ISSN:
2181-3906
2024

International scientific journal
«MODERN SCIENCE AND RESEARCH»
VOLUME 3 / ISSUE 2 / UIF:8.2 / MODERNSCIENCE.UZ

COMPOSITION AND MORPHOLOGY OF THE SURFACE OF Si (111) WITH SURFACE FILM OF SiO2 OF DIFFERENT THICKNESS

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https://doi.org/10.5281/zenodo.10629023

Abstract. *The composition, morphology, and electronic structure of SiO_2 nanofilms of different thicknesses created by thermal oxidation on the Si(111) surface were studied in this work. It was shown that up to a thickness of 30-40 Å the film has an island character. At $d \geq 60$ Å, a homogeneous continuous film of SiO_2 is formed, the stoichiometric surface roughness does not exceed 1.5 – 2 nm. Regardless of the thickness of the SiO_2 films, no noticeable interdiffusion of atoms is observed at the SiO_2-Si boundary. The patterns of changes in the composition, the degree of surface coverage, and the energy of plasma oscillations were determined when the thickness of the SiO_2/Si(111) films varied from 20 to 120 Å.*

Key words: *thermal oxidation, nanophases, nanofilms, plasma oscillation, surface roughness, Auger peaks, Raman spectra, optical-phonon mode, island growth.*

СОСТАВ И МОРФОЛОГИЯ ПОВЕРХНОСТИ Si(111) С ПОВЕРХНОСТНОЙ ПЛЕНКОЙ SiO2 РАЗНОЙ ТОЛЩИНЫ

Аннотация. *В работе исследованы состав, морфология и электронная структура нанопленок SiO2 различной толщины, созданных термическим окислением на поверхности Si(111). Показано, что до толщины 30–40 Å пленка имеет островной характер. При $d \geq 60$ Å формируется однородная сплошная пленка SiO2, стехиометрическая шероховатость поверхности не превышает 1,5 – 2 нм. Независимо от толщины пленок SiO2 заметной взаимной диффузии атомов на границе SiO2-Si не наблюдается. Определены закономерности изменения состава, степени покрытия поверхности и энергии плазменных колебаний при изменении толщины пленок SiO2/Si(111) от 20 до 120 Å.*

Ключевые слова: *термическое окисление, нанофазы, нанопленки, плазменные колебания, шероховатость поверхности, оже-пики, спектры комбинационного рассеяния света, оптико-фононная мода, рост островков.*

Introduction

Heterofilm structures of the SiO2/Si type and multilayer systems based on them are widely used and promising for the creation of new solid-state electronics devices, in particular, in the development of ultra-high-frequency MOS transistors, integrated circuits, memory elements and displays, photoconverters, solar cells, etc. Such structures They are mainly created by methods of thermal oxidation, ion-plasma deposition, and ion implantation.

Currently, the composition, structure and properties of SiO2/Si films of various thicknesses obtained by various methods have been well studied [1-5]. In this case, the most uniform nanofilms ($d \leq 50$-60 Å) of SiO2, as in the case of metal silicides [6-9], were obtained by the method of low-energy ion implantation in combination with annealing [4, 5].

The presence of excess silicon atoms or clusters in thin films of SiO_2 and metal silicides leads to a significant change in their physical properties [10-12]. In the case of thin films ($d \leq 10$

nm) SiO_2/Si, diffusion of Si atoms into the SiO2 film can occur. However, there is still no reliable information about the dynamics of changes in the morphology, composition, crystalline and electronic structure of SiO_2/Si nanofilms with a thickness from d ≈ 20 Å to 100 Å, obtained by thermal oxidation. Solving this problem was the main goal of this work.

Experimental technique

The objects of study were amorphous SiO_2 films created on the Si(111) surface by thermal oxidation in a dry oxygen atmosphere. Studies of the composition, electronic structure, emission and optical properties were carried out using the methods of Auger electron spectroscopy (AES), characteristic electron energy loss spectroscopy (CHLES), ultraviolet photoelectron spectroscopy (UFES) on the same ultra-high vacuum device at $P = 10^{-7}$ Pa.

The surface morphology and crystal structure were studied using standard scanning electron microscopy SUPRA-40, atomic force microscopy (XE-200) and Raman spectrometer. The depth distribution profiles of atoms were recorded using the OES method in combination with surface etching with Ar^+ ions.

Films with thickness d = 20, 40, 60, 80, 100 and 500 Å were mainly used. Before the study, the samples were evacuated at T = 900 K for 4-5 hours at a pressure of at least 10^{-7} Pa.

Results of experiments and their discussions

In Fig. Figure 1 shows an SEM image of the surface of a SiO2/Si film with d ≈ 20 Å. It can be seen that the film has an island character.

