Research Article / Review Article FUPRE JOURNAL 8(1): 108-116(2024)

FUPRE Journal
of
Scientific and Industrial Research

ISSN: 2579-1184(Print) ISSN: 2578-1129 (Online)

http://fupre.edu.ng/journal

OPTICAL PARAMETERS OF SILICON DIOXIDE THIN FILMS FORMED BY LOW-ENERGY IONS

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ARTICLE INFO

Received: 12/08/2023
Accepted: 22/11/2023

Keywords

IR spectra, Magnetron sputtering, Refractive index, Silicon oxide

ABSTRACT

In this work, optical properties of silicon dioxide thin film were studied. Optical parameters were measured using an IRTracer-100 spectrophotometer (Shimadze). Thin films of silicon oxide were formed on a substrate heated in high vacuum using a magnetron shaker, their absorption, transmission and reflection spectra were obtained, absorption coefficient, refractive index, bonding and vibrations of SiO_2 atoms were measured.

1. INTRODUCTION

One of the methods for directional change in the electrical and other properties of solids is the ion-plasma method, which has a number of advantages over other doping methods. Using low-energy ions, it is possible to control such parameters as the atomic and molecular transfer of oxygen to the silicon surface, the thickness of the doped layer, and the concentration of the introduced mixture, as a result of which the method has become widespread in semiconductor technology and microelectronics *(Stepanov, et at., 2003; Умирзаков, et al., 2012).*

Amorphous porous dielectric films are promising materials for micro-, nano-, and optoelectronics. These materials are used in LEDs, photodetectors, vacuum microelectronic cathodes, biological implants, gas sensors and membranes. Based on them, it is possible to manufacture unheated electronic sources and memory elements. One such material is porous silica. It holds great promise for creating humidity, gas, chemical and biological sensors, as well as other applications. The production and study of amorphous porous films is a priority direction in physical electronics *(Huasong, et al., 2018; Умирзаков, et al., 2022; Нормурадов, et al., 2019).*

In this work, dielectric SiO_2 films obtained by various oxidation methods were studied. There are several ways to produce silicon dioxide: in water vapor, in dry oxygen, in humid oxygen, in atmospheric pressure water vapor, by implantation of low-energy O^+_2 ions and by the ion-plasma method using a magnetron sputtering system. Experiments have shown that SiO_2 films obtained in water vapor are less perfect, while films obtained in an

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atmosphere of dry oxygen are oxidized evenly. Good adhesion, absence of defects and smooth surface are characteristic of SiO_2 films obtained by placing O_2 ions on silicon. In addition, it should be noted that the ion plasma method has advantages over other production methods, since it allows one to obtain films of a certain thickness, from 8 nm to several microns, with a high level of chemical purity *(Boschetto, et al., 2018).*

2. METHODOLOGY

In the chamber of the EPOS-PVD-DESK-PRO magnetron device, a high vacuum was created at a pressure of 10^{-6} Torr using a molecular turbopump. By introducing argon into the chamber, a pressure sufficient to create ion plasma was created, and this process was controlled on the SR-307 monitor of the Magnetron device. The current from the magnetron power supply was 657 mA, power 221 W, voltage 336 V. Air was sucked into the chamber to a pressure of 10^{-5} Torr using a turbopump. Initially, thin films of silicon oxide of various thicknesses were created at room temperature and a pressure of $3{\cdot}10^{-4}$ mbar using the ion-plasma method.

Elemental analysis of the resulting SiO_2 thin films was carried out using energy-dispersive X-ray spectroscopy, and the surface morphology was studied using a Quanta 200 microscope (Scios FEI).

3. RESULTS AND DISCUSSION

3.1 Results Presentation

SEM a thin film of silicon oxide (SiO_2) obtained a low-energy ion plasma method using a magnetron sputtering device, as well as the chemical composition and energy dispersive X-ray diffraction pattern of a SiO_2 sample obtained after oxide layers 160-240 nm thick at high temperature as a substrate prepared with using an energy dispersive device. Analysis were performed on a Quanta 200 microscope (Scios FEI) (Fig. 2). Results (O-wt.% - 34.27, At% -35.94), (Si-wt.% - 65.73, At% -64.06) elements were determined in fractions.

