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Configurational statistical model for the damaged structure of silicon oxide after ion implantation

B. Garrido, J. Samitier, and J. R. Morante
Laboratori de Caracterització de Materials per a la Microelectrònica, Departament de Física Aplicada i Electrònica, Universitat de Barcelona, Diagonal 645-647 E-08028 Barcelona, Spain

J. Montserrat and C. Domínguez
Centre Nacional de Microelectrònica, Consejo Superior de Investigaciones Científicas, Campus Universitat Autònoma Barcelona, E-08193 Bellaterra, Spain

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A configurational model for silicon oxide damaged after a high-dose ion implantation of a nonreactive species is presented. Based on statistics of silicon-centered tetrahedra, the model takes into account not only the closest environment of a given silicon atom, but also the second neighborhood, so it is specified whether the oxygen attached to one given silicon is bridging two tetrahedra or not. The frequencies and intensities of infrared vibrational bands have been calculated by averaging over the distributions and these results are in agreement with the ones obtained from infrared experimental spectra. Likewise, the chemical shifts obtained from x-ray photoelectron spectroscopy (XPS) analysis are similar to the reported values for the charge-transfer model of SiO_x compounds.

I. INTRODUCTION

The effects of different kinds of radiation on SiO_2/Si structures have been studied for many years. Particularly, ion implantation in SiO_2 is of great importance on account of its technological applications in microelectronics as well as its interest in the field of basic research in amorphous materials. In this context, several investigations have been devoted to the effects of ion implantation into SiO_2, reporting, for instance, the enhancement of its etching rate in wet solutions and therefore reflecting important modifications of the SiO_2 structure.[1,2]

The structure of amorphous SiO_2, as its crystalline polymorphs, is built up from basic SiO_4 tetrahedral units centered with silicon atoms. However, unlike the crystal forms, the Si-O-Si intertetrahedral angle of the amorphous material varies from one tetrahedron to another within the range 120°–180°.[3,4] The mean value of this Si-O-Si angle distribution is found to be 144°.[3,4] Ion implantation modifies this distribution in different ways thus producing structural damage. Some authors have reported that ion implantation into silica causes the local densification of the structure, as a consequence of the Si-O-Si angle diminution—the same that is found after x-ray or neutron irradiation.[5,6] Another effect of the implantation is to widen the bond-angle distribution, and hence increasing dispersion of the intertetrahedral angles which can be regarded as an increment of disorder. These modifications lead to shifts and broadenings of the vibrational spectra bands from which compaction and structural disorder can be quantified. Moreover, previous experimental studies of silicon oxide implanted with Ar and other heavy ions have confirmed the lack of porosity in these kind of samples, which is also in favor of densification.[5,7,9] However, as well as compaction and disorder, the most relevant phenomenon produced after high-dose implantation is structural damage, which is mainly originated by broken bonds and displaced atoms. In general, it is the presence of these point defects, which are connected with alteration of the environment of the silicon atom, that is mainly responsible for modifications on the vibrational spectra of implanted samples. For instance, the Si-O bond stretching mode is positioned at 1080 cm^{-1} when the structure is undamaged, and when oxygen is nonbridging two tetrahedra as a consequence of one broken bond, the value is around 1000 cm^{-1}.[8] Furthermore, infrared analysis reveals a strong reduction of the contribution of Si-O absorbing bonds with the increasing dose.[5,7,9] But, when the nuclear deposited energy reaches a critical value of about 10^{24} eV/cm^{-3}, damage saturates and the infrared spectrum of the oxide for higher doses does not become modified anymore. Etching rate measurements by Hiraiwa, Usui, and Yagi[2] reproduce this saturation behavior.