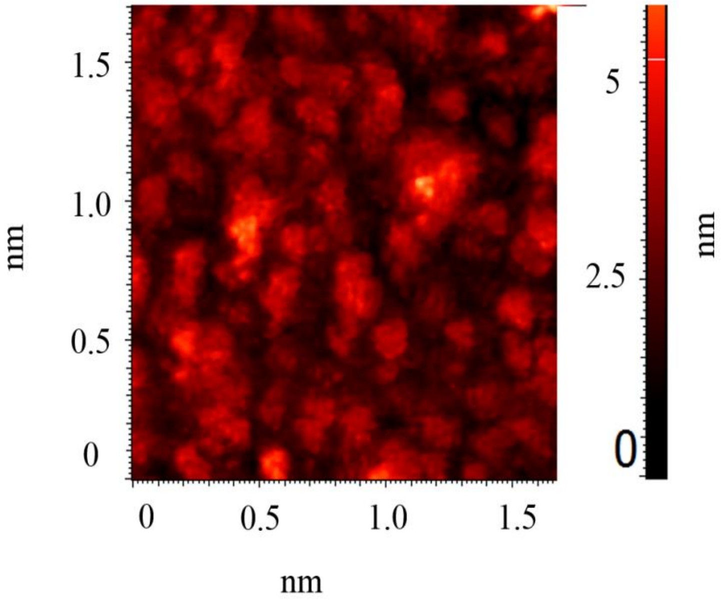

Fig. 1. SEM image of the surface of a Si film with a SiO_2 film 20 Å thick.

The average surface dimensions of the islands are 40–50 nm. Further studies showed that with increasing oxidation time, the sizes of the islands increase; starting from d ≈ 40 Å, the boundaries of neighboring islands overlap and a continuous SiO_2 film is formed.

In Fig. Figure 2 shows Auger spectra of SiO_2/Si(111) films of different thicknesses, recorded in the region E ≈ 70-100 eV.

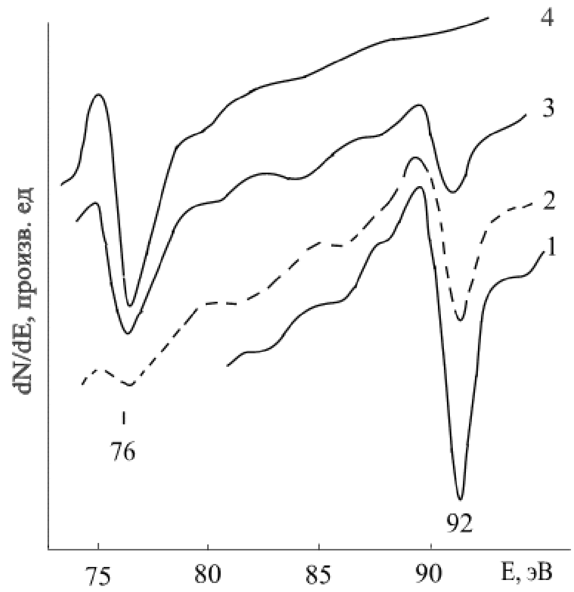

Fig. 2. Auger electron spectra of Si(III) with SiO_2 nanofilm of different thicknesses d, Å: 1-0; 2-20; 3-40; 4-80

Auger spectra were recorded at the primary beam electron energy Ep = 2500 eV. Already at d = 20 Å, a low-intensity SiO_2 peak with E ≈ 76 eV appears in the Auger spectrum. As d increases, the intensity of the SiO_2 peak increases and at d ≈ 60 Å reaches its maximum value, and the intensity of the Si peak decreases to zero (within the sensitivity of the Auger spectrometer).

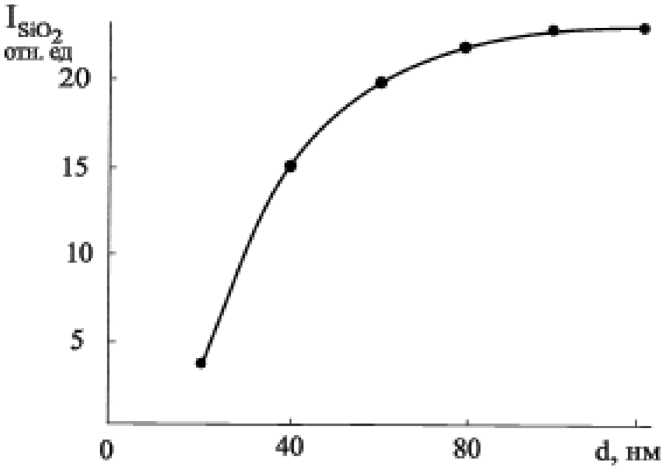

Fig.3. Dependence of the intensity of the Auger peak of SiO_2 (E = 76 eV) on the thickness of the SiO_2 film

As can be seen from Fig. 3, the intensity of $ISiO_2$ increases almost linearly up to d ≈ 40 Å, and exponentially in the range d = 40-80 Å. At d > 80 Å, the intensity of $ISiO_2$ remains virtually unchanged, and the Auger peak of pure Si completely disappears. Analysis of Auger electron spectra together with SEM images showed that in the range d ≈ 0-40 Å the linear growth of $ISiO_2$ is mainly associated with an increase in the size of surface islands, i.e. with the degree of coverage of the Si surface with SiO_2 islands. Due to the fact that at d ≈ 40 Å a continuous film of SiO_2 begins to form, the increase in $ISiO_2$ in the range d ≈ 40-80 Å is explained by a decrease in the influence of the substrate (silicon) on the yield of secondary electrons. At d ≥ 80 Å, Auger electrons emerge only from the SiO2 film. From these data it is clear that in the case of thin SiO_2/Si films, no noticeable diffusion of substrate atoms into the oxide film occurs.

