IR-SPECTROSCOPY ANALYSIS OF THE STRUCTURE AND COMPOSITION OF THE Si—O PHASE IN ULTRATHIN (10—15 nm) SiO$_2$ FILMS

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The structural features of ultrathin (10—15 nm) SiO$_2$ layers thermally grown at 850 °C both on standard and hydrogen-plasma-treated Si wafers have been studied by IR-spectroscopy, spectral ellipsometry, and computer simulation. The analysis of IR spectra has shown that the structure of standard SiO$_2$ layers (as compared to that grown on hydrogenated Si) is characterized by the presence of SiO$_2$Si$_2$ molecular complexes and the relatively large concentration of strained 4-fold rings of SiO$_4$ tetrahedra. This fact indicates a more ordered and less strained SiO$_2$ lattice as well as an improved Si—SiO$_2$ interface in the case of the oxide films on hydrogen plasma cleaned Si. These conclusions are in a good agreement with ellipsometric data which have demonstrated a higher level of silicon oxidation for the oxides grown on hydrogenated silicon.

Introduction

The main direction in the development of a new generation of metal-oxide-semiconductor (MOS) devices is the reduction of their dimensions down to submicron values. To solve this problem, the thickness of a gate dielectric (usually SiO$_2$ is used for this purpose) has to be of nanometer size and very soon can reach a limit of several nanometers [1]. Therefore, a further improvement of the oxide quality is required for the production of the high-quality MOS structures with reliable characteristics. The structure and the medium-range ordering of ultrathin silicon oxide layers as well as the thickness and the composition of interface Si—SiO$_2$ layers are being studied intensively and attract more and more attention of researchers [2].

Since the state of the surface of Si substrate can significantly influence the properties of a dielectric film grown on it [3], considerable efforts are applied to obtain the Si surface as clean and smooth as possible prior to oxidizing it. Recently, many various technological procedures are proposed worldwide to purify and modify the surface of Si substrates. Treatments in dry hydrogen plasma are considered very perspective among them [4].

That is why in this work, a comparative study of the structural characteristics of ultrathin SiO$_2$ films and the interface Si—SiO$_2$ layer has been carried out for the films obtained by a standard thermal oxidation of silicon, as well as by oxidation with the preliminary hydrogen plasma treatment of silicon surface. IR-spectroscopy with the analysis of the absorption band shape, spectral ellipsometry, and computer modeling of the Si—O phase structure have been chosen as the methods of investigation.

Experimental Methods

The Czochralski-grown (100) and (111) Si wafers ("Wacker") were used in our experiments. Prior to the oxidation, all the substrates were subjected to a standard RCA cleaning, which includes the cleaning in a H$_2$SO$_4$/H$_2$O$_2$ solution with the following dipping in a diluted HF solution and rinsing in deionized water. After this procedure, a part of substrates was additionally cleaned in hydrogen plasma in a planar reactor. The substrates were placed on an electrode whose temperature was kept at 20 or 300 °C. A 15-W RF-generator operating at 13.56 MHz was used as a plasma source. The hydrogen pressure during the plasma treatments for 15 min was fixed at 13.3×10^{-3} Torr. The oxidation of Si wafers was carried out in dry (the water concentration was less than 3 ppm) oxygen at 850 °C. Although each set of samples was oxidized under identical conditions, the oxide thicknesses were different depending on the pre-oxidation treatments of the Si surface as well as on the substrate orientation. These thicknesses varied from 10 to 15 nm. The description of the samples studied is presented in Table 1.

IR-spectra were measured under normal light incidence in the wave number range of 950 — 1150 cm^{-1} using an automatic differential spectrophotometer IKS-25. Taking into account that the difference in

oxide thicknesses and, hence, the difference between the measured spectra were small, the differential spectra of a standard oxide (sample A) and the oxides grown on hydrogenated Si (samples B and C) were additionally obtained. After this, the main absorption band of oxide (the Si—O valence oscillations) was deconvoluted into the elementary Gaussian components, according to the method described in detail in [5]. The precision of deconvolution procedure was characterized by a standard deviation of the sum of Gaussian profiles from the experimental spectrum. This deviation was about 10^{-2}.