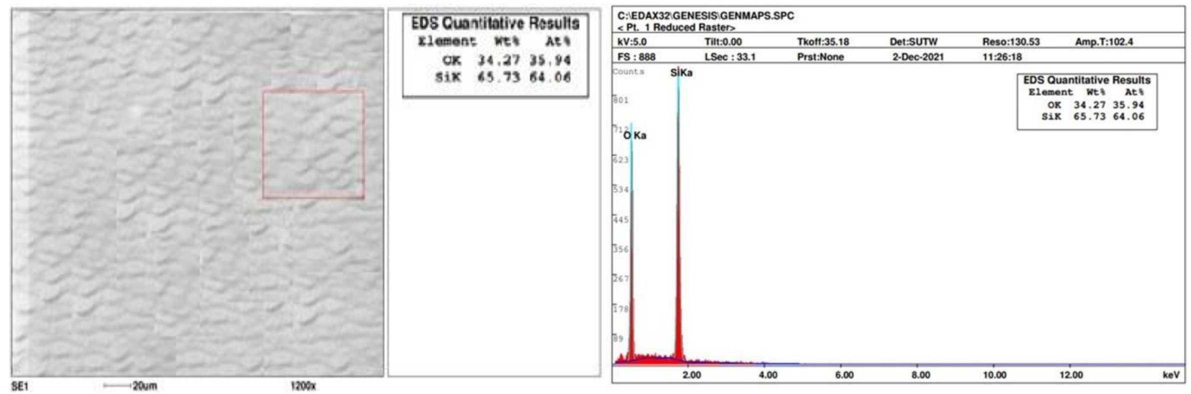

Fig. 1. SiO_2 chemical composition and energy dispersive X-ray diffraction analysis

The layer thicknesses of thin SiO_2 films grown on the silicon surface were measured by transmission methods and the single reflection ATR method (Ge prism) at incidence angles of 45° and 90°. The thickness of SiO_2 films is 250, 200 and

150 nm. Figure 2 shows the ATR measurement results. As the oxide layer becomes thinner, the peaks around 1258 cm^{-1} and 1164 cm^{-1} shift towards higher (or lower wavenumber) wavelengths.

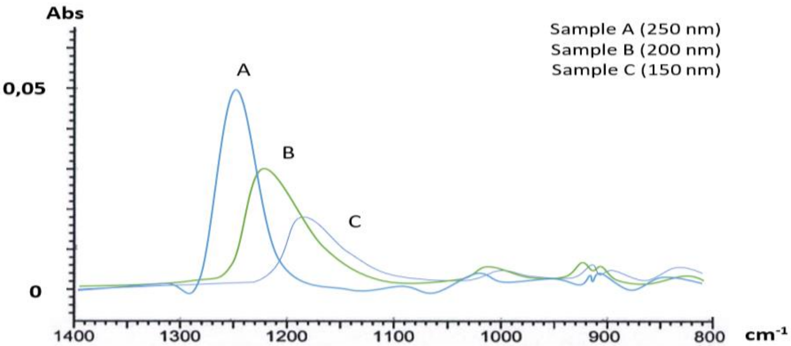

Figure 2. Results of ATR measurements of SiO_2 film

Structural changes in dielectric films were assessed using FTIR transmission spectroscopy and multiple attenuated total internal reflection (ATR) *(Milekhin, et al., 2006)*. An IR Fourier spectrometer "IRTracer-100" was used. To study the structure and composition of SiO_2 films by the ATR method, trapezoidal n-germanium samples with a resistivity of 18 Ω cm, which are transparent in the wavelength range of interest, were used.

To analyze SiO_2 glasses in the range of ~ 1565÷1271 cm^{-1}, high-resistivity silicon with a resistivity of 15 kΩ cm was also used as a Marv sample. The thicknesses of dielectric films were measured by the ellipsometric method. Scanning electron and atomic force microscopy were used to analyze the effect of high-temperature annealing on the structure of dielectric-semiconductor samples.

