ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 4, № 3 (2003) С. 407-413

PHYSICS AND CHEMISTRY OF SOLID STATE
V. 4, № 3 (2003) P. 407-413

PACS: 81.65.CF, 81.40. TV, 81.70.FY

ISSN 1729-4428

Ž. Rutkūnienė, A. Grigonis, A. Rėza[1], J.G. Babonas[1], A. Jotautis

Formation of Multilayer Structures on the Silicon Surface after Etching in Plasma

Kaunas University of Technology, 50, Studentų, Kaunas, 3031, Lithuania
[1]Semiconductor Physics Institute, 11, Goštauto, Vilnius, 2600, Lithuania
e-mail: Zivile.Rutkuniene@ktu.lt

Silicon surface was analyzed after radiation by CF_4, CF_4+H_2, CF_2Cl_2 plasmas in this work. Formation of multilayer structures on the silicon surface during plasma treatment was obtained after ellipsometric measurement. Their optical parameters were changed to 2 μm in the depth. Optical response strongly depends on the etching duration in the CF_2Cl_2 plasma and varying from pure silicon surface to samples having irregular interference image in the dielectric function spectra. Small deflections can be modeling as relatively thin and transparent layers (30-50 nm) formatted as SiO_2 or other transparent materials, like CH, SiF_x, which optical parameters and ε value is close to it. Polymerization on silicon surface is effective in CF_4+H_2 plasma and became more intensive when H_2 concentration increases. 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 while CF_x and C-CF_x bounds predominate. Si-F_x and Si-C bounds dominated in the second deeper layer. The third layer is silicon damaged by ion bombardment. Its refractive index equals 4.63.

Keywords: plasma etching, ellipsometry, chemical composition

Стаття поступила до редакції 19.05.2003; прийнята до друку 23.08.2003.

I. Introduction

Silicon integrated circuits are most by 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 poly silicon 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 the 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 the 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. Cl etches Si quite well when ion bombardment is added to chemical fluxes, because the activation energy of chlorine is lower than activation energy of fluorine (Ea = 0.108 eV for chlorine and Ea = 0.2 eV for fluorine) [5]. Ion bombardment causes not only the sputtering of material but also activates chemical processes such as polymerization, etching [6], and causes intermixing between surface atoms and atoms from the bulk [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 asymmetric diode system PK 2420 RIE (ADS), where the samples have had a negative

bias voltage (0.1-0.5 keV), and pressure varied from 0.1 to 26.6 Pa. The composition of the altered layer was subsequently analyzed "ex situ" by X-ray photoelectron spectroscopy (spectrometer KRATOS ANALITICAL) (XPS), ellipsometry (variable angle null ellipsometer EL11D, wavelength 632.8 nm, laser HeNe), scanning electron microscope (EM25), profilometry (TAYLOR HOBSON). The spectroscopic studies in the middle of infrared range 2-10 μm were performed making use of a standard spectrometer SPECORD M 82 supplied with additional unit for the measurements of specular reflectance. The experimental spectra were taken at the angle of incidence equal to 22.5°.

XPS spectra were obtained using a Al (Kα) radiation source. XPS spectra were separated to 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].

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

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 Ei ≤ 100 eV and W ≤ 3 W/cm^2 after 20 min. of etching became close to 60% of full surface atom 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 (halogen concentration was about 5%) [14].

