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Changes on the Silicon Surface Radiating it by Halocarbon and/or Hydrogen Plasma

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It is shown, that polymeric formation based on carbon-halogen is not dominant on surface when silicon etched in CF_2Cl_2 plasma. The A-Si_xC_{1-x}:H:F film formed on the silicon surface when it is treated in $CF_4 + H_2$ plasma. Concentration of impurities and predominating of bonds depend on condition of irradiation and etching duration. Concentration of free bonds in the structure increased with increasing of power of irradiation. Ellipsometry measurements of irradiated structures showed that four-layer model can be taken for the analysis.

Key words: silicon, surface, plasma.

Стаття поступила до редакції.

I. Introduction

Silicon integrated circuits are most widespread today. Silicon is easily processed in comparison to other semiconductor materials (GaAs, InP), and its oxide is used as an insulator. Control of reactions and their kinetics are very important using plasma etching methods. Reactive ion etching of silicon and other surfaces is an important material processing technique that is widely used by the semiconductor industry in the fabrication of integrated circuits or micro sensors [1]. Converting Si into volatile halides is today responsible for almost all silicon plasma etching: SiF_4 and $SiCl_4$ are usually the main final products. Initial products are produced by reactions between silicon and atomic or molecular halogens [2]. The elementary interaction of halogen with silicon is inherently complicated by temperature effects, morphology and crystallographic effects, trace impurities, ion bombardment, doping effects, and other factors that have not been identified yet [3]. The final products are not necessarily the same as the initial products emitted from the surface. $SiCl_2$, for example, is an initial product in ion-accelerated polysilicon etching, but it reacts with Cl and Cl_2 in the gas phase to form $SiCl_4$ [4].

Anisotropic etching of silicon in fluorine atom rich plasmas is practically impossible under most plasma etching conditions because of the rapid spontaneous chemical reaction between fluorine and Si. Low pressure plasmas with high substrate “bias” in CF_4 are an apparent exception, the gas phase concentration of F atoms but in this regime is lower relative to the adsorbed halocarbon species and flux of ions. The main goal is to achieve the anisotropy of etching using mixtures of gases with physical and chemical treatment; sidewall protection etching is a main requirement here. The Cl atoms, however, are substantially larger than the F atoms and have much greater difficulty forming a volatile silicon chloride molecule in the absence of ion bombardment. Because the activation energy of chlorine is lower than activation energy of fluorine ($E_a = 0.108$ for chlorine and $E_a = 0.2$ eV for fluorine) [5] Cl etches Si quite well when ion bombardment is added to chemical fluxes. The ion bombardment causes not only the sputtering of material but also activates chemical processes such as polymerization, etching and causes intermixing between surface atoms and atoms from the bulk [6,7].

II. Experiment

Single-crystal silicon substrates (111) of p-type 4.5 Ωcm have been etched in CF_4, $CF_4 + H_2$, CF_2Cl_2 gases in the 13.6 MHz of asymmetric diode system PK 2420 RIE (ADS), where the samples have had a negative bias voltage (0.1-0.55 keV), and pressure can be varied 0.1-26.6 Pa. The diameter of cathode is 0.1 m and vacuum chamber diameter – 0.88 m and high – 0.34 m, and pumping system MPB-35 was used in PK 2420 RIE system. Ion energy was definite from DC negative bias voltage expressed in eV. The composition of the altered layer was subsequently analyzed “ex situ” by X-ray photoelectron spectroscopy (XPS) (spectrometer KRATOS ANALITICAL), ellipsometry (variable angle null ellipsometer EL11D, wavelength 632.8 nm, laser HeNe), electron paramagnetic resonance analysis (EPR)

(E/X-2547 spectrometer), Raman spectroscopy (RS).

XPS spectra were obtained using a Al(K_{α}) radiation source. XPS spectra were separated into components by the least-square method in order to estimate the binding energy and photoelectron intensity of each component. Type of bonds was estimated from the previous reports [5,8-10].

