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The influence of high-energy electron irradiation and boron implantation on the oxide thickness in the SiO₂/Si system

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Abstract. The SiO₂/Si system exposed to irradiation with 11–12 MeV electrons was studied by soft-x-ray emission spectroscopy using the variable-exciting-electron-energy, optical ellipsometry, and nuclear reaction techniques. For the SiO₂/Si system prepared on an n-substrate, oxidation of Si was observed, and the thickness of the SiO₂ layer after electron irradiation was estimated. For the SiO₂/Si system prepared on a p-Si substrate, irradiation-induced oxidation was not observed. It was found that preliminary boron implantation in the SiO₂/n-Si system blocks oxidation of the n-Si substrate exposed to electron irradiation.

1. Introduction

It is known that interface states and fixed positive charges can be induced in metal–oxide–semiconductor (MOS) structures by electron irradiation [1, 2]. This effect is explained by the rupture of strained bonds [3, 4] and by the breaking of Si–H, Si–O, Si–OH, and Si–Si bonds [5] at the Si–SiO₂ interface as a result of irradiation.

One of the methods of characterizing interfaces is soft-x-ray emission spectroscopy. The application of x-ray emission spectroscopy for the analysis of interfaces is based on the high sensitivity of x-ray emission valence spectra to chemical bonding. Since the wave function of a core electron is quite localized, and its angular momentum symmetry is well defined, the valence states derived from the electronic transition to the core level are those projected onto the atomic site to which the core electron belongs, and their symmetries are determined by selection rules. Si L_{2,3} x-ray emission spectra (XES) correspond to the 3s → 2p transition, and probe the distribution of the Si 3s partial density of states in the valence band. It was shown in our previous publications [6–8] (see also [9]) that for the silicides, c-Si, a-Si, Si₃N₄, and SiO₂, the Si L_{2,3} spectra are distinct from each other. On the other hand, measurements of the Si L_{2,3} XES at different electron exciting energies can be used for the nondestructive depth-profiling phase analysis, because of a pronounced dependence of the x-ray yield on the electron excitation depth. With this method, we have constructed depth profiles of elements and phases within interfaces [10]. We used this method for characterization of interfaces in Fe⁺-implanted Si [10], W/Si multilayers [11],

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Si₃N₄ thin films irradiated by an excimer laser [6], and Hf/Si and Ir/Si systems after thermal annealing [12, 13].

In this work, this technique is applied to the study of the SiO₂/Si system prepared both on p-type and on n-type Si substrates, and irradiated with high-energy electrons ($E = 11$ – 12 MeV). The thickness of the dioxide layers, and the irradiation conditions (the duration of the electron irradiation and the preliminary boron implantation) are analysed. The the x-ray spectra results were verified by ellipsometry and nuclear reaction methods.

2. Experimental procedure

The sample substrates were n-type Si(111) (P-doped) wafers of resistivity $4.7 \Omega \text{ cm}$, and p-Si(100) (B-doped) wafers with $R = 10 \Omega \text{ cm}$. The thick layer of oxide was prepared using a standard cleaning process and thermal oxidation at $1050 \text{ }^\circ\text{C}$ in a 6% HCl ambient. The specimens were irradiated with high-energy 11–12 MeV electrons for 15, 30, 45, or 60 s in vacuum. High-energy electrons were generated by a cyclic accelerator. The beam current was about $I_e = 5$ – $9 \mu\text{A}$.

Table 1. Preparation conditions of the specimens

Series	Specimen	Substrate	SiO ₂ (Å)	Implantation	Irradiation	Time (s)
I	1	n-Si(111)	580	—	—	—
I	2	n-Si(111)	580	—	e [−] (12 MeV)	15
I	3	n-Si(111)	580	—	e [−] (12 MeV)	30
I	4	n-Si(111)	580	—	e [−] (12 MeV)	45
I	5	n-Si(111)	580	—	e [−] (12 MeV)	60
II	6	p-Si(100)	239	—	—	—
II	7	p-Si(100)	239	—	e [−] (12 MeV)	15
II	8	p-Si(100)	239	—	e [−] (12 MeV)	30
II	9	p-Si(100)	239	—	e [−] (12 MeV)	45
II	10	p-Si(100)	239	—	e [−] (12 MeV)	60
III	11	n-Si(111)	580	—	—	—
III	12	n-Si(111)	580	B ⁺ (26 keV)	—	—
III	13	n-Si(111)	580	B ⁺ (26 keV)	e [−] (11 MeV)	15
III	14	n-Si(111)	580	B ⁺ (26 keV)	e [−] (11 MeV)	60
III	15	n-Si(111)	580	B ⁺ (26 keV)	e [−] (11 MeV)	300

