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ScienceDirect
Applied Surface Science 253 (2006) 412–416
applied surface science
www.elsevier.com/locate/apsusc

Characterization of ion species of silicon oxide films using positive and negative secondary ion mass spectra

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Accepted 5 December 2005
Available online 24 January 2006

Abstract

Secondary ion species of silicon oxide films have been investigated using time-of-flight secondary ion mass spectrometry (TOF-SIMS). Characterization of thermally grown SiO_2 films on silicon has been performed. A diagram showing secondary ion spectra of SiO_2 films in both positive and negative polarities indicates the pattern of change in polarities and intensities of ion species from SiO^+ to $Si_5O_{11}^-$. The ions mostly change from positive to negative polarity between Si_nO_{2n-1} and Si_nO_{2n}. Ion peaks with the strongest intensities in the respective cluster ions correspond to the Si_nO_{2n+1} negative ion. Intensities of ion species of Si_nO_{2n+2} appear negligibly small. Ion species of Si_3O^+, $Si_3O_2^+$ and $Si_3O_3^+$ have been found at the interface between silicon and SiO_2 films. The intensity patterns of these ion species compared to those of SiO_2 films indicate that most of these species are not emitted from the SiO_2 films, but likely from the SiO structures.

PACS: 61.43.Fs; 68.49.Sf; 68.55.Jk

Keywords: Silicon oxides; Secondary ion species; Time-of-flight secondary ion mass spectrometry

1. Introduction

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a useful tool to characterize solid structures by detection of secondary ion species emitted from the solid materials with high sensitivity [1]. TOF-SIMS has been previously applied to study silicon [1,2] and silicon oxides [3], for instance, SiO_2 [4], silicon oxynitride [5] and silicon nanoclusters embedded in SiO_2 layers [6].

A silica glass, consisting of fused silicon dioxide, consists of a silicon–oxygen, Si–O, network in three-dimensions [7]. Si–O network systems have attracted increasing interest, particularly in thin SiO_2 and ultra-thin oxynitride films on silicon, as gate oxides as devices shrink in scale [8,9], and SiOx films for gas barrier applications [10,11]. The characterization of Si–O networks at the nano-scale will provide further information on the structural features of these materials.

As a Si–O network system, thermally grown SiO_2 films on silicon are interesting materials for study. The Si–O network structure is produced by the oxidation of a high-purity silicon surface, and the interface between silicon and SiO_2 is of great interest from a materials science viewpoint [12]. This interface has been primarily studied using spectroscopic ellipsometry until now [13]. With the assumption of an optical model, the presence of an identifiable thin transition layer at the interface with intermediate optical constants has been implied by many authors [12,14].

In TOF-SIMS, the identification and understanding of characteristic features in the fragmentation patterns is important to relate them to structural features of materials [15]. It is to be noted that many secondary ion species with positive and negative polarities are produced and detected in TOF-SIMS spectra, resulting from the breaking of bonds at many sites in the material, in association with possible re-arrangements relevant to the stability of ion structures upon impact of an accelerated primary ion [16]. In addition, the intensities of peaks in the spectra are frequently influenced by matrix effects, mostly due to variations in ionization probabilities [17]. These factors make the interpretation of spectra complicated.

In this paper, we report TOF-SIMS characterization of SiO_2 secondary ion species emitted from thermally grown SiO_2 films on silicon using spectra in both positive and negative polarities.

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doi:10.1016/j.apsusc.2005.12.118

We discuss the identification of ion species of Si_3O^+, $Si_3O_2^+$ and $Si_3O_3^+$ at the interface between silicon and the SiO_2 films.

2. Experimental

The samples used in this study were 25 nm thick thermally grown SiO_2 films on single-crystal p-type (1 0 0) silicon wafers (resistivity of 2–8 Ω cm), which were received from Mitsubishi Materials Co., Ltd. TOF-SIMS measurements were performed using an ULVAC-PHI TRIFT III TOF-SIMS spectrometer. Sputter etching was accomplished by Ar^+ ions at 1 kV and 200 nA rastering over a 1000 μm $\times$ 1000 μm area. This corresponds to an etching rate of approximately 0.04 nm/s for the SiO_2 films. Spectra were obtained at etching times of 50 and 450 s in the SiO_2 layer and in intervals of 10 s from 450 to 750 s near the Si–SiO_2 interface. TOF-SIMS analyses were performed in positive and negative polarities using a pulsed Au_3^+ primary ion beam operating at 22 kV and 2.0 nA. A bias voltage of +3 and −3 kV was applied to the sample holder in this instrument for measurements of positive and negative secondary ions, respectively. This results in a difference in the actual acceleration voltage of a primary ion, with values of 19 and 25 kV for measurements of positive and negative secondary ions, respectively. The beam was rastered on a 100 μm $\times$ 100 μm surface area. Secondary ions in the mass range from 0 to 1860 atomic mass units (amu) were collected for 300 s. No charge compensation using an electron flood gun was required. The working pressure was in the 10^{-7} Pa range. Identifications of peaks of the secondary ion species were carried out using the masses of peaks with an accuracy of within 0.01 amu.