Raman spectra was taken under the argon laser of 514.5 nm wavelength and 20 mW power excitation at a 2-mm spot size. Data were collected in backscattering geometry at room temperature. Distribution curves were fitted with the same Gaussian shapes at a linear background using the least square fitting software. Raman spectra were taken in the range of 400-2000 cm^{-1} but the fitting process was performed for the 1000-1800 cm^{-1} range only.

A steady – state condition on the surface occurs some 20-40 minutes after the interruption etching process and depends on the adsorption of admixtures from the surroundings. We estimate dominating radicals in the plasma and on the surface in comparison to our experimental results with other published authors [10-13].

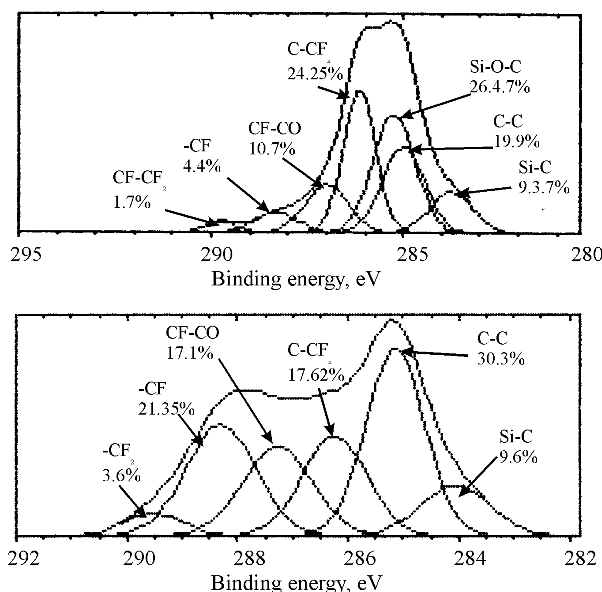

Fig. 1. XPS C1s spectra after silicon etching in CF_2Cl_2 plasma: a) ion energy 100 eV, b) ion energy 400 eV Etching duration 10 min.

III. Results and discussion

a) Etching in CF_2Cl_2 plasma

Etching velocity and surface state depend on bombarding ion energy and power density of irradiation. Carbon concentration on the surface increased when $E_i \leq 100$ eV and $W \leq 3$ W/cm^2 and after 20 min. of etching became close to 60% of full surface atoms concentration. It decreased to 45% and became established when etching was longer (t = 20-40 min.). Silicon concentration conversely decreased and after 40 min. of etching it was close to 15% and later did not change. Concentrations of oxygen, fluorine and chlorine were established in all etching process (halogens concentration was about 5%) [14].

Concentration of carbon per 1-2 min. came to 40% and later has not changed when $E_i = 400$ eV and $W > 3.2$ W/cm^2. Silicon concentration decreased and after 10 min. it amounted 15-20% of surface atoms. Fluorine (chlorine) concentration gradually increased and after 60 min. make up to 35% of surface atoms, whereas oxygen concentration gradually decreased. Synthesis of silicon (Si 2p) XPS peak showed that silicon on the surface is unbounded or in SiF_x ($SiCl_x$) bounds when energetic radiation is low, but concentration of unbounded silicon quickly decreased and higher concentration of silicon was obtained in composition of SiC, SiF_x ($SiCl_x$) bounds when ion energy increased [14] Type of these silicon bonds and unbounded silicon was obtained in all etching duration. Desorbtion energies of SiF_x ($SiCl_x$) are high (especially for $SiCl_2$ and $SiCl_3$), so they can stopped silicon etching when plasma temperature is low (T < 800 K) [15,16].

Domination of bounds in carbon C1s spectra depends on condition of irradiation (Fig. 1). As shown, formation of polymeric layers based on C-CF_x or CF-CCl bonds is hardly impossible especially when ion energy is high. RS measurements also have not fixed it.