Three series of the specimens were prepared (see table 1). The specimens of the first series (specimens 1–5) were prepared on the n-Si(111) wafers with the oxide 580 Å thick. One of the samples was not irradiated, but the others were irradiated with 12 MeV electrons for 15–60 s.

The specimens of the second series (specimens 6–10) were prepared on the p-Si(100) wafers and have the oxide thickness 239 Å. One of the samples was not irradiated, and the rest were irradiated with 12 MeV electrons for 15–60 s.

The specimens of the third series (specimens 11–15) were prepared on the n-Si(111) wafers with the oxide thickness of 580 Å. One sample was not irradiated, and the rest were implanted with 26 keV boron ions with the dose $D = 1.2 \times 10^{12} \text{ cm}^{-2}$. One of the specimens was only implanted, and the others were implanted and irradiated with 11 MeV electrons for 60 s and 5 min.

The thickness of the SiO₂ films was measured by the ellipsometry method, with an accuracy of about $\pm 2 \text{ } \text{Å}$. The optical ellipsometry measurements were carried out by the

Beatty method, using an automatic ellipsometer. The angle between the light beam and the normal to the surface of the sample was 62°.

Si L_{2,3} x-ray emission spectra were measured on a small-spot x-ray spectrometer with a diffraction grating ($N = 600$ lines mm⁻¹, $R = 2$ m) [15] having high spatial (~ 5 μm) and energy resolution ($\Delta E \sim 0.4$ eV). Electron excitation of the x-ray spectra was used, with the accelerating voltage applied to the x-ray tube varied from 2 to 10 kV, and the anode current 130 nA.

Measurements of the surface density of oxygen atoms were made by the nuclear reaction technique on a 2 MV Van de Graaf accelerator. To measure the surface oxygen atom density, two reactions, $^{16}\text{O}(d, p_1)^{17}\text{O}$ and $^{16}\text{O}(d, p_0)^{17}\text{O}$, can be used. Since the $^{16}\text{O}(d, p_0)^{17}\text{O}$ reaction has a small cross-section, the nuclear reaction $^{16}\text{O}(d, p_1)^{17}\text{O}$ was used here. The energy of the primary deuteron beam and the irradiation dose were 900 keV and 160 μC, respectively. The experimental details are described more fully in reference [14].