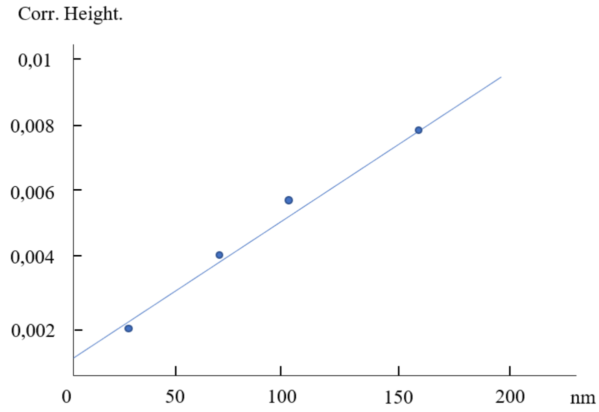

Figure 3. Photometric graphical results of silicon oxide films of different thicknesses

Peak height is plotted on the vertical axis and film thickness is plotted on the horizontal axis to determine the relationship between peak intensity and film thickness in the 45° transmittance spectra. Fig. 3 shows the results for low wavelengths. These results indicate that a

good correlation was achieved between peak intensity and film thickness.

The IR transmission and absorption spectra of films deposited in the region characteristic of the Si-O vibrational zones are shown in Figure 8. They are very similar because they have similar chemical composition and structure. The overall higher intensity in the IR spectra of samples A (green) and B (red) is due to the larger film thickness. The assignment of IR vibration bands to the spectra of films deposited under various plasma conditions is given in Table 1.

As can be seen from Fig. 4, the IR spectra show characteristic vibrational bands at 1080, 800 and 445 cm^{-1}, corresponding to stretching, bending and out-of-plane strain of Si-O bonds, respectively. It has a transmittance of 35.21% at wavenumber 893 cm^{-1} of the main Si-O vibration line and a transmittance of 50% at 758 cm^{-1}. In the absorption spectrum, 45.3% of the light is absorbed at a wavelength of 11197.7 nm. The absorption at 13192.6 nm was 30%, and a well-defined shoulder indicates the stoichiometric structure of silica. At the same time, bands associated with impurities are also observed. The main peaks of light transmission were 893.04 cm^{-1}. Therefore, the existence of stretching vibrations of Si and OH groups at these peaks can be emphasized.

When silicon oxidizes (naturally in an air atmosphere or under the influence of high temperature), Si-OH hydroxyl groups are formed on its surface, and SiO_x groups are formed in the surface layer. The presence of hydroxyl groups leads to the adsorption of atmospheric moisture and corresponding changes in the spectra of the samples. The absorption and transmission spectra of SiO_2 films obtained by the ion-plasma method were obtained on an IRTracer-100 spectrophotometer using the Happ-Ganzel method. In the range of 400÷4000 cm^{-1}, in order to reduce the influence of water vapor (H_2O) and carbon dioxide (CO_2) molecules, several of the following corrections were made: addition, smoothing, baseline zero correction, normalization, filtering and ATR. Correction *(Селезнев, and Федоров, 2017).*

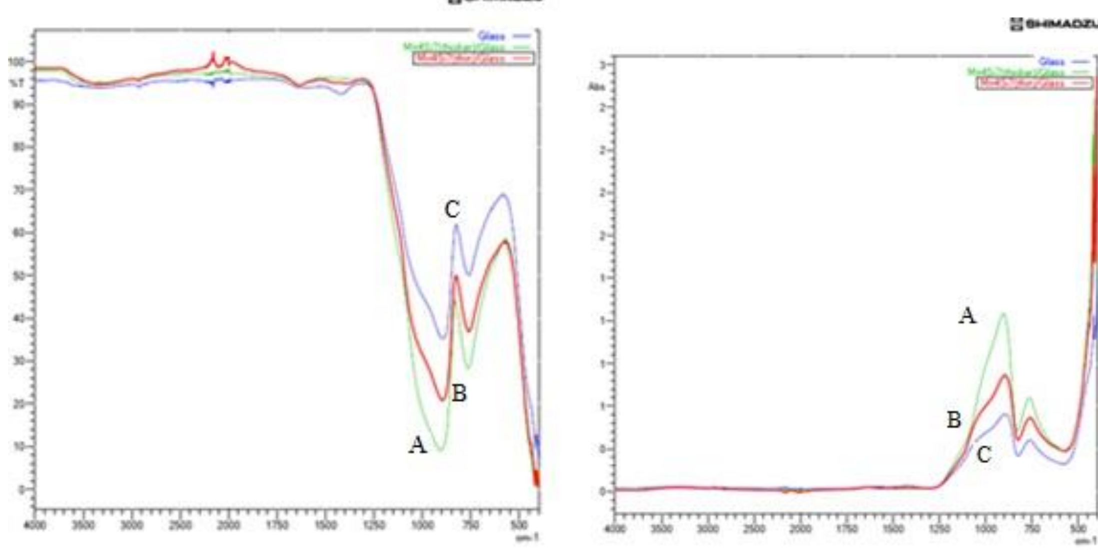

Figure 4. Transmission and absorption spectra of thin SiO_2 films of various thicknesses formed by low-energy O^+ ions