Irradiated samples have two characteristic EPR signals: intensive with $\Delta B = 0.74$ mT and g factor 2.006±0.0003 and low (g = 2.002±0.0007). These EPR

Table 1

Intensity of EPR center in silicon samples after irradiation in halocarbon plasma (decrement 10dB)

Plasma	Plasma addition, %	Etching duration, min.	Ion energy, eV	Intensity of EPR center with g = 2.0060, a.u	Intensity of EPR center with g = 2.0020, a.u
CF_2Cl_2		5	100	2	2
		40	100	3.75	3
		5	400	2	2
		40	400	8	5
CF_4	-	20	540	1.25	1.25
	10 O_2	20	540	5	4
	5 H_2	20	540	3.5	3
	20 H_2	20	540	4.25	4

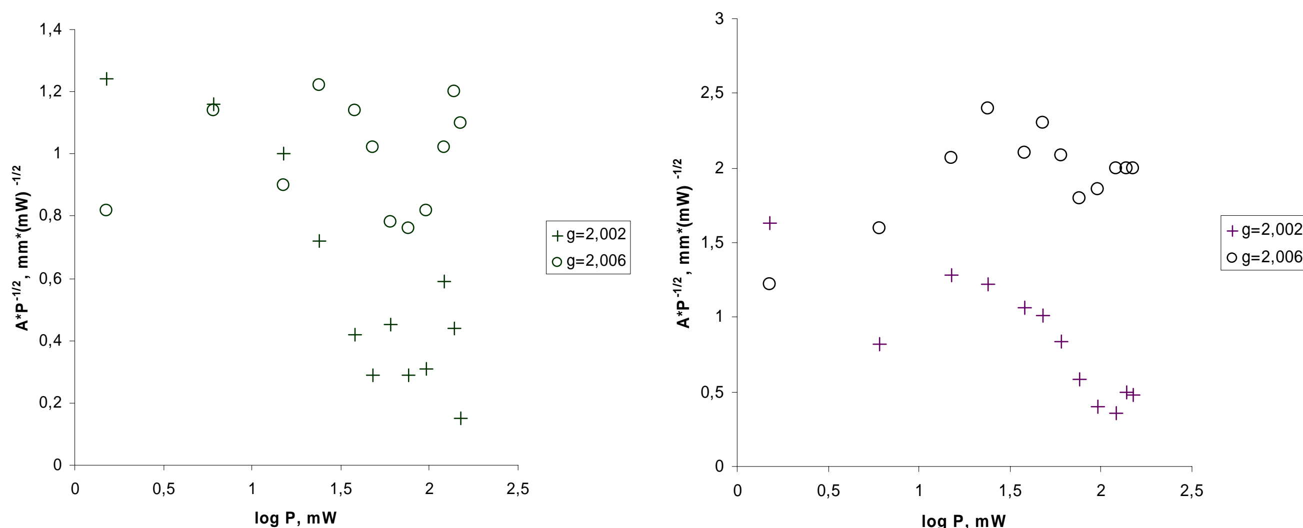

Fig. 2. Dependence $A/\sqrt{P} = f(\log P)$ for Si samples after 40 min. etched in CF_2Cl_2 plasma, when ion energy: a) 100 eV, b) 400 eV.

centers are complex and their spectra overlap. Lower signal is in major slope. Amplitude slowly depends on parameters of irradiation. Intensity of both centers slowly varied with etching duration (thickness of film) and ion energy (table 1).

Concentration of free radicals quickly increased with increasing of irradiation intensity ($E_i = 400$ eV) and etching duration. Ellipsometry measurement shows that film thickens also increased with increasing of radiation time. Variation of dependence $A/\sqrt{P} = f(\log P)$ (where P – power of microwaves, A – amplitude of signals) let compare EPR centers. As shown in Fig. 2, this dependence for signal with g = 2.006 were not saturated, but saturated for signal with g = 2.002 and power of microwaves for these saturations is different. So, different EPR centers can be created in the samples with same g = 2.002 and they depend from condition of irradiation. Part of them related with typical hydrogen paramagnetic centers H_1 and H_2. The next paramagnetic centre (g = 2.006) can be the same and can be interpreted as carbon vacancy [17,18].

b) Etching in CF_4 and $CF_4 + H_2$ plasma

Surface carbon concentration is measurable when silicon is etched in CF_4 plasma, and addition of oxygen (10%) does not interrupt accumulation of it. XPS measurements showed that width and mean of C1s peak depend on ion energy. Peaks maximum is in the binding energy interval of 284.6-285 eV when ion energy is $E_i = 0.7$-1 keV [19]. It means that carbon is unbounded or is in the SiC bonds. Maximum of peak is shifted to higher energy side (0.5-1 eV) when ion energy has decreased ($E_i < 0.5$ keV). So, carbon existed in the bonds with oxygen (C-O-C, C-O) and unbounded carbon is obtained on surface, and it is correct, because lower quantity of ion is penetrated in the crystal bulk when ion energy decreases. But, accumulating of thin, amorphous and porous carbon layer not interrupted etching.