Concentration of carbon per 1-2 min. came to 40% and later has not changed when Ei = 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 SF_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

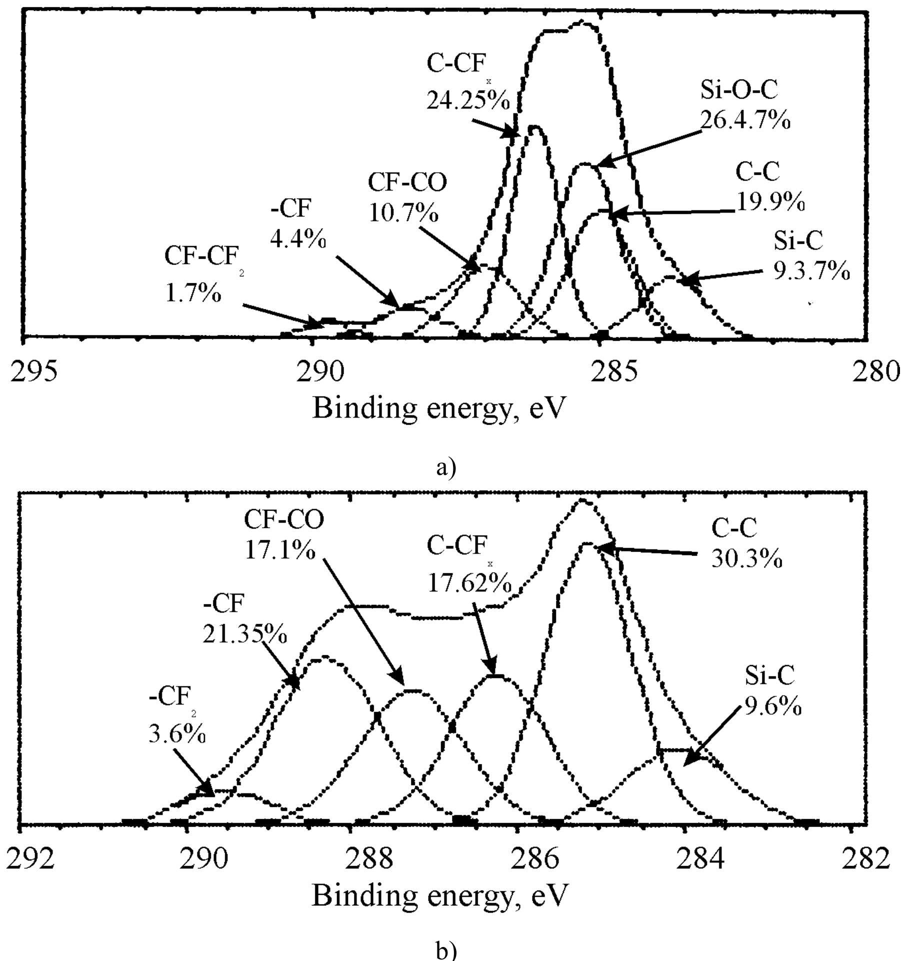


Fig. 1. XPS C1s spectra after silicon etching in CF_2Cl_2 plasma: a) ion energy 100 eV, b) ion energy 400 eV Etching duration 10 min.