Table 1: Results of IR analysis of SiO_2 films of various thicknesses

Vibrational modes of chemical bonds	Sample A (d=150 nm) O_2 flow, 3 sccm	Sample B (d = 200 nm) O_2 flow, 10 sccm	Sample C (d=250 nm) O_2 flow, 14 sccm
Bending vibrations from Si-O plane strain	Large peaks superimposed on the strong band at 445cm^{-1}	Large peaks superimposed on the strong band at 445 cm^{-1}.	Large peaks superimposed on the strong band at 445 cm^{-1}.
Si-OH stretching Stretching vibrations	760 cm^{-1} weak band	760 cm^{-1} strong band	760 cm^{-1} strong band
Si-O - Stretching vibrations-Si stretching	890 sm^{-1}	895 cm^{-1} with a well-defined step	895 cм$^{-1}$ with a well-defined step
Si-OH deformation; CH bending vibrations	Very small peaks located at 1500-1700 cm^{-1}.	small peaks located at 1500-1700 cm^{-1}.	small peaks located at 1500-1700 cm^{-1}.

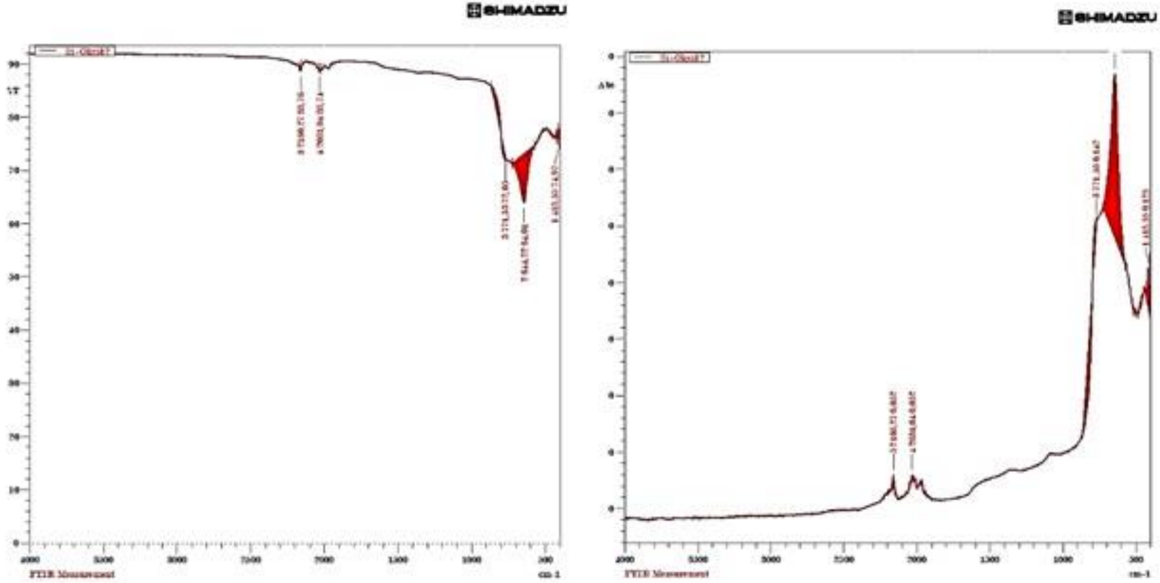

Figure 5. Smoothing analysis of transmission and absorption spectra of SiO_2/Si

Fig. 5 shows the infrared absorption and transmission spectra of the SiO_2 film formed on the silicon surface. In the absorption spectrum, a peak was observed at 769.60 cm^{-1}. These lines correspond to the antisymmetric stretching vibrations of the Si-O-Si groups, respectively. The peak of the transmission spectrum in the region of 644.22 cm^{-1} corresponds to the “fingerprint” region of the spectrum of pure silicon. Silica layers have three absorption bands: a low-frequency band at 418.55 cm^{-1}, a weak band at 771.53 cm^{-1}, and an intense broadband band with a maximum at 644.22 cm^{-1}. These lines are associated with pendulum vibrations, symmetric and antisymmetric stretching of Si-O-Si groups (Нормурадов, et al., 2022) [9]. Depending on the brittleness, the last line of the oxide can have a half-width from 95 cm^{-1} to 140 cm^{-1} for a dense oxide. The study of silicon oxides showed that during deposition SiO_x ($x=1\div2$) is formed, and during annealing with decreasing x, the limit of the maximum of the lower wave numbers of the n-band (Si–O–Si) shifts to the region (915 cm^{-1} at x= 1, 980 cm^{-1} at x=2). on the contrary, it increases from 780 to 835 cm^{-1}; the

pendulum's oscillation frequency increases with x (Fig. 4).