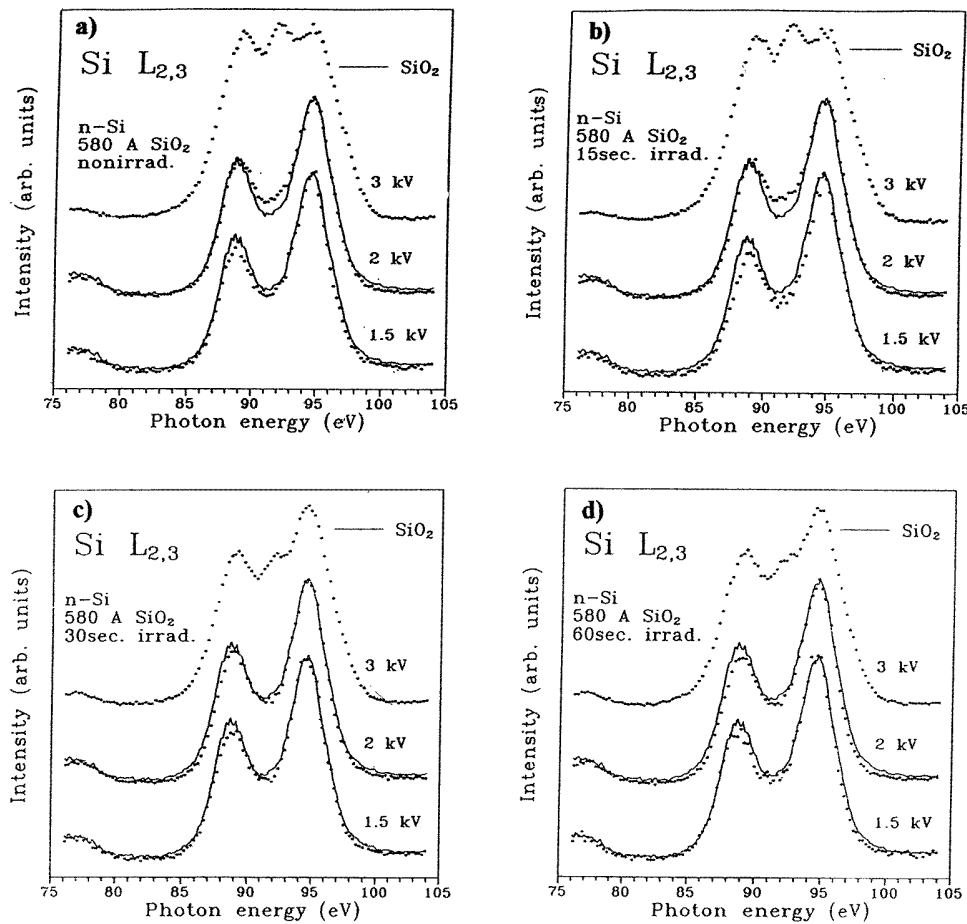


Figure 1. The dependences of Si L_{2,3} x-ray emission spectra of the SiO₂ (580Å)/n-Si system for the specimens that were not irradiated (a) and for those that were irradiated with high-energy electrons ($E = 12$ MeV) ((b), (c), (d)) on the exposure time: $\tau = 15$ s (b), $\tau = 30$ s (c), and $\tau = 60$ s (d).

3. Results and discussion

Figure 1 shows the x-ray emission Si $L_{2,3}$ spectra for the first series of the specimens. One can see that the Si $L_{2,3}$ x-ray emission spectra (XES) of the SiO₂ (580 Å)/n-Si system measured at the electron exciting energies 1.5 and 2.0 keV (the accelerating voltage applied to the x-ray tube was 1.5 and 2.0 kV, respectively) are very similar to those of SiO₂.

Si $L_{2,3}$ spectra measured at $V = 3$ kV split into three peaks centred at the photon energies 89, 92, and 94.5 eV. The relative intensities of these peaks depend on the electron irradiation conditions. The spectra for the initial sample and for the sample irradiated with $E = 12$ MeV electrons for 15 s (figures 1(a) and 1(b), respectively) are similar to each other. Noticeable changes in the Si $L_{2,3}$ XES ($V = 3$ kV) appeared for the specimens irradiated for periods not less than $\tau = 30$ s (specimen 3; figure 1(c)), and these persisted after irradiation for $\tau = 45$ and 60 s (specimens 4 and 5; figure 1(d)).