The structure of amorphous silicon-based alloys, such as SiO_x, SiN_x, $Si_xN_yH_z$, have been treated in terms of statistical microstructural models based on random mixture of different configurations of silicon-centered tetrahedra. In these models, the fundamental structural units or configurations determine the vibrational response of the alloys. This method was introduced by Philipp to obtain the optical response for amorphous silicon-based alloys,[10] and was further developed by Aspnes and Theeten,[11] Yin and Smith,[12] and Bustarret *et al.*[13] Si-centered random tetrahedra models have also been employed for determining Si-H, Si-N, and Si-O bond stretching frequencies[14–15] and Si 2*p* core-level binding energies measured by x-ray photon spectroscopy[16] (XPS) in those amorphous alloys. An XPS approach to the microstructure of *a*-SiN_x has been reported by Ingo *et al.*[17] and Hasegawa *et al.*[20] on the basis of these models.

However, these forementioned studies have always been applied to materials with complete bond saturation. Neither broken bonds nor vacants or interstitials are allowed in the structure. In this framework, this paper presents a random bonding model of silicon-centered tetrahedra which is applied to the nonsaturated structure of damaged silicon oxide. The frequencies and intensities of infrared vibrational bands have been calculated from the theoretical distributions obtained and they have been compared with experimental infrared results. Furthermore, as XPS analysis of Si 2*p* core-level binding energy gives information about the nearest environment of the silicon atom, it is also used to test the theoretical results.

II. THEORETICAL ANALYSIS

From theoretical point of view, the structural damage caused by ion implantation is quantified as the total number of broken bonds relative to the initial number of absorbing Si-O bonds, which is determined by infrared absorption spectroscopy, and is analyzed by considering a statistical model based on tetrahedral configurations which differ on their number of vacants, nonbridging oxygens (NBO's) and bridging oxygens (BO's).

If we consider one basic tetrahedral unit of an undamaged oxide, only oxygen atoms would saturate the four sp^3 hybrids of silicon. But, in damaged oxides, we must take into account that some hybrids could end up not being saturated and if saturated with oxygen, it could be a bridging oxygen or not. Consequently, we have three fundamental units which can "saturate" each silicon hybrid (the square refers to a dangling bond or a hole so each broken bond gives rise to two dangling bonds): Si-O-Si, Si-O-□, and Si-□. Therefore, the number of different tetrahedra that can be built is $(4+3-1)!/4!(3-1)!=15$. Each configuration will be denoted with three numbers, i,j,k, which stand, respectively, for the number of the -O-Si, $-$O-□, and $-$□ units attached to one given silicon atom.

It is worth noting here that all the statistical calculations are based on the assumption that broken bonds (squares) are randomly distributed within the sample. This is obviously false for low implantation doses, since broken bonds arise from displacements and they would be in groups of two or four depending on whether the displaced atom is oxygen or silicon. On the contrary, high implantation doses give rise to the rearrangement of the whole structure regarding that nearly all the atoms will have been displaced. Therefore, what we consider random is the final distribution of broken bonds after a great amount of damage.

If we consider all the units, a "chemical formula" for damaged oxides can be written as

$$\mathrm{Si}_x\mathrm{O}_y\Box_z(\mathrm{O}\Box)_t(\Box\mathrm{O}\Box)_s\ , \tag{1}$$

where coefficients are related by the following. (a) As all the silicon bonds must be "saturated" by one of the above units: $4x=2y+z+t$. (b) As the number of O atoms is twice the number of Si atoms: $y+t+s=2x$. (c) As each broken bond introduces two dangling bonds, one for Si and one for O: $z=t+2s$.

