

## INFRARED SPECTROSCOPY STUDY OF Si-SiO<sub>2</sub> STRUCTURES IRRADIATED WITH HIGH-ENERGY ELECTRONS

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Si-SiO<sub>2</sub> structures, fabricated on n-type Si wafers by thermal oxidation in dry oxygen or in wet ambient, were studied by means of infrared transmission spectroscopy in the wavenumber range 800-1400 cm<sup>-1</sup>. Three series of samples were irradiated with 23 MeV electrons at a flux of about 10<sup>13</sup> electrons cm<sup>-2</sup> s<sup>-1</sup> for different durations: 30, 120 and 7200 s. A Si substrate without an oxide film was used as a reference sample. It was demonstrated that as a result of high energy electron irradiation, the main absorption band shifts towards higher wavenumbers and the shape of the absorption band is changed. The absorption band peak position shifts monotonically with increasing electron irradiation dose. The shift depends on the oxide type, varying in the range 7-14 cm<sup>-1</sup>. This effect is most pronounced for samples with wet oxide. Analysis of the absorption band shape enabled us to conclude that the irradiation changes the contribution of 4 and 6-fold SiO<sub>4</sub> tetrahedral rings into the oxide lattice.

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### 1. Introduction

The importance of the Si-SiO<sub>2</sub> structure in the contemporary semiconductor device industry is based on the fact that an extremely stable Si-SiO<sub>2</sub> interface with a low interface state density can be achieved. Electrical methods have commonly been used for rapid technical measurement of interface states at the Si-SiO<sub>2</sub> interface. In particular, radiation-induced interface states, created by various kinds of irradiation, are investigated by electrical methods.

However, employment of spectroscopy analyses such as infrared transmission spectroscopy gives additional valuable information about the structural changes at the Si-SiO<sub>2</sub> interface after irradiation. In this paper, we report the results of an experiment in which the infrared spectra of two groups of Si-SiO<sub>2</sub> samples irradiated with 23 MeV electrons are examined. We compare the structural changes at the Si-SiO<sub>2</sub> interfaces of structures with wet and dry oxide. A rearrangement of the oxide lattice is observed after irradiation. This leads to the formation of the oxygen bridges with larger Si-O-Si bond angles, which are connected with the irradiation-induced traps created during irradiation. This effect depends on the kind of the oxide, i.e. on the ambient in which oxidation was carried out, as well as on the electron irradiation dose.

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## 2. Investigated samples and experimental technique

Si-SiO<sub>2</sub> structures fabricated on two-side polished n-type Si wafers were prepared with different Si-SiO<sub>2</sub> interfaces, as the Si wafers were oxidized in different ambients. Some of the wafers were thermally oxidized in dry oxygen, and some were thermally oxidized in a wet ambient at 1050 °C to produce (in the both cases) 200 nm oxide thickness. Then, both groups of Si-SiO<sub>2</sub> samples were simultaneously irradiated with 23 MeV electrons for different durations: 30, 120 or 7200 s. The average electron beam flux during irradiation was  $8 \times 10^{12}$  el/cm<sup>2</sup>s. The distance between the Microtron window and the sample was 150 mm. The energy (23 MeV) was high enough for electrons to penetrate through the whole Si-SiO<sub>2</sub> structure. Electron irradiation was carried out in a Microtron MT-25, at the Flerov Laboratory of Nuclear Reactions of Joint Institute of Nuclear Research, (FLNR, JINR) Dubna, Russia.

The subsequent investigation was carried out by Infrared (IR) transmission spectroscopy. Spectra were measured in the range 800–1400 cm<sup>-1</sup>, using an IKS-25M automated spectrometer, before and after each dose of high-energy electron irradiation to the samples. A Si substrate without an oxide film was used as a reference sample.

## 3. Experimental results and discussion

The 23 MeV electron influence on the IR spectra on the two kinds of Si-SiO<sub>2</sub> structure is illustrated in Figs.1 and 2. From these figures, it is seen that due to the different doses of high-energy electron irradiation, three important results are observed:

- the intensity of the absorption band increases;
- the maximum position ( $\nu_M$ ) of the main absorption band is shifted towards higher wavenumbers;
- the shape of the absorption band is changed.

The shift of the absorption band is illustrated in the inserts of both figures.