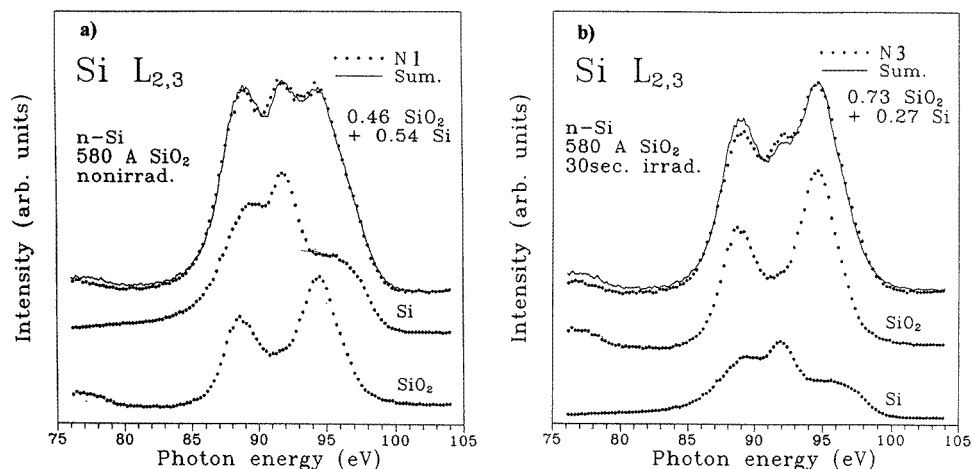


Figure 2. The simulation of the Si $L_{2,3}$ XES of specimens 1 (a) and 3 (b) measured at $V = 3$ kV by means of the superposition of the spectra of SiO₂ and c-Si.

With the aim of simulation, we represented the spectra measured at $V = 3$ kV by the superposition of the spectra of the reference specimens SiO₂ and c-Si. As is seen from figures 2(a), and 2(b), the fine structure of the Si $L_{2,3}$ XES of the nonirradiated SiO₂ (580 Å)/n-Si system (and of the one irradiated with $E = 12$ MeV electrons for $\tau = 15$ s) is reproduced quite well by the superposition of the spectra of SiO₂ and c-Si taken in the ratio 0.46:0.54 (see figure 2(a)). This means that, with the excitation of the Si $L_{2,3}$ XES at $V = 3$ kV, we probe the interface states with the above-mentioned contribution of SiO₂ and c-Si.

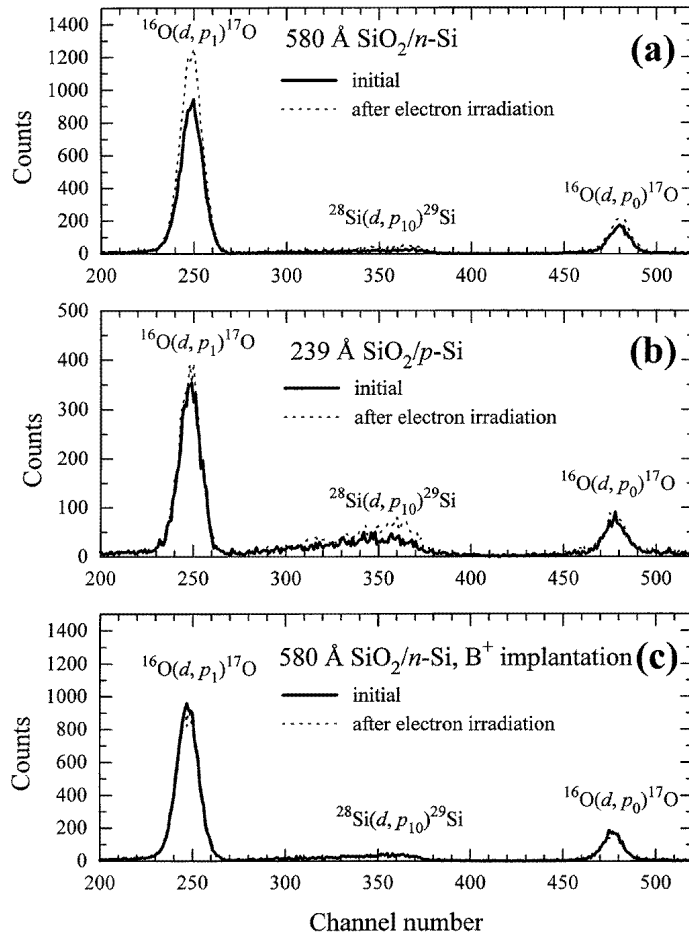
To check this conclusion, we estimated the Si $L_{2,3}$ intensity distribution in the SiO₂/Si system (see the appendix and table 2). One can see that for $V = 1.5$ and 2.0 kV, the model calculations give SiO₂ contributions of 1.0 and 0.797, respectively. This corresponds well with the conclusion that at these electron exciting energies, only the 580 Å SiO₂ layer is analysed. At $V = 3$ kV, the calculated contribution of SiO₂ (0.448) agrees closely with the measured one (0.46).