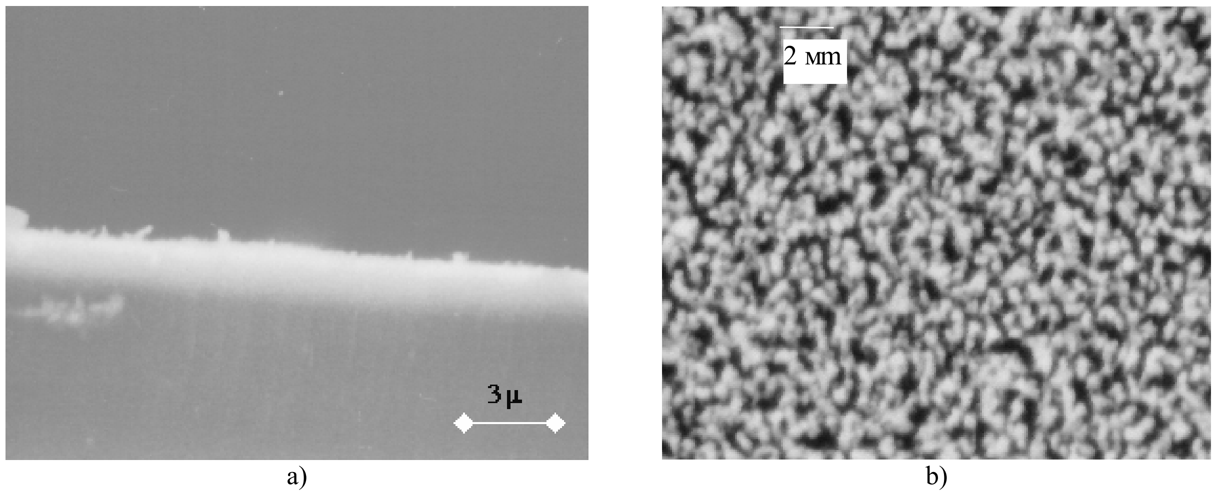
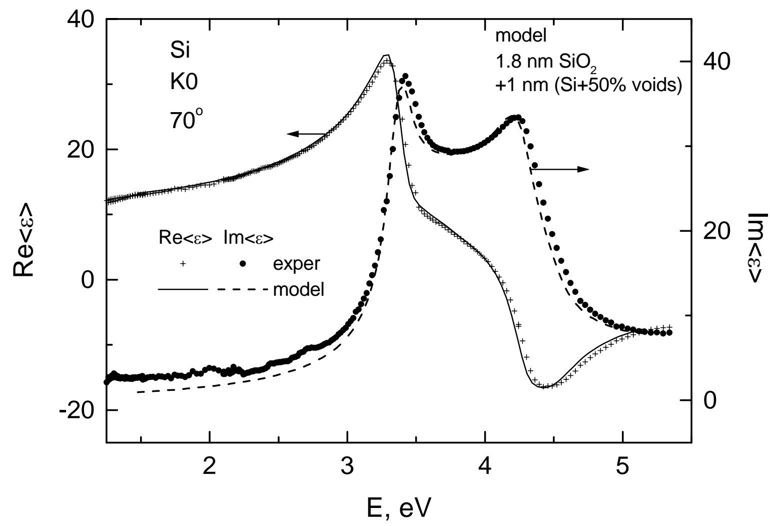
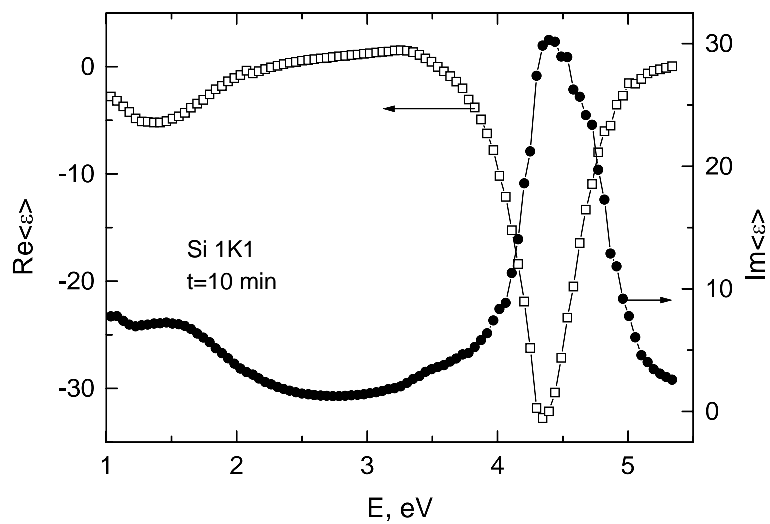


Fig. 2. Cross section (a) and surface (b) scanning electron microscope images of *p*-Si exposed to ion-etching for 10 and 40 min, respectively.



a)



b)

Fig. 3. Dielectric function for initial Si sample (a) and for the sample etched for 20 min (b).