Ellipsometric measurements were carried out at a light incidence angle of $70°$ in the spectral range of 280—633 nm. The error of the angles of a polarizer, an analyzer, and light incidence did not exceed $\pm 0.01°$. The systematic errors of ellipsometric angles Δ and Ψ were eliminated by averaging the results of measurements in four zones.

Computer modeling of the Si-O phase structure was done using the results from IR spectroscopy and the "OUP Molecular Modelling Package" software. Modeled clusters consisted of about 90 atoms and were obtained after the minimization of energy, according to the principles described in [6]. The results of modeling allowed us to estimate the fundamental structural characteristics of the vitreous Si-O phase, namely the distribution of Si—O—Si bond angles and the interatomic distance.

Results and Discussion

The results obtained by spectral ellipsometry are presented in Table 1. It can be seen that the treatment of silicon in hydrogen plasma prior to oxidation influences significantly the stoichiometry of the interface Si—SiO$_2$ layer, which is a layer of SiO$_x$. For hydrogenated oxides, this layer is characterized by a far higher degree of silicon oxidation, comparing to the standard oxide (the stoichiometry indices of the interface region, x, are equal to 1.4 and 0.8, respectively). In this case, the temperature of plasma treatment has almost no influence on the effect found out.

The main absorption band of silicon oxide films (with a maximum at $1070 - 1100$ cm^{-1} depending on the thickness of film) related to the antisymmetric valence oscillations of the atoms of the bridge oxygen in Si—O—Si "molecules" can be presented as a superposition of Gaussian profiles, the number of which depends on oxide thickness and changes from 2 ($d < 40$ nm) to 6 ($d > 475$ nm) [7]. At the same time, the positions of Gaussians and their half-widths do not depend on the thickness of a SiO$_2$ layer. The analysis of the nature of these elementary contributions was carried out using the method described in [5 and 8]. In particular, the positions of the maxima of Gaussian profiles allow us to calculate the respective angle of a Si—O—Si bond, θ, using the approximation of a Si—O—Si "molecule" (Fig. 1):

$$\omega_{TO}^{OS} = [(2/m)(\alpha \sin^2(\theta/2) + \beta \cos^2(\theta/2))]^{1/2}, \tag{1}$$

$$\omega_{LO}^{OS} = [(2/m)(\alpha \sin^2(\theta/2) + \beta \cos^2(\theta/2) + \gamma)]^{1/2}, \tag{2}$$

where $\gamma = Z^2 \rho/[\varepsilon \varepsilon_v(2m + M)]$, α and β are the power constants, m and M are the masses of the atoms of oxygen and silicon, respectively, ρ is the film density (~ 2.2 g/cm^3 for Si oxide), ε is the static electron permittivity (~ 2.14 for SiO$_2$), ε_v is the absolute vacuum permittivity, Z is the transverse dynamic effective charge of the motion of stretching of the oxygen atom (-3.95×10^{-19} C) [9].

The power constants are independent of the bonding angle and are determined by the frequencies of the valence oscillations of Si atoms and the deformation oscillations of a Si—O bond:

$$\omega^{Si} = [(4/3m)(\alpha + 2\beta)]^{1/2}, \tag{3}$$

$$\omega^{D} = [(2/m)\beta]^{1/2}. \tag{4}$$

The values of ω^{Si} and ω^{D} for the samples under investigation were equal to ~ 808 and ~ 461 cm^{-1}, respectively, which allowed us to determine $\alpha \cong 610$ and $\beta \cong 100$ N/m. It should be stressed that, for these values of α and β, their ratio $\beta/\alpha \cong 0.164$ coincides with the known value [10] with the 10 % precision.

The dependences obtained from expressions (1) and (2) are presented in Fig. 1. It is obvious that two oscillation zones should exist in the absorption in the films under investigation, which are related to the

T a b l e 1. Conditions of Si treatment and characteristics of the interface Si—SiO₂ layer