For specimens 3–5 irradiated for $\tau = 30, 45,$ and 60 s, the SiO₂ contribution in the interface region increases from 0.46 to 0.73 after electron irradiation.

It is shown in figure 2(b) that the Si $L_{2,3}$ spectra measured at 3.0 kV for the SiO₂/n-Si

Table 2. Comparison of the calculated and measured SiO₂ contributions.

Electron energy (keV)	SiO ₂ (580Å)/n-Si		SiO ₂ (239 Å)/p-Si	
	Experimental	Calculated	Experimental	Calculated
1.5	1.0	1.0	0.45	0.459
2.0	1.0	0.797	0.26	0.244
3.0	0.46	0.448	0	0.103
4.0	—	0.330	—	0

**Figure 3.** Nuclear reaction spectra of the SiO₂/n-Si samples before and after irradiation: (a) series I (specimens 1 and 3); (b) series II (specimens 6 and 8); (c) series III (specimens 11 and 14).

specimen irradiated for 30 s can be simulated by the sum of the spectra of SiO₂ and c-Si, taken in the ratio 0.73:0.27. The changes can be attributed to oxidation of the n-Si substrate of the SiO₂ (580 Å)/n-Si system as a result of electron irradiation. Using the method of calculation presented in the appendix, we have estimated that such a ratio of SiO₂ and c-Si

concentrations occurs for the SiO₂ layer with a thickness of about 860 Å.

It follows from the study by means of the nuclear reaction technique that electron irradiation of the SiO₂/n-Si specimen leads to a 32% increase in the oxygen surface density, in comparison with that of the initial specimen. This means that the thickness of the SiO₂ layer is 765 Å. This value agrees satisfactorily with that determined by the x-ray emission method. The nuclear reaction spectra of SiO₂ before and after electron irradiation (for the specimens of the first series) are given in figure 3. A similar conclusion about the increase of the SiO₂ layer thickness in the first series of the specimens was reached using optical ellipsometry. According to these measurements, the SiO₂ thickness of the specimen after irradiation is equal to 745 Å.