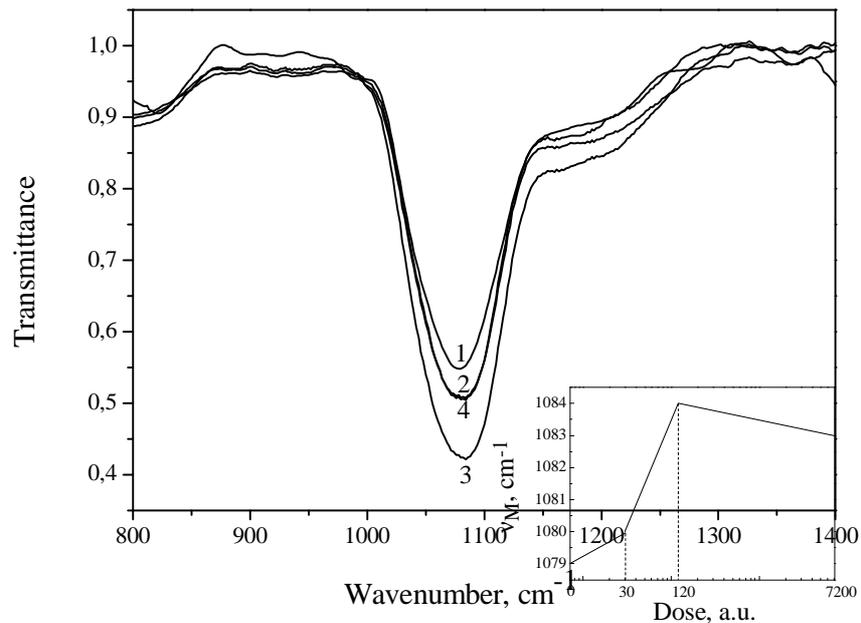


Fig. 1. Effect of 23 MeV electron irradiation on the IR spectra of SiO<sub>2</sub> films, fabricated in dry oxygen before irradiation (1); and after irradiation for 30 s, 120 s and 7200 s, respectively (2, 3 and 4).

Fig. 1 presents the IR spectra of Si-SiO<sub>2</sub> structures prepared in dry oxygen. The initial curve (1) is drawn before electron irradiation. Curves 2, 3 and 4 present the IR spectra of samples irradiated for 30 s, 120 s and 7200 s, respectively. It is seen that curve 4 coincides with that obtained after the first step of irradiation (curve 2). This means that high dose electron irradiation restores the oxygen structural arrangement to the position existing after the lowest irradiation dose.

The results presented in the insert of Fig. 1 show that the shift of the absorption band depends on the electron irradiation dose. In particular, after 30 s irradiation it was about 2 cm<sup>-1</sup>. The shift then increases and achieves a maximal value (about 5 cm<sup>-1</sup>) after 120 s of electron irradiation. At the highest doses, the shift decreases.

Fig. 2 presents the IR spectra of Si-SiO<sub>2</sub> structures with an oxide thermally grown in wet oxygen. Curves 1- 4 are measured under the same conditions as in the previous case. However, in this case the behaviour of the IR spectra of the samples differs from that for the samples with dry oxides. Significant changes in these IR spectra are observed immediately after 30 s electron irradiation. The spectral curves for the samples irradiated with higher doses differ only slightly.

The shift of the absorption band of the samples with oxide produced in a wet ambient is illustrated in the insert of the Fig. 2. It is rather significant (up to 12 cm<sup>-1</sup>). Hence, its value depends on the type of oxide – the effect is higher for the wet oxides. In contrast to the samples with dry oxides, the samples with wet SiO<sub>2</sub> films are characterized by a monotonic dose dependence of the  $\nu_M$  shift value. The maximal changes take place at the beginning of irradiation (after 30 s) and then the curve practically achieves saturation.

The main absorption band for SiO<sub>2</sub> connected with stretching vibrations of bridging oxygen atoms is known to be within the wavenumber range 1000–1100 cm<sup>-1</sup>, and the position of the peak depends on the structural arrangement of the oxygen atoms [1, 2]. The absorbance ( $A = \log(1/T)$ , where T is the transmittance) spectral curves were deconvoluted into Gaussian profiles, whose main characteristics, specifically the positions and intensities of the peaks, were analyzed in the context of the random bonding model. Details of this procedure and the accuracy of the results obtained for SiO<sub>2</sub> films have previously been described [2–4]. The purpose of the analysis was to estimate the contribution of the different kinds of SiO<sub>4</sub> tetrahedral rings to the oxide according to the approach previously suggested by us [3, 4].