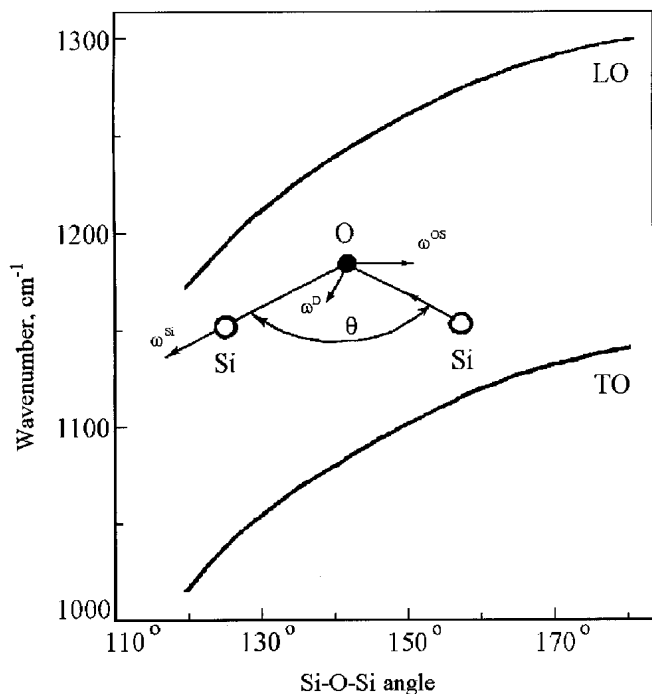| Sample	Pre-oxidation treatment	Stoichiometric composition of the interface layer, x
A	RCA-cleaned	0.8
B	RCA-cleaned and hydrogen-plasma-treated at 20 °C	1.4
C	RCA-cleaned and hydrogen-plasma-treated at 300 °C	1.4

Fig. 1. Frequencies of the transverse and longitudinal modes of the valence oscillations of an bridge oxygen atom vs the bond angle. In the inset, a model of an oscillating Si-O-Si "molecule" and the types of oscillations are shown

Fig. 2. IR-transmission spectra of samples A, B, and C (the curve marking is analogous to that in Table 1)

transverse and longitudinal valence oscillations of the atoms of bridge oxygen: the frequencies of the mentioned oscillations are distributed in separate regions, $1010 < \nu < 1140$ cm^{-1} and $1190 < \nu < 1300$ cm^{-1} in the range of $120° < \theta < 180°$.

The dependences shown can be used also for the analysis of components of the main absorption band of silicon oxides SiO$_x$ ($x < 2$), whose position changes in the range of $1000 - 1080$ cm^{-1} depending on the value of x [11]. In any case, according to a random-bonding model, which describes the structure of the vitreous Si—O phase, the angle of a Si—O—Si bond characterizes the structural elements of a film, i.e. it is unambiguously related to the type of the tetrahedron rings of SiO$_4$ in the lattice of vitreous SiO$_2$, or to the type of the molecular clusters of Si—O$_y$—Si$_{4-y}$ ($1 \leq y \leq 4$) in the lattice of amorphous SiO$_x$.

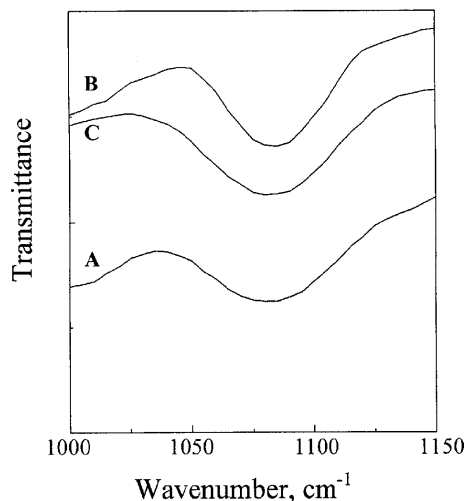The IR-transmission spectra of some oxides studied are shown in Fig. 2. It can be seen that the positions of absorption bands remain almost unchanged, but the shapes of the spectral curves for plasma-treated samples differ from those for the spectrum of standard oxide.

This observation is supported by Fig. 3, in which the results on the deconvolution of the absorption spectra into Gaussian profiles are presented. The results of the mathematical treatment of spectra are summarized in Table 2. It can be seen that the bands with the maxima at ~1055 and 1085 cm^{-1} give the main contribution to the absorption spectra of all the oxides (both standard and hydrogenated). The angles of a Si—O—Si bond are equal to 131 and 143° for the respective structural units.