Addition of 5% of hydrogen in the CF_4 plasma stimulates condensation of polymeric compounds on the silicon surface. From XPS spectra we obtained that carbon, silicon, hydrogen, fluorine and oxygen are in the composition of formatted film. Oxygen is only on the film surface – it is adsorbed from surrounding (XPS measurements going "ex situ"). As result, we obtained that variable composition and complex thin film of a-Si_xC_{1-x}:H:F is formatted on the silicon surface. As measurements show, etching velocity depends on surface carbon state. After 10 min. of etching it was obtained from XPS C1s spectra that carbon can create such kind of bonds: C-CF_x (30%), C-C or C-H (47%) and can be in the composition of $(CHFCH_2)_n$ compounds. Dependence of carbon bonds on etching duration were analyzed [20], and it was obtained that not only carbon in C-CF_x bonds become predominating, but also fluorine concentration increased there when etching duration increased. Stage of surface carbon also depends on hydrogen concentration in plasma, power density of discharge and on etching duration [20]. Concentration of $(CH_2)_n$ and $(CHFCH_2)_n$ bonds decreased with increasing of discharge power density and ion energy (Table 2). Peak of C1s shifted to higher energy side and it means that $(C\text{-}CF_2)_n$ stable inhibitor has formed on the surface.

After the analysis of RS spectra it was obtained that formatted film is amorphous and have high concentration of impurities (Fig. 3). Several peaks have such characteristic as: 519 cm^{-1} (silicon substrate conditioned it and the peak showed that film is transparent); 1150 cm^{-1}- in our opinion it belongs to a single C-C bond with C-H trend, but other authors referred it to nanocrystaline (1-100 nm) carbon formation and related it with small size of crystallites or/and with disorder in tetrahedron structure [21-22]. Sharp peak with 1650 cm^{-1} is conditioned adsorbing water. Synthesis of spectra show, that typical DLC lines (D – 1350 cm^{-1}, G – 1550 cm^{-1}) are substantially shifted to lower energy side: D-line to 1303 cm^{-1} and G-line to 1508 cm^{-1} after 10 min. of etching in CF_4 + 20% H_2 plasma. It is influencing of impurities, because silicon shifted D and G peaks [22].

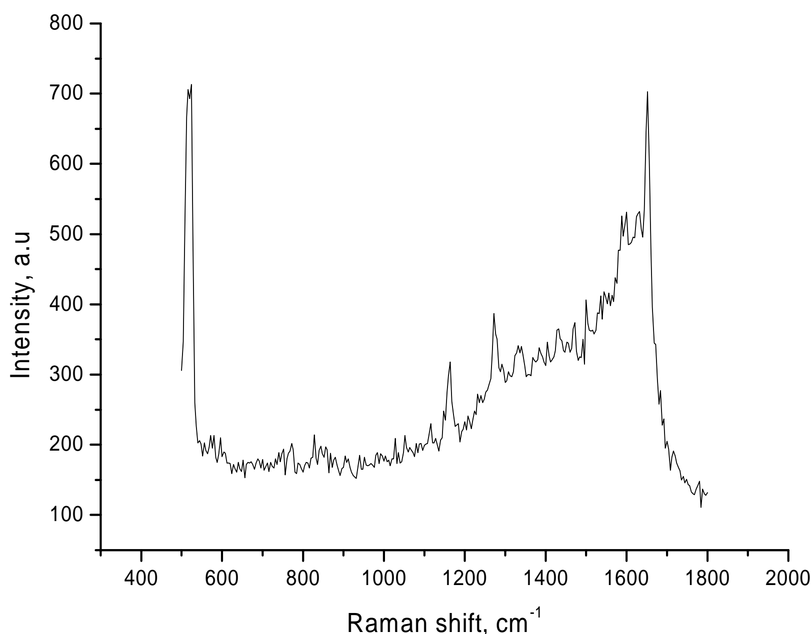

Fig. 3. Typical RS spectra after silicon etching in CF_4+H_2 plasma.