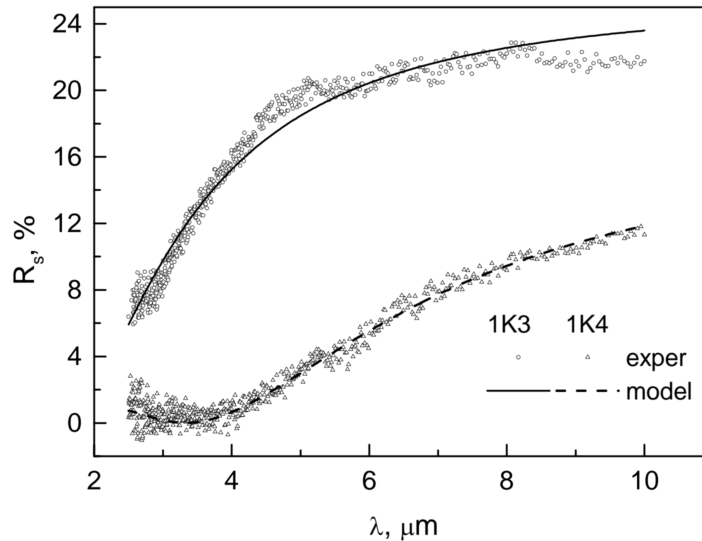


Fig. 4. Spectral dependence of the specular reflection coefficient for two Si samples exposed to ion-etching in CF_2Cl_2 for 30 min (sample 1K3) and 40 min (sample 1K4).

SiC, SF_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 stop 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.

The scanning electron microscope images (Fig. 2) are obtained by means of electron microscope EM25 show the samples of ion-etched Si. As it is seen, an extended surface layer up to 1 μm of order is observed (Fig. 2a) in the cross section of the Si sample etched for 10 min. The porous-like layer with grains up to 0.1-0.5 μm is formed on the Si sample surface after longer etching time up to 40 min (Fig. 2b).

The major part of experimental results on the spectral dependence of ellipsometric parameters Ψ and Δ were considered in the approximation of pseudodielectric function (PDF) $<\varepsilon>$, which is efficiently used [17] for the analysis of the optical response of complex multilayer structure:

$$<\varepsilon>= \sin^2\theta\left[\left(\frac{1-\rho}{1+\rho}\right)^2\tan^2\theta+1\right],$$

where θ is the angle of light incidence. The approximation of pseudodielectric function $<\varepsilon>$ is particularly descriptive in the case of thin surface layers, when the optical response is close to that for the initial sample before the surface treatment is applied. In the case of the samples exposed to the ion-etching for a relatively short time of order 1 min, the surface layer is quite thin and the optical response is expected to be close to pure Si surface. In the case of etching time of 10-20 min. order the optical response of ion-etched Si samples is strongly changed (Fig. 3) as compared to that for pure Si surface.

The data obtained at two angles of incidence (50° and 80°) for sample 1K2 exposed to ion-etching for 20 min. were analyzed by the model of five homogeneous surface layers. It was assumed that Si substrate was coated by five layers in which the dielectric function was changing linearly from upper layer (εH) to lower layer at the substrate (denoted as εL). The thickness of five layers was assumed to be 5x25 nm. The analysis of experimental results obtained of this series of samples clearly illustrate that the surface layer is not homogeneous.

In the case of Si samples exposed to ion-etching for the longest times of 30-40 min. the reflection coefficient in the UV-VIS was significantly reduced. The experimental values were ~1.0 and ~0.2-0.5 for real and imaginary parts of PDF. On the basis of SEM observations (Fig. 1b) it was reasonable to assume that the optical response of these samples was strongly influenced by roughness of the surface.