This fact is rather known [5, 12]. Most likely, it is related to the 4- and 6-fold rings of SiO$_4$ tetrahedra in the Si oxide lattice [8, 13]. However, one more Gaussian profile is present in the case of light absorption in a standard sample, whose maximum lies at ~1045 cm^{-1}. Its contribution is rather small comparing to the main contributions, but really exists, which can be supported by the data presented in Fig. 4. Here, the differential

T a b l e 2. Parameters of elementary contributions in the absorption of the films studied

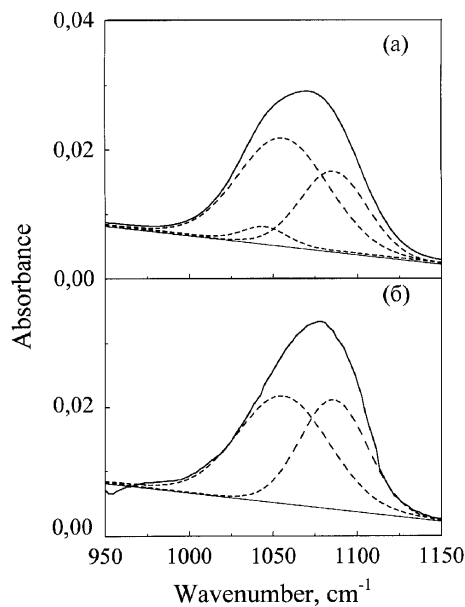| Contribution	Maximum position, cm^{-1}	Si—O—Si bond angle	Dominating structural element
1	1045 ± 2	$\sim 128°$	Molecular complexes SiO$_2$Si$_2$
2	1055 ± 3	$\sim 131°$	4-fold SiO$_4$ rings
3	1085 ± 4	$\sim 143°$	4- and 6-fold SiO$_4$ rings

Fig. 3. Deconvolution of a Si—O absorption band into Gaussian profiles for the standard oxide (*a*) and for the oxide grown on hydrogenated silicon (*б*)

Fig. 4. Differential IR-transmission spectrum of samples A and C (the parameters of elementary components are shown in Table 2)

spectrum of samples A and C is shown. The obtained spectral curve can be described by a single Gaussian profile with the maximum position just at $\sim$1045 cm^{-1}. The angle of a Si—O—Si bond for the respective structural unit is equal to 128° (see Table 2). Such an angle of the bond is typical of the SiO_2Si_2 molecular complex, which is one of the components of the lattice of SiO_x films [8, 9]. Thus, this result shows that the standard oxide has an additional quantity of under-oxidized silicon comparing to the oxides grown on plasma-treated Si substrates. Most likely, this underoxidized silicon is in the interface region between Si and oxide. This conclusion agrees well with the results obtained by spectral ellipsometry (see Table 1), namely, the oxides grown on the hydrogenated silicon are characterized by a better stoichiometry of the interface.

The result presented *prima facie* contradicts to the known data [12], according to which the absorption band of the thin ($d < 40$ nm) films of thermally grown Si dioxide consists only of two Gaussian profiles (at $\sim$1055 and 1085 cm^{-1}). However, it should be noted that the data mentioned were measured for the SiO_2 films obtained by the thermal oxidation of silicon in the mixture of O_2 + HCl. The presence of hydrogen and chlorine in the oxidizing atmosphere leads to a noticeable improvement of the structure of oxide and the interface
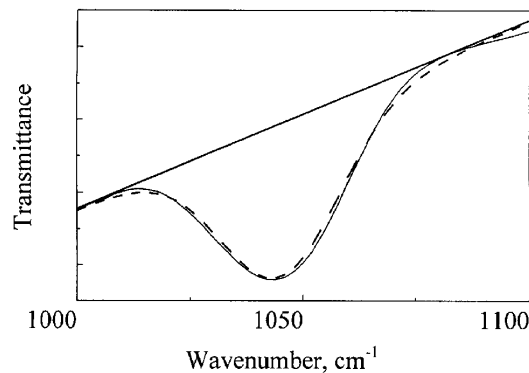
Si—SiO_2 layer [3]. This can also mean that the hydrogenation of Si substrates with the following oxidation in dry oxygen is to a certain extent analogous to the oxidation of Si wafers in the HCl-containing atmosphere, carried out after a standard cleaning.