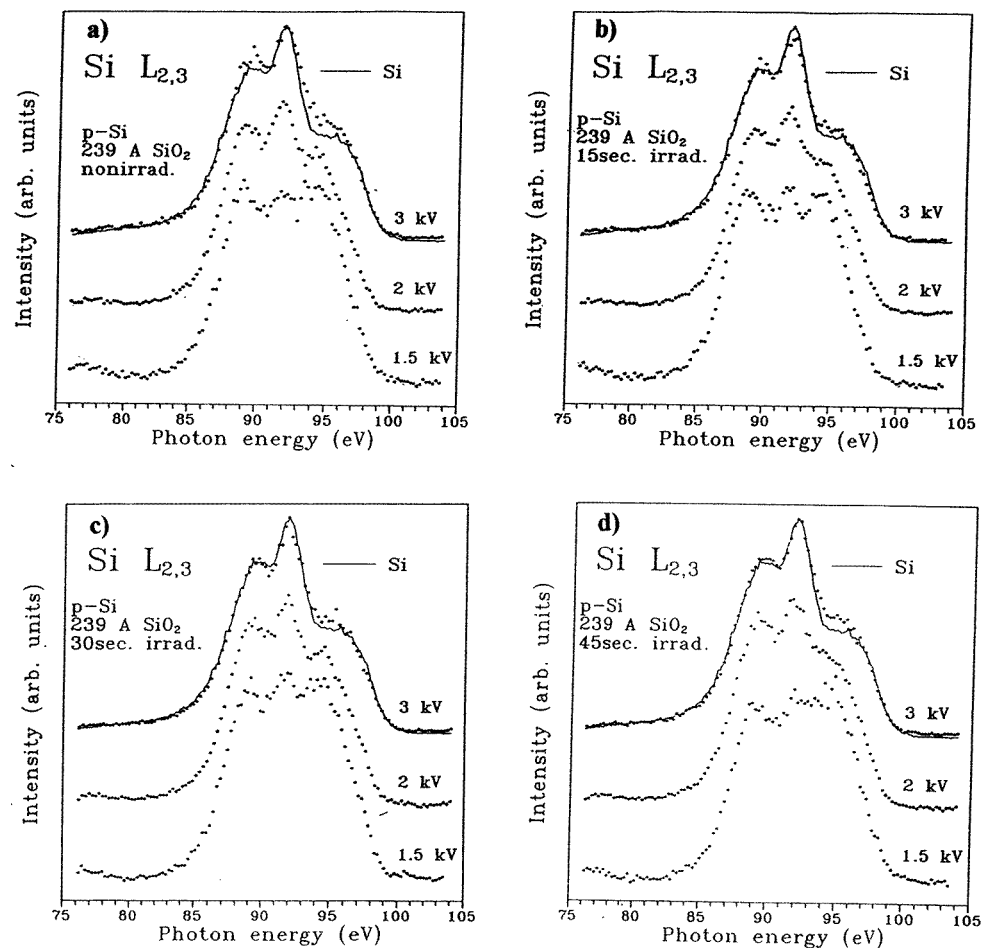


Figure 4. The dependences of the Si L_{2,3} x-ray emission spectra of the SiO₂ (239 Å)/p-Si system for the specimens that were not irradiated (a) and for those that were irradiated with high-energy electrons ($E = 12$ MeV) ((b), (c), (d)) on the exposure time: $\tau = 15$ s (b), $\tau = 30$ s (c), and $\tau = 45$ s (d).

The specimens of the second series were prepared on p-Si substrates, and had a SiO₂ layer 239 Å thick. The x-ray emission Si L_{2,3} spectra of these samples are given in figure 4. One can see that the spectra did not change upon electron irradiation. The spectra measured

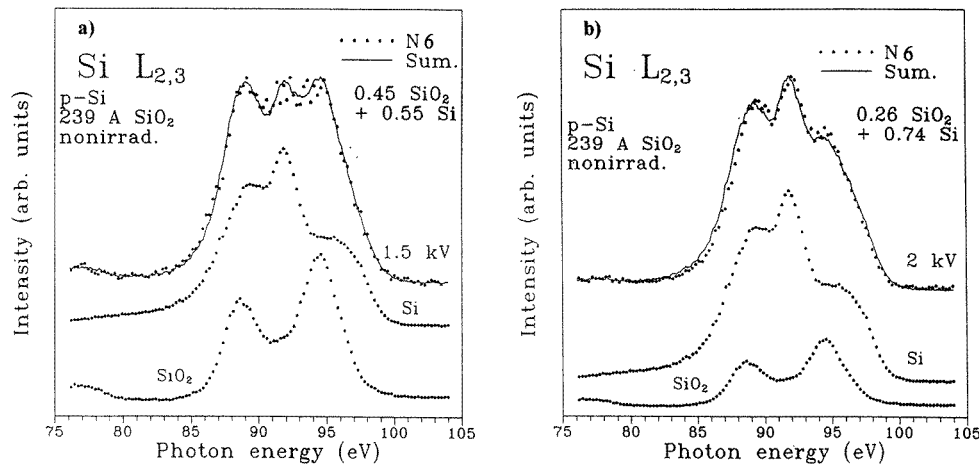


Figure 5. The simulation of the Si L_{2,3} XES of specimen 6 measured at $V = 1.5$ kV (a) and 2.0 kV (b) by means of the superposition of the spectra of SiO₂ and c-Si.

at 3 kV are close to the ones for pure c-Si. The spectra measured at $V = 1.5$ and 2.0 kV indicate a contribution of both SiO₂ and c-Si in the area studied. The simulation of these spectra is shown in figure 5. The spectra are well reproduced by the superposition of the ones for SiO₂ and c-Si taken in the ratios 0.45:0.55 for $V = 1.5$ kV and 0.26:0.74 for $V = 2$ kV. These values are well reproduced in the model calculation (see table 2). The irradiation time has no effect on the spectral shape.

Measurements made by the nuclear reaction technique show that the surface density of oxygen atoms is unaffected. Likewise, the ellipsometric parameters for the SiO₂/n-Si system are also unaffected.