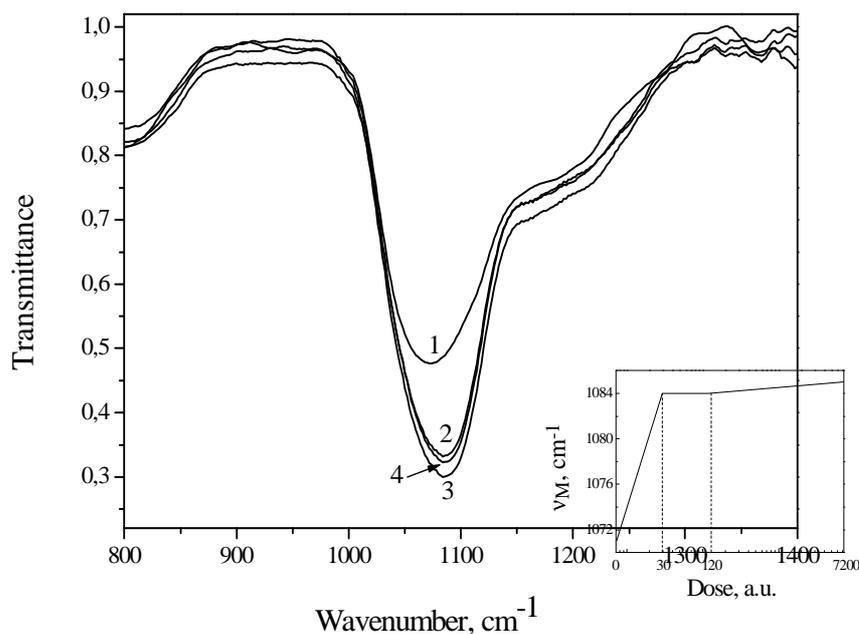


Fig. 2. Effect of 23 MeV electron irradiation on IR spectra of the SiO<sub>2</sub> films, fabricated in wet oxygen (1) before irradiation; (2,3 and 4) after irradiation for 30s, 120 s and 7200 s, respectively.

The shift of the  $\nu_M$  towards higher wavenumbers may be connected with rearrangement of the oxide lattice, leading to the formation of oxygen bridges with larger Si-O-Si bond angles. The analysis of the results of the mathematical deconvolution of the spectral curves is evidence in favor of this assumption.

Table 1. Parameters of the elementary bands (for wet oxides grown on n-Si).

Band	Maximum position, $\text{cm}^{-1}$	FWHM, $\text{cm}^{-1}$	Mode	Si-O-Si angle	Structural component	Contribution of elementary bands %			
						Before irradiation	After irradiation for 30 sec	After irradiation for 120 sec	After irradiation for 7200 sec
1	1050	60	TO	$130^\circ$	4-fold $\text{SiO}_4$ rings	39	34	33	34
2	1090	46	TO	$143^\circ$	4- and 6-fold $\text{SiO}_4$ rings	21	38	36	37
3	1150	52	TO	$180^\circ$	Linear chain of Si-O-Si	14	13	13	12
4	1206	70	LO	$127^\circ$	4-fold $\text{SiO}_4$ rings	26	15	18	17

The parameters of the elementary bands are presented in Table 1. As a result of high energy electron irradiation, the area of the elementary band 1 decreases, while that of the elementary band 2 increases. Band 1 is connected with oxygen atoms incorporated only in 4-fold  $\text{SiO}_4$  tetrahedral rings, while band 2 is connected with oxygen atoms incorporated both in 4-fold and 6-fold rings [3, 4]. Hence, the observed changes in the areas of the bands means that the concentration of the 4-fold rings decreases, while the concentration of 6-fold rings increases. This fact seems to be rather natural, taking into account that 4-fold rings (coesite-like structures) are more deformed and strained, contrary to the case for the more stable 6-fold rings. It is easy to break such strained Si-O bonds by irradiation. Another explanation of this effect may be connected with additional silicon oxidation under electron flow: because the 4-fold rings are known to be predominantly situated near the  $\text{SiO}_2$ -Si interface [4], the lattice of thicker oxides contains a larger contribution by the 6-fold  $\text{SiO}_4$  rings [3].

The decrease of the absorption band area due to high dose electron irradiation may be explained by the formation of radiation-induced defects, including broken Si-O bonds.

Taking into account that the high-energy electron irradiation was performed under vacuum, one may suppose that oxygen atoms which are necessary for silicon oxidation diffuse from the silicon substrate through the radiation defects generated during high-energy electron irradiation [5]. In fact, our investigations have shown that the radiation stimulated oxidation during high-energy electron irradiation depends on the ambient in which irradiation is carried out [6].

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