The results presented in Fig. 3 show one more peculiarity of the IR spectra of SiO_2 films grown on hydrogen-plasma-treated silicon. The contribution of the band with the maximum position at $\sim$1085 cm^{-1} is greater as compared to the standard sample. Taking into account the results summarized in Table 2, we may explain this observation by that fact that the lattice of SiO_2 layers grown on hydrogen-plasma-cleaned silicon has a greater contribution of 6-fold SiO_4 rings. Of course, the SiO_2 lattice composed of 6-fold tetrahedral rings is ordered (up to the formation of a crystalline phase in the limiting case [13, 14]). The appearance of 4-fold rings leads to a lattice disordering [5]. This yields that a comparatively small contribution of 4-fold rings, typical of oxides grown on plasma-treated hydrogenated silicon, allows one to obtain more ordered and less strained SiO_2 lattices. This conclusion also agrees well with the estimations made from spectral ellipsometry data: the oxides grown on hydrogenated silicon have smaller internal strains at the interface of Si—SiO_2 [15].

According to the results obtained for the oxides grown in the mixture of O_2 and HCl, the contribution of the band with the maximum position at $\sim$1055 cm^{-1} to the absorption is three times as great as that of the band with the maximum position at 1085 cm^{-1} [12]. In our case, this ratio is considerably smaller (Fig. 3). In other words, the specific weight of the 6-fold tetrahedral rings of SiO_4 in the structure of hydrogenated oxide is higher than that in the structure of chloride oxides. This fact
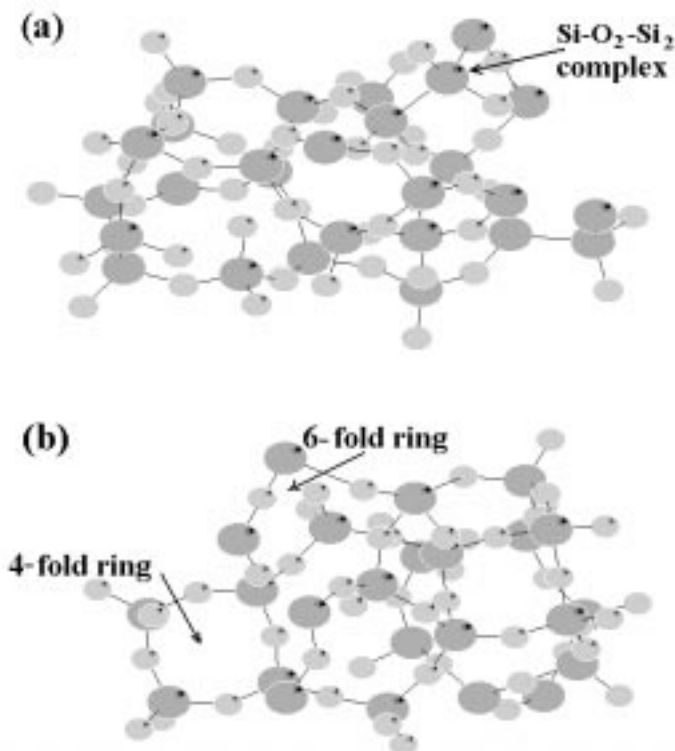
Fig. 5. Geometric structure of a standard oxide film (*a*) and the oxide film grown on hydrogen plasma-cleaned silicon (*b*). Dark and gray spots are Si atoms and oxygen atoms, respectively

can mean that the treatment of silicon in hydrogen plasma influences more effectively the structure of an oxide film, comparing to the technology applying HCl.

Fig. 5 illustrates the structure of a film of silicon oxide obtained by computer modeling on the base of IR-spectroscopy results. The oxide lattice consists of the 4- and 6-fold rings of mutually joined SiO_4 tetrahedra in the case of the oxide on hydrogenated silicon, and additional built-in SiO_2Si_2 molecular complexes are added in the case of the standard oxide (Fig. 5,*a*). It is clearly seen that the appearance of these complexes really distorts the oxide lattice.