HPEE spectra also provide rich information about the surface composition and the density of state of the valence electrons. In particular, measuring plasmon energy can serve to identify samples. In Fig. Figure 4 shows the SEE of $SiO_2/Si(111)$ films of different thicknesses.

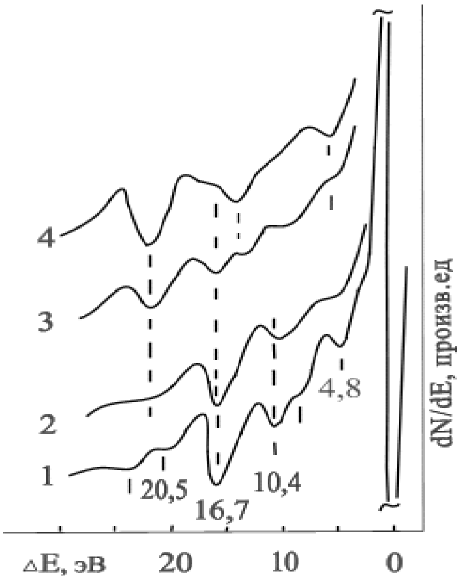

Fig. 4. Si XPEE with SiO2 film with thickness d, Å: 1-0; 2-20; 3-40; 4-60.

It can be seen that with increasing film thickness, the contribution of Si (substrate) to the yield of electrons with characteristic losses decreases, and that from the SiO2 film increases accordingly. At $dSiO_2 = 20$ Å, along with the intense peaks of plasma vibrations (hωs, hωv, 2hωs) of Si, a low-intensity peak of the bulk plasmon SiO2 with E ≈ 22 eV appears in the spectrum. As d increases, the intensity of this peak increases, and the intensity of the Si peaks decreases. Starting from d = 40 Å, another peak is detected at E = 14.5 eV, associated with the excitation of the SiO2 surface plasmon. Apparently, the excitation of the SiO2 surface plasmon occurs after the formation of a continuous film. At d ≈ 60 Å, the CPEE spectrum characteristic of bulk SiO2 films is completely established.

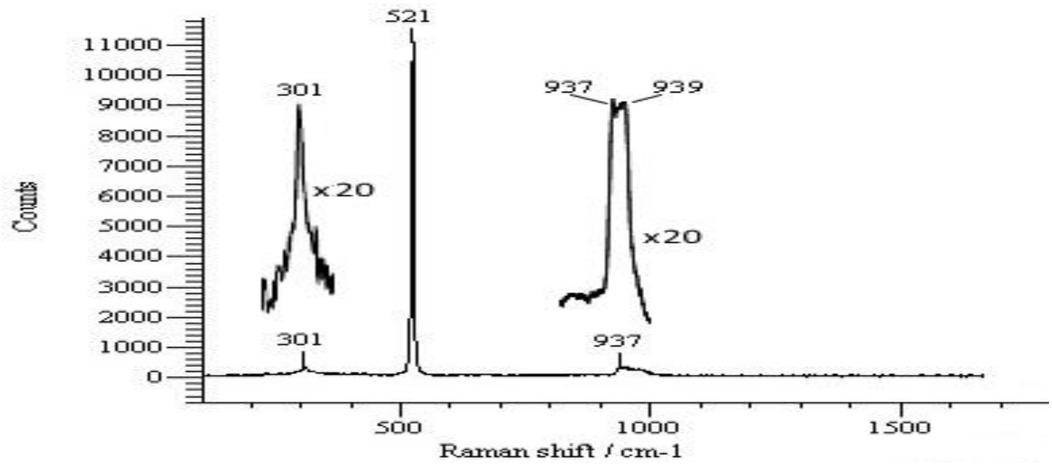

Fig. 5. Raman spectra of Si(111) with a SiO2 film 100 Å thick.

In Fig. Figure 5 shows the Raman spectra of Si(111) with a SiO2 film 100 Å thick. It can be seen that at ~520 cm^{-1} a very intense peak of the optical phonon mode of pure single-crystal Si is detected. The peak of the optical phonon mode of Si of the second order (943 – 980 cm^{-1}) is greatly broadened, which is associated with the presence of a thin amorphous layer of SiO_2 on the Si surface.

Conclusion

Based on the analysis of the results obtained in the work, the following conclusions can be drawn: SiO2 films obtained by the method of thermal oxidation of Si to a thickness of -40 Å have an island character; at d ≥ 60 Å, a continuous amorphous homogeneous film is formed. In all cases, the SiO2 films have good stoichiometry and no interdiffusion of atoms is observed at the SiO2/Si(111) interface. Already at a thickness of 20 Å, a peak appears in the CPEE spectrum at $\Delta E \approx 22$ eV, characteristic of the bulk plasmon of SiO2, and at a thickness of 40 Å, a peak of surface plasmon.

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