The penetration depth of infrared light depends on the sample and the refractive index of the crystal. Because the refractive index is wavelength dependent, ATR spectra have slightly different intensity ratios across the spectrum and may require adjustment for comparison with transmission spectra.

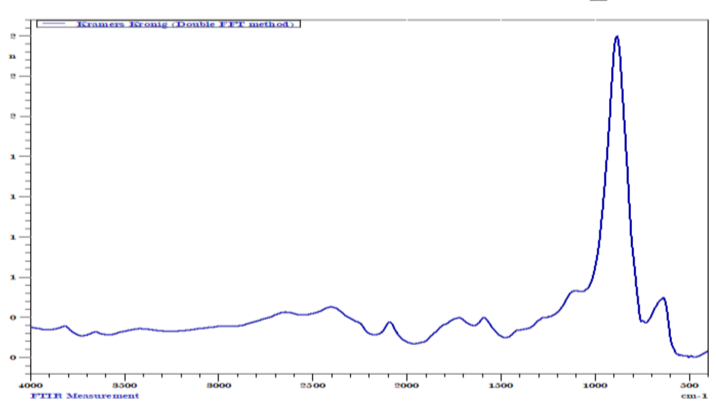

Figure 6. Spectrum of silicon Kramers-Kronig SiO_2/Si obtained using measuring FT-IR spectroscopy using the "double FFT" method.

We used the following modified Sellmeyer Edwards et al. expression, which is the most appropriate dispersion equation for ambient temperature *(Некрашевич, and Гриценко, 2014).*

$$n^2 = \varepsilon + \frac{A}{\lambda^2} + \frac{B\lambda_1^2}{\left(\lambda^2 - \lambda_1^2\right)}$$

here λ_1 =1,1071 μm, ε=1.16858:101, A=9,39816·10^{-1} and B=8,1046·10^{-3}. The results obtained gave λ=1,99807 microns for silicon and λ=1,0111223 microns for silicon oxide.

Knowing the angle of incidence and refractive index in the "calculate film density" function in the data processing unit of the IRTracer-100 spectrophotometer, you can measure the film thickness, the average number of interference fields and the standard deviation. Table 2 below shows the measured parameters of films of various thicknesses obtained on a magnetron device.

Table 2: Comparative comparison of optical parameters of Si and SiO_2 films

Sample	**Si(111)**	**SiO_2/Si(111)**	**Ref, Si(111)**
Range(cm^{-1})	503	465 – 1397	587,6 *(Queeney, et al., 2000)*
Refractive index	3,45323	1,494	3,9766 *(Queeney, et al., 2000)*
Angle of incidence	45°	90°	
Middle edges of intervention	24	122	
Thickness (μm)	51,34	12,36	
Standard Deviation (μm)	10,06	64,32	
Absorption coefficient	0,03241	0,00423	0,030209 *(Queeney, et al., 2000)*
Minimum Peak (%)	47.6527	64.007	23.47
Maximum Peak (%)	96.5350	92.099	64.35