Only two equations out of the three are independent. If we write t and z as a function of s, the result is

$$t=(2x-y)-s\ ,\quad z=(2x-y)+s\ . \tag{2}$$

Let N_R be the number of broken bonds and $4N_t$ the total number of possible bonds, where N_T is the number of silicon atoms. If the distribution of broken bonds is random among all the oxygen atoms, the probability for a given O bond to be unsaturated is $N_R/4N_T$. Therefore, the statistical weight for the three possible units when centered in oxygen is

$$\begin{aligned} P(\text{Si-O-Si})&=\left[1-\frac{N_R}{4N_T}\right]^2 ,\\ P(\text{Si-O-}\Box)&=2\left[\frac{N_R}{4N_T}\right]\left[1-\frac{N_R}{4N_T}\right] ,\\ P(\Box\text{-O-}\Box)&=\left[\frac{N_R}{4N_T}\right]^2 . \end{aligned} \tag{3}$$

As the total number of oxygens and silicons is $2N_T$ and N_T, respectively, we can write

$$\frac{s}{x}=\frac{2N_T(N_R/4N_T)^2}{N_T}=2\left[\frac{N_R}{4N_T}\right]^2\equiv a\ . \tag{4}$$

After Eqs. (2) and (4), only x and y are independent. But, as we see later, probabilities only depend on the ratio y/x so there will only be one free parameter.

From the point of view of the silicon atom, let f be the fraction of the basic units attached to silicon which can be rewritten by using (4) as

$$\begin{aligned} f(\Box)&=\frac{z}{4x}=\frac{2x-y+ax}{4x}\ ,\\ f(\mathrm{O}\Box)&\frac{t}{4x}=\frac{2x-y-ax}{4x}\ ,\\ f(\mathrm{O})&=\frac{y}{2x}\ . \end{aligned} \tag{5}$$

Now, the quotient y/x can be easily related with the number of broken bonds N_R, and the number of silicon atoms N_T, by considering that the quantity of broken bonds is the total number of □ units connected with silicon:

$$\frac{z}{4x}4N_T=\left[\frac{2x-y+ax}{4x}\right]4N_T=N_R \tag{6}$$

and with the aid of Eq. (6), the set (5) can be put in terms of the fraction of broken bonds which is the experimentally determined parameter. The following expressions are obtained:

$$\begin{aligned} f(\Box)&=\frac{N_R}{4N_T}\ ,\\ f(\mathrm{O}\Box)&=\frac{N_R}{4N_T}-\frac{a}{2}=\left[\frac{N_R}{4N_T}\right]-\left[\frac{N_R}{4N_T}\right]^2 ,\\ f(\mathrm{O})&=1+\frac{a}{2}-\frac{N_R}{2N_T}=\left[1-\frac{N_R}{4N_T}\right]^2 . \end{aligned} \tag{7}$$

Finally, by using the multinomial coefficients, the probability for each of the 15 i,j,k configurations, as a function of the number of broken bonds is

$$P_{i,j,k} = P(\text{Si-O-(O}\square)_j - \square_k, i+j+k=4) = \frac{4!}{i!j!k!} f(\text{O})^i f(\text{O}\square)^j f(\square)^k . \quad (8)$$

III. RESULTS AND DISCUSSION

Figure 1 shows the probability for some of the i,j,k configurations, obtained from the above expressions, as a function of the relative number of broken bonds $N_R/4N_T$. These probabilities let us compute the theoretical vibrational spectra if frequencies are assigned to each tetrahedron. This can be done by calculating the normal vibrational modes of a cluster consisting of some structural units as it has been done by Furukawa, Fox, and White,[8] who considered in their work three-, two-, and one-zero-dimensional structures with increasing content in the number of NBO's. $P_{i,j,k}$ units of our damaged oxide have been classified according to dimensionality criteria and BO and NBO frequencies for each of them have been calculated by averaging Furukawa's BO and NBO frequencies. If the unit has nonsaturated silicon bonds (Si-□), the frequencies for them are taken as 0. These calculated values are given in Table I for some i,j,k units.

For the experiments, 2500 Å of thermal silicon oxide has been grown by wet oxidation at 950° C on Si(100) N-type silicon wafers. In different samples we have done Ar implantations with doses ranging from 3.2×10^{12} cm^{-2} to 3.2×10^{16} cm^{-2}, two doses in every decade, with an energy of 130 KeV so that the maximum of the Ar-implanted distribution stays in the middle of the layer and the damaged thickness comprises most of the layer. Structural analysis was performed from Fourier transform infrared (FTIR) measurements in transmission and reflexion mode by using a BOMEM DA3 spectrometer and from XPS analysis by using a Perkin Elmer PHI 5500.