Fig. 4 presents the measurement data for two samples exposed to ion etching for 30 and 40 min. As it is seen, the coefficient for speculars reflection increases more or less steeply with increasing the wavelength. For sample 1K3 the Rs-value tends to saturate at ~ 0.22 which is close to R_o = 0.29 for non-doped Si. The experimental data are well understood by the change of the optical response of rough surface from diffuse to seculars reflection [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

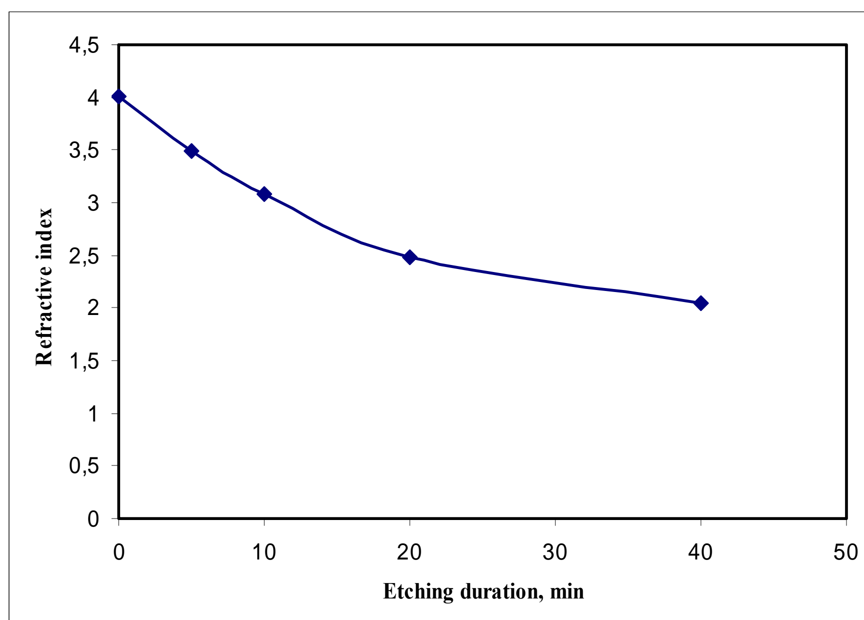


Fig. 5. Refractive index dependence on silicon etching duration in CF_4 + 20% H_2 plasma, (E_i = 400 eV).

(10%) does not interrupt accumulation of it. XPS measurements showed that width and mean of C1s peak depend on ion energy. Peak's maximum is in the binding energy interval of 284.6-285 eV when ion energy is Ei = 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 (Ei < 0.5 keV). So, carbon existed in the bonds with oxygen (C-O-C, C-O) and unbounded carbon is obtained on the 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 α-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 1). Peak of C1s shifted to higher energy side and it means that $(C\text{-}CF_2)_n$ stable inhibitor has formed on the surface.

Measurement of ellipsometry shows that refractive index depend on etching duration also. Refractive index of surface varied from 4 to 2, and it can be interpreted as carbon layers (fig. 5.). 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 (Table 2.) 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 bonds are predominant) to n = 1.48, d ≈ 22 nm (etching duration is 40 min., CF_x and

Table 1.

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
400 eV	6%	52%	25%	9%	8%
200 eV	16%	50%	22%	7%	5%

Table 2.
Variation of optical properties of first and second layers in the altered layer of silicon on etching duration in CF_4+20%H_2 plasma.

	Etching duration	5 min	10 min	20 min	40 min
I layer	Refractive index, n	1.8	1.8	1.48-1.8	1.58-1.48
	Thickness d, nm.	0.33	5.5	4-4.4	20.2-21.8
	Dominating bond	C-H	C-H	C-H arba C-F	C-C, C-F
II layer	Refractive index, n	1.54	1.54	1.54	1.54-2.63
	Thickness d, nm.	1	3	3	3-1.6
	Dominating bond	Si-F_x	Si-F_x	Si-F_x	Si-F_x or Si-C
	Etching velocity, nm/min	0.6	0.4	-0.02	0