Table 2

Variation of carbon bond concentration when silicon etching in CF_4+20% H_2 plasma, for pressure P = 0.1 Pa, W = 0.9 W/cm^2, gas flow 24 cm^3/s

Ion energy	$(CH_2)_n$	-C-C and/or -C-CH	-C-CF_x	$(CHFCH_2)_n$	-CF
400eV	6%	52%	25%	9%	8%
200eV	16%	50%	22%	7%	5%

Also peaks shifted to lower means when radiation and film formation duration increased. Peak of D-line shifted per 13 cm^{-1}, G-line -31cm^{-1} after 40 min. of etching. Position of peaks and their width (ΔG = 164.5 cm^{-1}) showed that film is amorphous. Changes of carbon bonds in the film and quick removal of graphite stage with active reagents (H,F) make film more transparent – the peak of silicon substrate increased.

EPR signals are low after etching in CF_4, CF_4+5% H_2 plasma, but the signal is intensive when oxygen or 20% of hydrogen was addition into the plasma. Means of g-factor and saturation is analogical as in CF_2Cl_2 plasma; saturation is getting only for g = 2.002. Power of microwaves is not in phase with any accident of CF_2Cl_2 plasma when dependence saturated, so centers are different.

Measurement of ellipsometry shows that refractive index depend on etching duration also. Refractive index of surface varied from 4 to 2, and this can be interpreted as carbon layers. Few layers model was taken for the analysis, and after calculating it was obtained that four-layer structure formatted on the surface when silicon is treated in CF_4 + 20% H_2 plasma. Fluorinated and hydrogenated carbon is predominant in the first layer. Refractive index and thickness of this layer intensively varied from n = 1.8, d = 0.33 nm (etching duration is 5 min., C-H and C-C bonds are predominant) to n = 1.48, d ≈ 22 nm (etching duration is 40 min., CF_x and C-CF_x bounds predominate). Si-F_x and Si-C bonds dominated in the second deeper layer. Thickness of this layer (3 nm) does not depend on the treatment duration, but refractive index shifted from 1.54 (specified for the Si-F_x) to the values specified for the SiC (n = 2.63) if etching duration is more than 20 min. The third layer is silicon damaged by ion bombardment. Its refractive index equals to 4.63, depth – 2 μm. The fourth layer is bulk silicon with n = 3.85.

IV. Conclusions

1. Polymeric formation based on carbon-halogen is not dominant on surface when silicon etched in CF_2Cl_2 plasma.

2. A-Si_xC_{1-x}:H:F film formed on the silicon surface when it is treated in CF_4 + H_2 plasma. Concentration of impurities and predominating of bonds depend on condition of irradiation and etching duration.

3. RS and XPS measurements showed that polymer like film having high concentration of sp^3 bonds formed on the silicon surfaces when it etched in CF_4 + H_2 plasma.

4. Concentration of free bonds in the structure increased with increasing of power of irradiation. Ellipsometry measurements of irradiated structures showed that four-layer model can be taken for the analysis.

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Зміни на кремнієвій поверхні опроміненій, гало-вуглецевою і/або водневою плазмою

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Показано, що утворення полімерів на основі вуглецевого галогену, не домінує на поверхні, при травленні кремнію в плазмі CF_2Cl_2. Плівки $A\text{-}Si_xC_{1-x}$:H:F, сформовані на поверхні кремнію обробляли в плазмі $CF_4 + H_2$. Концентрація домішок і переважаючі зв'язки залежать від умов опромінення і його тривалості. Концентрація вільних зв'язків у структурі, зростає із збільшенням потужності опромінення. Еліпсометричні вимірювання опромінених структур показали, що при аналізі можна використовувати 4-шарову модель.