Figure 2 displays the strong modification of the silica stretching band (TO$_3$) after the implantation process. The evolution of the TO$_3$ band with dose consists of (i) shifts to lower frequencies, (ii) broadening, and (iii) decrease of the intensity and area. A saturating law is observed after doses of the order of 10^{14} cm^{-2}, which corresponds to a nuclear deposited energy density of 4.65×10^{23} eV/cm^3. As far as damage is concerned, Smakula's relationship, which involves the complex dielectric function of the layers, has been used for calculating the number of absorbing Si-O bonds and hence the number of broken bonds N_R. Thus, the dispersion analysis was carried out by fitting the experimental infrared spectra with suitable complex dielectric functions for amorphous materials.[8,21] The number of broken bonds obtained N_R is plotted in Fig. 3 as a function of the implantation dose. The maximum number of broken bonds reached is 15.5% of the total initial number $4N_T$. The statistical weight for some i,j,k configurations in the saturation region is given in the last column of Table I.

TABLE I. Vibrational frequencies of the BO and NBO oxygens for the most probable configurations of the damaged oxide. The last column refers to the probability when the number of broken bonds reaches the saturation value (15.5%).

Conf.	k_{BO} (cm^{-1})	k_{NBO} (cm^{-1})	Probability
$P_{1,0,0}$	1083		0.2575
$P_{3,1,0}$	1071	968	0.1904
$P_{2,2,0}$	1056	1013	0.0528
$P_{1,3,0}$	1054	1012	0.0065
$P_{3,0,1}$	1071		0.2255
$P_{2,0,2}$	1056		0.0741
$P_{1,0,3}$	1054		0.0108
$P_{2,1,1}$	1056	1013	0.1251
$P_{1,2,1}$	1054	1012	0.0231
$P_{1,1,2}$	1054	1012	0.0274

From the values of Table I, we have calculated the final frequency for BO and NBO modes, for the whole material by averaging those frequencies weighted with its corresponding $P_{i,j,k}$. We obtain for doses in the saturation re-

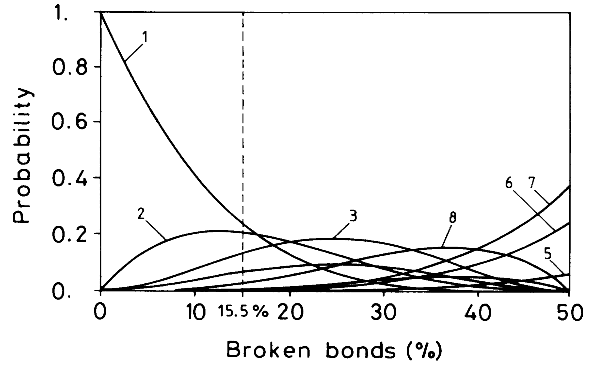

FIG. 1. Theoretical probability of some selected configurations as a function of the relative number of broken bonds, $N_R/4N_T$, in percentage. The value 15.5% marked on the plot corresponds to the saturation value of the number of broken bonds. The numbers marked stand for $1=P_{1,0,0}$, $2=P_{3,1,0}$, $3=P_{2,2,0}$, $5=P_{0,4,0}$, $6=P_{0,1,3}$, $7=P_{0,2,2}$, and $8=P_{1,2,1}$ [see Eq. (8)].