C-CF_x bonds predominate). The surface, subjected to ion bombardment, is in thermodynamically unstable state, therefore the formation of mechanical stresses and defects in near- surface region (up to 15 nm) takes place. In this region due to penetration of bombarding ions and diffusion the interface with increased Si-C, Si-F, species are formed. So, 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 inclusions, defects and mechanical stresses change electrical properties of near surface region. The thickness of layer with altered electrical properties depends on energy of bombarding ions, etching rate, pressure and extens to 7 μm. So, the third layer we take as silicon damaged by ion bombardment. Its refractive index equals to 4.63, depth – 2 μm, because ion energy is only 400 eV. The fourth layer is bulk silicon with n = 3,85. As it is show in table 3, modeling ellipsometric results have good correlation with XPS

IV. Conclusions

Polymeric formation based on carbon-halogen is not formatted on the surface when silicon etched in CF_2Cl_2 plasma, but polymeric films of α-Si_xC_{1-x}:H:F formatted on the surface when it is treated in CF_4+ 20% H_2 plasma. Concentration of impurities and predominating of bonds depend on condition of irradiation and etching duration. Ellipsometry measurements of irradiated structures showed that few-layer model can be taken for the analysis. Type of bonds and thickness of the first carbonized layer is the main factor influenced to etching rate. The optical response of the ion-etched in CF_2Cl_2 plasma Si samples depends strongly on the etching time. For a short etching time of order 1 min the optical response is quite close to that of pure Si. It can be modeled by the influence of a thin transparent surface layer (30-50 nm) possessing a small gradient of optical constants in depth. The optical response of the samples exposed to ion-etching for 10-20 min was interpreted by the system of homogeneous layer with linearly changing dielectric functions. The optical response of the Si-samples etched for 30-40 min is mainly caused by surface roughness and is characterized by dominating diffuse reflection in UV-VIS whereas in the middle of IR range it is caused by the increase of the specular reflection coefficient. The surface roughness of thick surface layers is of order 2-4 μm.

[1] D.E. Hanson, A.F. Voter, J.D. Kress. // *J. Appl. Phys.*, **7**(82), p. 3552 (1997).
[2] T. Engel. Fundamental aspects of the reactions of thermal and hyperthermal F, F_2, Cl, and Cl_2 with Si surface // *Jpn. J. Appl. Phys.*, **35**(4B), pp. 2403-2409 (1996).
[3] W. Ensinger. Low energy ion assist during deposition - An effective tool for controlling thin film microstructure // *Nucl. Instr. and Meth. B*, **127**, pp. 796-808 (1997).
[4] D.L. Flamm. Plasma Chemistry, Basic Process and PECVD in Plasma Processing of Semiconductors // *Eds. P.F. Williams Kluwer Academic Publishers,* Netherland, pp. 23-59 (1997).

