Effect of heat treatment temperature on the properties of silicon dioxide films derived from film-forming solutions

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Abstract. The effect of the heat treatment temperature on the physical properties of sol-gel silicon dioxide films derived from film-forming solutions is investigated experimentally. The dependencies of the thickness of the films, their refractive index, electrical strength, resistivity, etching rate, and the level of internal mechanical stresses on the treatment temperatures in the range from 700 to 1150 °C are obtained. It was found that the dependencies of the electrical strength, the etching rate, and the level of internal mechanical stresses have the sections with different characters. The transition region between these sections corresponds to the heat treatment temperature equal to 900-950 °C.

Keywords: film-forming solution, tetraethoxysilane, silicon dioxide film, refractive index, dielectric strength, internal mechanical stresses

1. Introduction
Thin films based on silicon dioxide obtained by sol-gel method are widely used in various technique applications [1, 2]. The constituent part of the process of obtaining these films from film-forming solutions is the thermal treatment of the spin-coated or sprayed films, as a result of which its final formation is occurred. During heat treatment, the main factors determining the properties of the films are the temperature and processing time, as well as the environment in which the films are processed. Among these factors, the heat treatment temperature has the greatest influence.

The effect of heat treatment temperature on properties of the silicon dioxide films obtained by sol-gel method was studied in many papers [3-10]. These papers considered the dependences of the following properties of the films on the heat treatment temperature: film shrinkage [3], film refractive index [3, 4], intrinsic stress [3, 5, 7-9], film thickness [4, 5, 7-9], film porosity [4, 6, 9], dielectric constant [6], leakage current density [6], transmittance spectra [10], infrared absorption spectra [7]. However, the results presented in the above papers are not complete. First, the change in the properties of films at high-temperature treatment (more 700 °C) has not been enough considered. Second, there is no comparison of changes in various properties of the films in the range of the heat treatment temperatures.

The aim of this work is to comprehensively study the effect of high-temperature treatment on the physical properties of silicon dioxide films derived from film-forming solutions.

2. Experiment details
The solution for the deposition of silicon dioxide films have been prepared by hydrolytic polycondensation of tetraethoxysilane. The substrates were silicon wafers with the (111) orientation and the resistivity of 7.5 Ohm•m. The silicon dioxide films were derived by spin coating at a rotation speed of 2000 rpm. The heat treatment of the films was carried out in the temperature range from 700 to 1150 °C in an oxygen atmosphere during 5 minutes.
The thickness of the obtained films and their refractive index were measured using an LEM-3M ellipsometer with a wavelength of 632.8 nm. The dielectric strength of the films was found as the ratio of the breakdown voltage to the film thickness. The breakdown voltage of silicon dioxide films was determined from the current jump in the electrode-film-substrate system at a voltage change rate of 20 V/s. The resistivity of the films was determined from the measured resistance of the “electrode-film-substrate” system. Internal mechanical stresses in the films were found by measuring the deformation of the “film-substrate” structures using a prism interferometer, which makes it possible to study the deformations of samples with a deflection arrow of 0.3–150 µm. Taking into account that the silicon dioxide film is much thinner than the substrate and isotropic, the maximum internal stress in the film can be calculated as follows [11]

\[
\sigma_{\text{max}} = \frac{E t_s^2 h}{3(1 - \nu) t_f r^2},
\]

where

- \(E\) – the Young's modulus of the substrate material, equal to 169 GPa;
- \(\nu\) – the Poisson's ratio of the substrate material equal to 0.2624,
- \(t_s, t_f\) – the thickness of the substrate and film, respectively;
- \(h\) – the deflection of the "film-substrate" structure in the centre;
- \(r\) – the radius of the substrate.

3. Results and Discussion
The changes of the thickness and refractive index of the silicon dioxide films depending on the heat treatment temperature are shown in figures 1 and 2, respectively. With increasing the treatment temperature the thickness of the films decreases and their refractive index grows. In the entire investigated temperature range, the film thickness decreases by about 13 percent.

Figure 1. Thickness of the silicon dioxide film as a function of the heat treatment temperature.
Figure 2. Refractive index of the silicon dioxide film as a function of the heat treatment temperature.

The dielectric strength (figure 3) of the films increases with increasing the heat treatment temperature. At the dependence of the dielectric strength, the two sections can be distinguished: section I – from 700 to 900 °C; section II – from 900 to 1150 °C. In section I, there is a sharp increase of the dielectric strength of the films by a factor of 2.5. In section II, the dielectric strength continues to increase monotonically with increasing the treatment temperature, but this increase is insignificant. The dependence of the resistivity of silicon dioxide films on the heat treatment temperature is shown in figure 4. With increasing the temperature, the resistivity of silicon dioxide films increases significantly approximately in 10 times.

Figure 3. Dielectric strength of the silicon dioxide film as a function of the heat treatment temperature.
The important parameter characterizing the structure of the film is an etching rate. Figure 5 shows the dependence of the etching rate of silicon dioxide films in the P-etchant (15 parts hydrofluoric acid (49%), 10 parts nitric acid (70%), and 300 parts water) [12] on the treatment temperature. For the films processed at temperatures from 700 to 900 °C, the etching rate decreases linearly with increasing temperature. For the films obtained with the heat treatment at temperature range of 900-1000 °C, the significant decrease of the etching rate is observed. This decrease is by more than 2.5 times. The etching rate of the films heat-treated at the temperatures above 1000 °C, continues to decrease. For the films derived at these temperatures the values of etching rate in P-etchant are close to the ones typical for thermal silicon oxide thin films (less than 1 nm/s).
The dependence of the internal stress level in the silicon dioxide film on the heat treatment temperature is shown in figure 6. As it can see from the given dependence, at treatment temperatures of about 900 °C, the sign of the internal stresses in the film changes. Tensile stresses are typical for films with treatment temperatures below 900 °C. The absolute value of these stresses decreases with increasing the treatment temperature. For the films, the treatment temperature of which was above 900 °C, compressive stresses are characteristic, as well as for silicon dioxide films obtained by thermal oxidation. In this case, with increasing the treatment temperature the absolute value of these stresses increases. Since the thickness of the silicon dioxide films decrease with increasing the treatment temperature (see figure 1), and the heat treatment time was only 5 minutes, this effect cannot obviously be associated with additional oxidation of the silicon substrate. This fact can be regarded as the evidence that the internal stresses in silicon dioxide films obtained with the heat treatment at the temperatures above 900 °C are caused by the difference in the thermal expansion coefficients of the silicon dioxide film and the substrate, as well as for the silicon dioxide films obtained by thermal oxidation. This also indicates that the structure of silicon dioxide films derived from film-forming solutions with the subsequent heat treatment above 900 °C is close to the structure of the silicon dioxide films obtained by thermal oxidation. In its turn the internal stresses in the silicon dioxide films obtained with the heat treatment at temperatures below 900 °C are intrinsic stresses which associated with the formation process of these films from thin-forming solutions.

It is also necessary to pay attention to the coincidence of the heat treatment temperatures of the silicon dioxide films, at which the sign of the internal stresses in the films and the etching nature of them change.

![Figure 6. Internal stress in the silicon dioxide film as a function of the heat treatment temperature.](image)

4. Conclusion
Thus, the processing temperature significantly affects the physical properties of the silicon dioxide films derived from film-forming solutions. Moreover, at the heat treatment temperature of about 900 °C, the nature of the internal stresses in the films changes. With increasing the heat treatment temperature the tensile stress in the films transform in the compressive one. The same temperature range causes a noticeable change in the temperature dependence of other properties of silicon dioxide films.
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