In comparison with the results obtained for the first series, we have found in this case a high resistance of the p-Si substrate to oxidation induced by high-energy electron radiation under the same conditions. This conclusion is in agreement with our previous measurements of the Si L_{2,3} XES of porous silicon [16]. According to those measurements, porous silicon prepared by anodizing p-Si is more stable against oxidation than that prepared by anodizing n-Si. Photoemission studies [17] have also shown that even porous silicon freshly made from the n-Si substrate is oxidized to some extent. Fu *et al* [18] reported also that even γ -irradiation increases the oxide thickness in porous Si.

The Si L_{2,3} spectra of the third series of specimens (specimens 11–15; see table 1) are shown in figures 6(a)–6(d). The samples of these series are identical to those of the first series with one exception. The SiO₂ (580 Å)/n-Si specimens were initially implanted with boron ions ($E = 26$ keV, $D = 1.2 \times 10^{12}$ cm⁻²) before the high-energy electron irradiation was carried out ($E = 11$ MeV; $\tau = 15, 60,$ and 300 s). The Si L_{2,3} spectra measured at $V = 3.0$ kV for all of the specimens are identical, and similar to those of the nonborated specimens (specimens 1–5). We have not found in this case any traces of oxidation of the n-Si substrate as a result of electron irradiation. This effect is supported by the measurements done by the nuclear reaction and optical ellipsometry techniques. According to the ellipsometry measurements, the thickness of the SiO₂ layer before the electron irradiation is equal to 580 Å, and after the irradiation it is 590 Å.

This means that preliminary treatment of the SiO₂ (580 Å)/n-Si system by boron implantation blocks oxidation of the n-Si substrate which might otherwise be induced by