[5] M. Horie. Plasma structure dependence of the growth mechanism of plasma - polymerized fluorocarbon films with resdidual radicals // *J. Vac. Sci. Technol. A*, **13**(5), pp. 2490-2497 (1995).
[6] K. Gamo, S. Namba. Ion beam asisted etching and deposition // *J. Vac. Sci. Technol. B*., **8**(6), pp. 1927-1931 (1990).
[7] R.S. Averback, M. Ghaly. A model for surface damage in ion -irradiated solids // *J. Apl. Phys*., **76**(6), pp. 3908-3918 (1994).
[8] N. Hirashita, Y. Miyakawa, K. Fujita, J. Kanamory. Reaction studies between fluorocarbon films and Si using temperature - programmed X-ray photoelectron and desorption spectroscopes // *Jpn. J. Appl. Phys*., **34**(4B), pp 2137-2141 (1995).
[9] Arai K. Tsujimoto, S. Tachi. Deposition in dry etching gas plasmas // *J. Apl. Phys*., **31**, pp. 2011-2019 (1992).
[10] *Practical surface analysis by Auger and X-ray photoelectron spectroscopy.* Eds. D.Brigs, M.P Seach, UK, 589 p. (1983)
[11] J.W. Coburn, H.F Winters. Ion and electron assisted gas-surface chemistry - an importanteffect in plasma etching // *J. Apl .phys*., **50**, pp. 3189-3196 (1979).
[12] Y. Khairallah, F. Arefi and J. Amouroux. Surface fluorination of polyethylene films by different CF_4 glow discharges: effects of frequency and electrode configuration // *Thin Solid Films*., **241**(1-2), pp. 295-300 (1994).
[13] R. Knizikevičius. Real dimensional simulation of SiO_2 etching in CF_4+H_2 plasma // *Vacuum,* **65**, pp. 101-108 (2002).
[14] A. Grigonis, R. Knizikevičius, Ž. Rutkūnienė, M. Pucėta. Kinetics of composition of polymeric layer during silicon etching in CF_2Cl_2 plasma // *Appl. Surf. Sc*., **199**(1-4), pp. 270-277 (2002).
[15] Y. Teraoka, I. Nishiyama. Stimulated etching of Si (100) by Cl_2 molecular beams with hyperthermal translation energies // *J.Apl.phys*., **82**(6), pp. 3137-3142 (1997).
[16] I. Bello, W. H. Chang, W. M. Lau. Mechanism of cleaning and etching Si low energy chlorine ion bombardment // *J.Appl.phys*., **75**(6), pp. 3092-3099 (1995).
[17] G.-J. Babonas, L. Leonyuk, V. Maltsev, R. Szymczak, A. Rėza, M. Baran, and L. Dapkus**.** Physical Properties of $(M_2Cu_2O_3)_m(CuO_2)_n$ (M = Ca, Sr, Bi) Single Crystals with Bi-2212 Phase on their Surface // *Acta Phys. Pol. A,* **100**, p. 553 (2001).
[18] M. Born. *Principles of Optics.* Oxford, Pergamon Press (1968).
[19] A. Galdikas**,** A. Grigonis, L. Pranevičius, J. Vosylius. Formation on the altered layer in silicon during RF reactive sputtering // *Solid - State Electron*, **37**(11), pp. 1891-1895 (1994).
[20] Ž. Rutkūnienė, A. Grigonis. Formation of polymeric layers using halogen-carbon plasmas // *Vacuum,* **68**(3), pp. 239-244 (2003).

З. Руткунуне, А. Грігоніс, А. Реза[1], Й.Г. Бабонас[1], А. Йотойтіс

Формування багатошарових структур на силіконовій поверхні після протравлення в плазмі

Каунаський технологічний університет, вул. Студента, 50, м. Каунас, 3031, Литва
[1]Інститут фізики напівпровідників, вул. Гостаута, 11, м. Вільнюс, 2600, Литва

В роботі проводиться аналіз поверхні кремнію після плазмового випромінювання CF_4, CF_4+H_2, CF_2Cl_2. Еліпсометричні вимірювання показали утворення багатошарових структур на поверхні кремнію через плазмове випромінювння. Їхні оптичні параметри були змінені до 2 mm по глибині. Оптична відповідність сильно залежить від тривалості офорту в плазмі CF_2Cl_2 і варіювання від чистої поверхні кремнію до зразків що має нерегулярне інтерференційне зображення в діелектричних спектрах функції. Малі відхилення можна моделювати як відносно тонкі і прозорі шари (30-50 nm), утворені як SiO_2 або іншими матеріалами, подібними до CH, SiF_x, оптичні параметри яких і значення ε є близьким до нього. Полімеризація на поверхні кремнію є ефективною в плазмі CF_4+H_2 і стає інтенсивнішою, коли концентрація H_2 зростає. 4-шарова структура утворюється на поверхні, коли кремній знаходиться в плазмі CF_4+ 20%H_2. Вуглець же є домінуючим у першому шарі. Коефіцієнт заломлення і товщина цього шару інтенсивно варіюється, поки переважають границі CF_x і C-CF_x. Границі Si-Fx і Si-C превалювали у другому глибшому шарі. Третій шар є кремнієм, ушкодженим через іонне бомбардування. Коефіцієнт заломлення рівний 4,63.