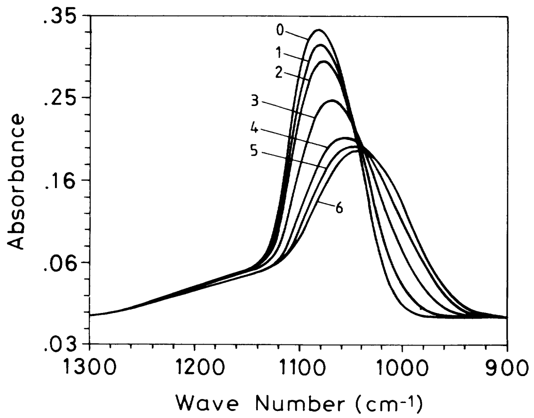

FIG. 2. Transmission spectra of the SiO$_2$ layers with the implantation dose as a parameter. Numbers stand for doses: 0=unimplanted, $1=3.2\times10^{12}$, $2=1.0\times10^{13}$, $3=3.2\times10^{13}$, $4=1.0\times10^{14}$, $5=3.2\times10^{14}$, and $6=3.2\times10^{15}$ cm^{-2}.

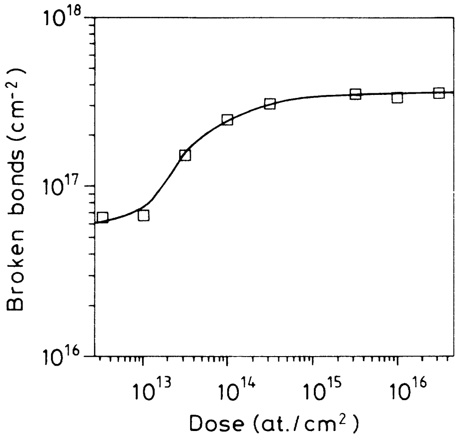

FIG. 3. Absolute number of broken bonds for layers which before implantation had 2.25×10^{18} bonds/cm^2, obtained from FTIR analysis, as a function of the implanted dose.

gion: $\omega_{BO}=1068$ cm^{-1} and $\omega_{NBO}=1006$ cm^{-1} and the ratio of the averaged intensities is $I_{BO}/I_{NBO}=2.7$. On the other hand, from the experimental infrared spectra, the absorption band of the layers implanted with high doses can be fitted with two Gaussian modes centered at these frequencies. The experimental area ratio obtained is 2.9 so it is in accordance with the result given above. Considering that the number of broken bonds is not as important in samples with lower implantation doses, the accordance is poorer in these samples. This is to be expected since the model considers that there is a random distribution of broken bonds, which is only achieved at high doses. The broadening caused by deformation and disorder of the intertetrahedral angles were considered by increasing the width of the Gaussian modes.

The developed model has also been tested by means of XPS analysis, which is complex since Si 2*p* core-level spectra have different components arising from chemical shifts. Such a chemical shift has been understood to be brought about by the charge transfer from Si to more electronegative atoms such as O.[16] Important chemical shifts are expected in damaged oxides since broken bonds and oxygen vacants mean that silicon oxidation number is less than 4 (Si^{+1},Si^{+2}, and Si^{+3}). This situation is similar (but not the same) to the determination of suboxide concentrations near oxide-silicon interface.[18,19] Hence, the area of each component is expected to be proportional to the population of the corresponding tetrahedron arrangement. As XPS is sensitive mainly to the nearest neighborhood, we have simplified our analysis by using only five tetrahedral configurations. Thus, the two bonding units Si-O-Si and Si-O-□ will be considered equivalent from the point of view of the XPS analysis. Therefore, the probabilities are now given by

$$P(\text{Si-O}_i\text{-}\square_{4-i})=\frac{4!}{i!(4-i)!}\left[1-\frac{N_R}{4N_T}\right]^i\left[\frac{N_R}{4N_T}\right]^{4-i}. \quad (9)$$