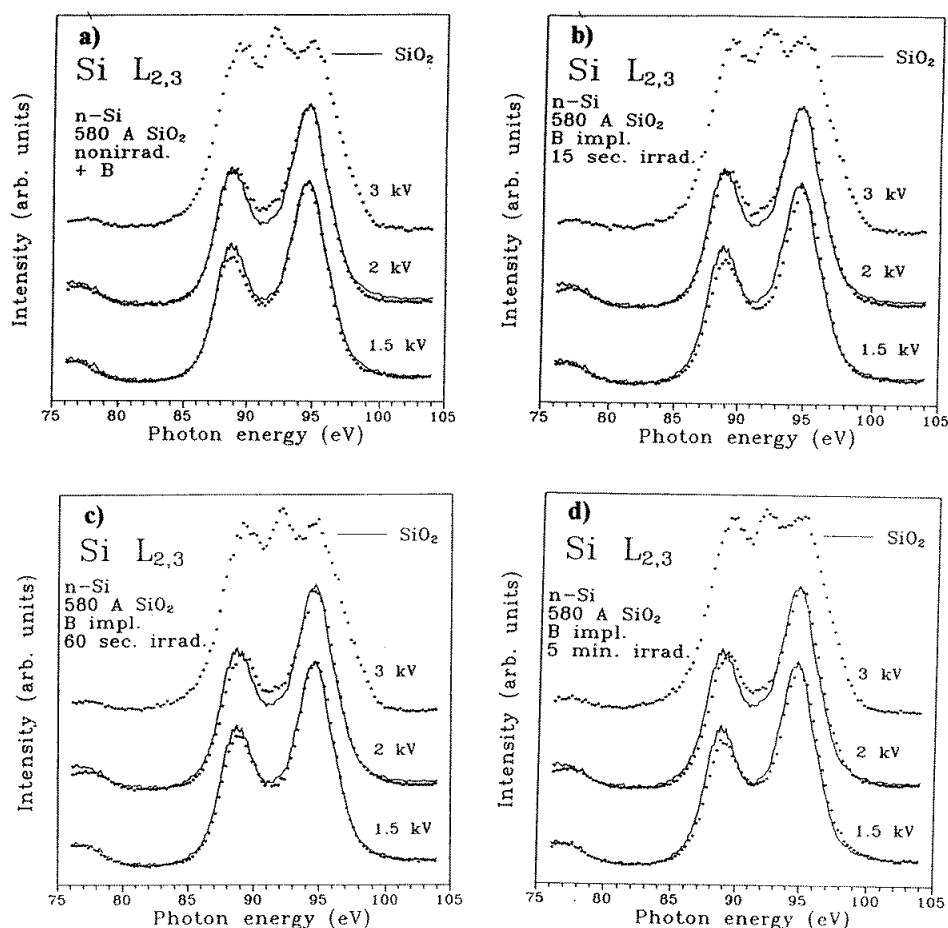


Figure 6. The dependences of the Si $L_{2,3}$ x-ray emission spectra of the SiO_2 (580 Å)/n-Si system initially implanted with boron ions ($E = 26$ keV; $D = 1.2 \times 10^{12}$ cm $^{-2}$) for the specimens that were not irradiated (a) and for those that were irradiated with high-energy electrons ($E = 11$ MeV) (b), (c), (d) on the exposure time: $\tau = 15$ s (b), $\tau = 60$ s (c), and $\tau = 5$ min (d).

high-energy electron irradiation.

Our results present no way of deducing the character of the oxidation: does the oxide growth occur during or after the electron irradiation? This question remains open. New experiments are needed.

4. Conclusion

In summary, the techniques of soft-x-ray emission Si $L_{2,3}$ spectroscopy with variable exciting electron energy, nuclear reactions, and optical ellipsometry have been used to study the dependence of the SiO_2 /Si system on the type of substrate (n-Si or p-Si), the SiO_2 layer thickness, and the irradiation conditions (the duration of the irradiation, and the preliminary boron implantation). It is found that oxidation of the n-Si substrate takes place as a result

of electron irradiation ($E = 12$ meV) for the SiO₂/n-Si system beginning at the exposure time of 30 s. This effect is absent for the electron-irradiated SiO₂/p-Si system under similar conditions. Preliminary boron implantation of the SiO₂/n-Si system blocks oxidation of the n-Si substrate, which might otherwise be induced by electron irradiation.

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Appendix A

As was mentioned in section 3, x-ray emission spectroscopy utilizing variation in the energy of the incident electrons allows one to perform an analysis of the different layers, since the x-ray yield depth is a function of the electron excitation energy. In figures 2 and 5 we estimate the size of the SiO₂ contribution in the SiO₂/Si system probed by the Si L_{2,3} XES for different accelerating voltages applied to the x-ray tube by means of the superposition of the spectra of SiO₂ and c-Si. In order to check the information regarding the depth output obtained experimentally, we have calculated the Si L_{2,3} intensity depth distribution for the electron energies 1.5, 2.0, 3.0, and 4.0 kV, for the SiO₂/Si system with layers of SiO₂ 580 and 239 Å thick. The x-ray intensity $I(\rho z)$ generated by atoms at the depth z was presented as the product of the electron distribution $\varphi(\rho z)$ and the absorption factor $\exp(-\mu_m \rho z / \cos \psi)$. Here ρ is the material density, μ_m is a mass absorption coefficient, and ψ is the collection angle of the x-rays with respect to the normal to the sample surface. The electron distribution function $\varphi(\rho z)$ was approximated by a parabola extending from φ_0 (at $\rho z = 0$) with the maximum at $\rho z = h$, and for $\rho z \geq 1.5h$ as an exponent [19]. The maximum depth of the electron penetration (in Å) was calculated using the expression given in reference [20]: $(\rho z)_{\max} = 250(E^n - E_c^n)A/Z^{n/2}$. Here, A and Z are the effective mass and the atomic number of the target material, E and E_c are the energy of the incident electrons and the ionization energy of the probed core level (keV), respectively, and $n = 1/(1 - 0.29 \log_{10} Z)$. The method of calculation is described in more detail in reference [11]. The results of the calculations are presented in table 2.

One can see that the experimental and calculated values of the SiO₂ contribution for the SiO₂/Si system obtained using the Si L_{2,3} XES with variation of the accelerating voltage applied to the x-ray tube are in good agreement. This means that our experimental determination of the increase in the SiO₂ contribution for the first series of the specimens resulting from high-energy electron irradiation can be used for quantitative estimations.

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