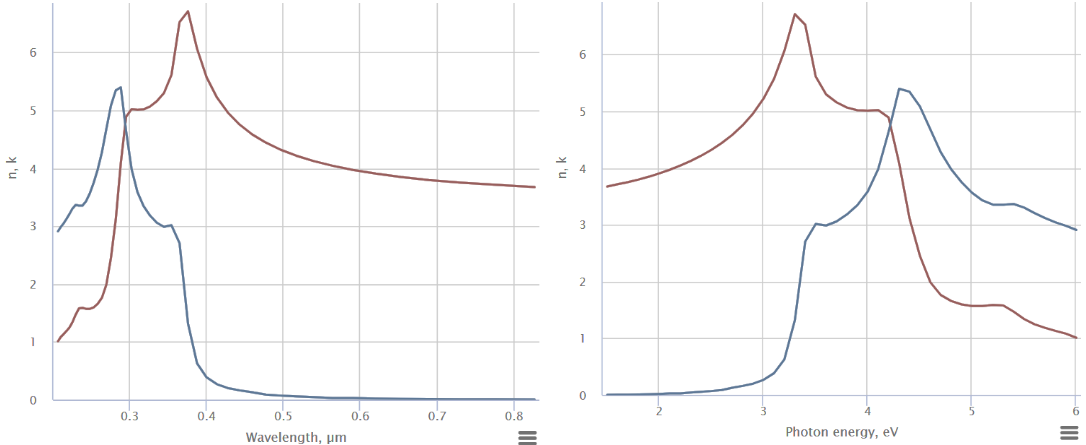

Figure 7. Refractive index and absorption coefficient of Si sample *(Queeney, et al., 2000; Hamelmann, et al., 2005)*

The data in the cited sources is as follows wavelength 0.5876 µm, refractive index: n=3.9766, absorption coefficient k=0.030209, complex refractive index (n+ik) *(Queeney, et al., 2000).*

Fig. 8 shows the spectral dependence of the refractive index of samples A, B and C, as well as the refractive index of stoichiometric thermally grown SiO_2. The physical composition of the films was analyzed using ellipsometric data. The results showed a slightly lower stoichiometric composition of $SiO_{1.985}$ for sample A and $SiO_{1.938}$ for sample C. However, increasing the oxygen flow rate to 12 cm^3 results in the formation of voids with a volume fraction of ~1.5%. This result explains the observed lower refractive index values with decreasing film thickness.

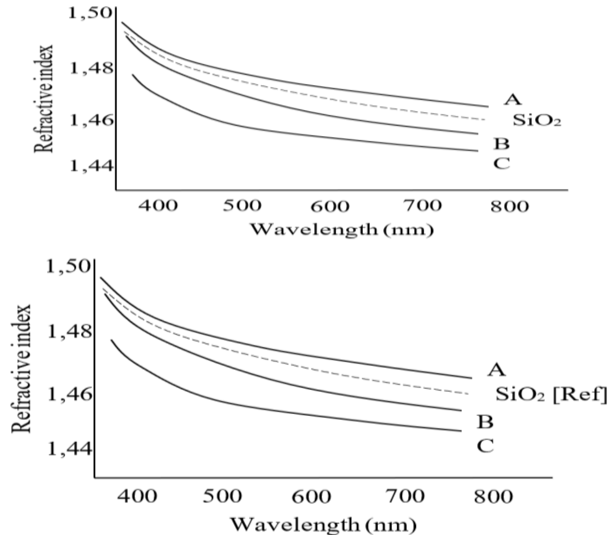

Figure 8. Refractive index dispersion of silicon oxide films deposited at different thicknesses

As can be seen from Fig. 8, both the refractive index and extinction coefficient of the SiO_2 film change with wavelength, indicating that the SiO_2 film has a certain dispersion. The refractive index and extinction coefficient of the deposited SiO_2 thin films at a wavelength of 250 nm are 1.494 and 0.00423, respectively.

3.2 Discussion

In this paper, the optical properties of dielectric SiO2 films obtained by magnetron sputtering and thermal oxidation in a dry oxygen atmosphere were studied. A silicon oxide film obtained by magnetron sputtering was studied using energy dispersive X-ray spectroscopy using elemental analysis of the sample; surface morphology was studied using a Quanta 200 microscope (Scios FEI), optical parameters were measured using an IRTracer-100 spectrophotometer (Shimadze).
The obtained results confirm the qualitative and quantitative analysis of the formation of thin layers of silicon oxide grown with the help of low-energy ions by ion-plasma method, SiO2-Si interface, as well as vibrational methods of chemical bonding, absorption and transmission spectra of nanofilms. The thickness and refractive index of the thin film were measured by analytical and experimental methods. Refractive index for silicon is n=3.45323 and for silicon oxide n=1.494. "Mean noise limits" were measured for silicon oxide and pure silicon. The penetration depth of infrared light into the crystal was measured. The results show that the as-deposited SiO2 thin films can be used in optical films with low refractive index.

Acknowledgments
We are very grateful to Elena Nikolaevna Vlasova, head of Laboratory No. 21 of the Institute of Macromolecular Compounds of the Russian Academy of Sciences (IMC RAS) for her review of this work.

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