The XPS spectra were measured both before and after etching the oxide layer to half its thickness, in a buffered HF mixture, with the aim of comparing concentration of defects at surface and in bulk conditions. Surface deviations from bulk concentration are expected to be caused by contamination and oxygen depletion after the ion implantation. To overrule contamination, a cleaning of the surface was previously made. On the other hand, the etching itself could affect the concentration of defects. By comparing the two series of spectra in order to limit the accuracy of the data extracted from them, we can point out that only slight differences are observed. Position and width modifications of the Si 2*p* band are always smaller than 5% of the absolute values, so either surface or bulk spectra give a correct account for defect concentration within these limits. Moreover, as the characteristic spectra features caused by different doses are retained in both series of measurements, we expect deviations not to be of great importance. Nevertheless, the spectra from bulk conditions were selected for further calculations because of their smallest superficial contamination and because we expect them to give better knowledge of average concentrations.

Decomposition of the XPS spectra into five components using a curve-fitting method is not unique because of the uncertainty in the linewidth and separation energy for each component. Therefore, as a starting point to fit the XPS spectra we have used the charge-

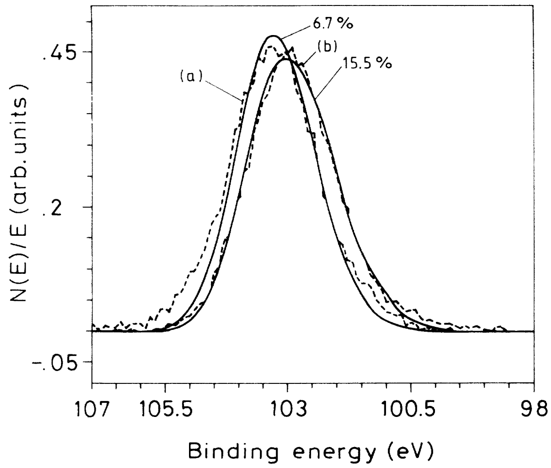

FIG. 4. XPS Si 2*p* core-level experimental spectra (broken line) for implantation doses of 3.2×10^{13} cm^{-2} (a) and 3.2×10^{15} cm^{-2} (b) and simulated spectra (continuous line) with the values 6.7 and 15.5% for the relative number of broken bonds ($N_R/4N_T$).

TABLE II. Chemical shift from the silicon 2*p* level and FWHM (full width at half maximum) for the different components, obtained after fitting the experimental XPS spectra of all the samples with component areas bounded to the statistical weights given by the model. All the quantities are in eV.

	Si^{+1}	Si^{+2}	Si^{+3}	Si^{+4}
"Shift"	1.0	1.95	2.95	3.86
FWHM	0.7	0.95	1.1	1.3

transfer model together with the random bonding model for SiO_x compounds[16–20] in which Si $2p$ binding energy is $\Delta E_B = 10.2 P_{Si}$ (eV), where P_{Si} is the averaged partial charge on the silicon atom and the reference energy is the position for silicon. Thus, the peak energy for each of the five components has initially been considered almost equally spaced between silicon Si^0 and silica Si^{+4}. Furthermore, the area of each component has been bound to be proportional to the statistical weight given by the model [Eq. (9)]. On the whole, we have allowed chemical shifts and linewidth of the components to vary around the reported values[15–19] for all the samples.

Figure 4 shows the experimental and fitted XPS spectra for two samples, before and after saturation. The goodness of the fit has been evaluated from the chi-square function, whose value has been always smaller than 0.02 for all the samples. As a result of the fitting process, the values obtained for the chemical shifts and linewidths of the components are written in Table II. These values are quite close to the ones quoted for SiO_x compounds result, which is in favor of the similar treatment—statistical models—for both under stoichiometric oxides and damaged oxides.

To summarize, the configurational statistical random model presented to account for the microstructure of damaged silicon oxide is able to explain structural characteristics of such materials. Macroscopic characteristics such as vibrational spectra can be justified by averaging frequencies of each configuration with the statistical weights given by the model. The model has also been tested experimentally by means of XPS analysis and the results show that the chemical shifts of the components arising from different tetrahedral configurations are close to the value for SiO_x compounds.

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