanning tunnelling microscopy could also provide information on the size of the porosities of plasma-etched materials like silicon, because of its capacity to probe many topographic scales.

Very recently, molecular dynamics calculations (Silverman *et al* 1990) were performed to analyse fluorine diffusion in amorphous silicon. It was shown that diffusion of Si–F molecules is energetically favourable, and diffusion-law determinations are in progress. Such work is very important because the authors introduce the existence of voids in their numerical amorphous silicon and hope to reproduce fluorine–silicon chemical bonds in the sample.

In conclusion, it is inferred that plasma etching of silicon, and probably other semiconductor materials (Menon and Allen 1986, 1987, 1988) proceeds in the following way: ions are responsible for amorphization of the surface via energy transfer through collision cascades; the induced current density results in the porosity, and deep fluorine diffusion can take place below an oxyfluorinated overlayer throughout the pores; and formation of volatile SiF_4 and subfluorinated (SiF_x, $x \leq 3$) occurs due to bond breaking by the diffusing F atoms (Si–F bond energy is higher than Si–Si and Si–O bond energies). Also, it becomes necessary to systematically probe such surfaces with at least two kinds of analysis: one for the outermost surface, and the other(s) for the underlying layers down to the unreacted bulk in order to allow completeness of the analysis and to verify whether the outermost surface is really the only region subject to reaction.

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