The modification of the lattice geometry due to the incorporation of different quantities of excess Si atoms is illustrated in Fig. 6. Here, the histograms of the distribution of Δ (a change of the distances in angstroms between the neighboring unbound Si atoms in the modeled SiO_x clusters, relative to the initial SiO_2 cluster) are shown. In Fig. 6, the concentrations of excess silicon atoms are equal to 3 (*a*), 10 (*b*), and 17% (*c*), respectively.
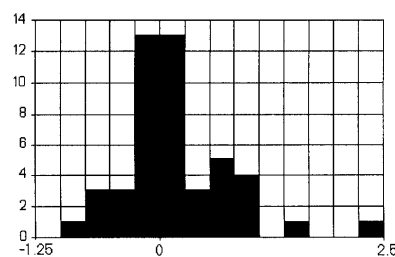
As can be seen from this Figure, the value of Δ shifts to the positive region of the histogram with adding Si
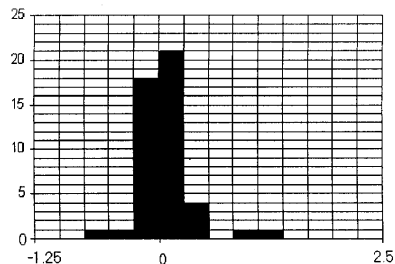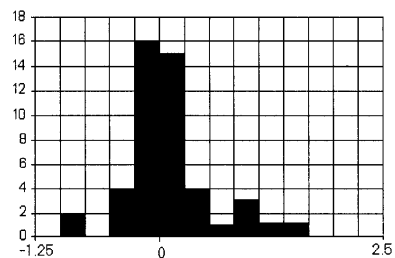
$$\Delta, \text{Å}$$

Fig. 6. Change of the histograms of the distribution of Δ with addition of excess Si atoms in the lattice of SiO_2

atoms. This shows that the lattice of interface layer expands, i.e. the distance between the neighboring Si atoms increases with the concentration of molecular complexes SiO_2Si_2. Therefore, the interface $Si\text{—}SiO_2$ layers obtained by thermal oxidation of preliminary hydrogen plasma-treated Si substrates are characterized by denser packing of atoms and hence, have better properties comparing to those of interface oxide layers after only RCA cleaning.

Conclusion

The analysis of the IR spectra of SiO_2 films deposited on hydrogenated silicon has shown that the structure of

such layers is characterized by a greater concentration of 6-fold tetrahedral SiO_4 rings comparing to that of the oxides obtained by the standard technology. This points to a more ordered and less strained SiO_2 lattice. This conclusion is based on the results of calculations which show a relatively small percent of 4-fold rings, which is typical of the oxides grown on plasma-treated hydrogenated silicon. The results of spectral ellipsometry confirm these data, namely the oxides grown on hydrogenated Si are characterized by lower internal strains.

The obtained results are perspective for the application in the production of MOS-structures, which is especially up-to-date according to the tendency of reducing their sizes down to submicron values. These results indicate the possibility to improve, in principle, the technology of thermal oxidation of silicon.

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АНАЛІЗ МЕТОДОМ ІЧ-СПЕКТРОСКОПІЇ СТРУКТУРИ ТА СКЛАДУ КРЕМНІЙ-КИСНЕВОЇ ФАЗИ В НАДТОНКИХ (10—15 нм) ПЛІВКАХ SiO_2

І.П. Лісовський, В.Г. Литовченко, Д.О. Мазунов, А. Секереш

Р е з ю м е

Методами ІЧ-спектроскопії, спектральної еліпсометрії та комп'ютерного моделювання проведено вивчення структурних особливостей надтонких (10—15 нм) шарів SiO_2, отриманих окисленням при температурі 850 °C як стандартних кремнієвих підкладок, так і підкладок, оброблених у водневій плазмі. Аналіз ІЧ-спектрів показав, що структура стандартних шарів SiO_2, у порівнянні з вирощеними на гідрогенізованому кремнії, характеризується наявністю молекулярних комплексів SiO_2Si_2 та відносно великим вмістом напружених чотиричленних кілець тетраедрів SiO_4. Це свідчить про більш впорядковану та менш напружену ґратку SiO_2, а також про поліпшення межі поділу Si—SiO_2 для оксидних плівок на кремнії, попередньо очищеному у водневій плазмі. Такі висновки добре узгоджуються з даними спектральної еліпсометрії, які говорять про якісніше окислення кремнію для оксидів, вирощених на гідрогенізованому кремнії.