3. Results and discussion

SiO_2 surface TOF-SIMS spectra were investigated in this study. To prevent the influence of contamination on the spectra, the surface was sputter-etched for 50 s, which corresponds to a depth of approximately 2 nm from the top surface. Fig. 1 shows the TOF-SIMS spectra in the mass range from 0 to 400 amu. The spectra are presented as a diagram showing both positive (up) and negative (down) polarities. This diagram shows the spectra of fragment ion species of both positively and negatively charged ions simultaneously. Prominent $^{28}Si^+$ and $^{16}O^-$ peaks emitted from SiO_2 can be observed in Fig. 1. The spectra at an enlarged intensity scale (by a factor of 30) in the mass range from 100 to 400 amu are illustrated in the inset. It is to be noted that periodic negative ion peaks with mass intervals of 60 can clearly be seen. The ion species from 76 to 316 amu, for which the intensity showed 49 counts, are assigned to SiO_3^-, $Si_2O_5^-$, $Si_3O_7^-$, $Si_4O_9^-$ and $Si_5O_{11}^-$, respectively. The mass interval of 60 corresponds to SiO_2 chain units as parts of broken pieces of the SiO_2 matrix.

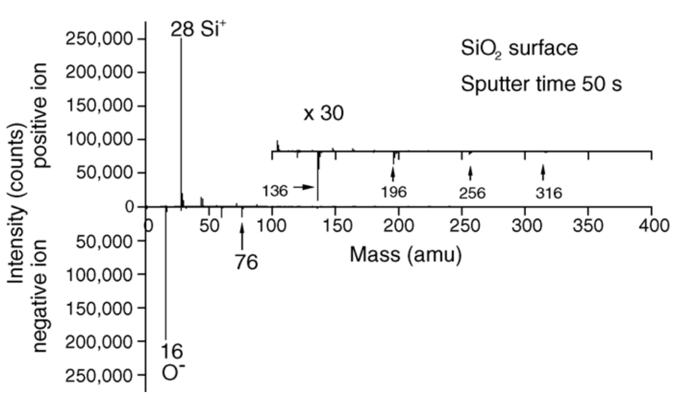

Fig. 1. TOF-SIMS spectra diagram of the surface of a 25 nm thick thermally grown SiO_2 film on silicon sample showing both positive (up) and negative (down) polarities in the mass range from 0 to 400 amu. The sputter etching time is 50 s. The inset shows the spectra in an intensity scale enlarged by a factor of 30 in the mass range from 100 to 400 amu. Periodic negative ion peaks appear in the figure.

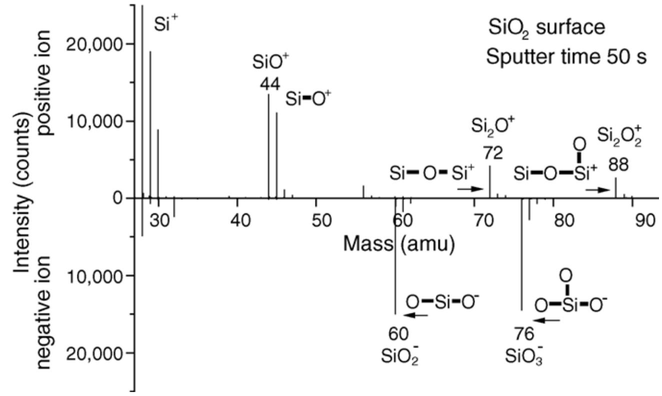

Fig. 2. TOF-SIMS spectra diagram of the SiO_2 surface in the mass range from 27 to 93 amu. The series of SiO_n (n = 1–3) and Si_2O_m (m = 1–2) ions are presented. Possible fragment structures are shown. The ion polarity is clearly shown to change from positive to negative polarity between SiO and SiO_2 ion species.

The spectra were further investigated in the selected mass ranges. Fig. 2 shows the diagram of TOF-SIMS spectra of the SiO_2 surface in the mass range from 27 to 93 amu. Possible fragment structures corresponding to the respective peaks are shown in the figure. Spectra peaks with mass intervals of 16 are observed in both positive and negative polarities, which correspond to a series of SiO_n (n = 1–3) ion species and Si_2O_n (n = 1–2). The diagram shows a variation in the intensity of the peaks and polarity with ion species, especially relevant to the number of oxygen atoms bonded to silicon atoms. For the SiO_n ion species, most of the ions changed from a positive to a negative polarity between SiO and SiO_2, resulting in their existence as SiO^+ and SiO_2^- ion species. The intensities of SiO_2^- and SiO_3^- appear almost to be the same. It is to be noted that the peak at a mass of 92, corresponding to SiO_4^-, appeared negligibly small, less than 30 counts of the intensity.

Fig. 3 shows a diagram of the TOF-SIMS spectra of the SiO_2 surface in the mass range from 110 to 200 amu. A series of peaks with mass intervals of 16 are observed in both positive and negative polarities from 116 to 196 amu. These peaks are assigned to $Si_3O_2^+$, $Si_3O_3^+$, $Si_3O_4^+$, $Si_3O_5^+$, $Si_3O_6^-$ and $Si_3O_7^-$, namely the ion species in the series of Si_3O_n (n = 2–7), respectively. $Si_2O_4^-$ and $Si_2O_5^-$ are also shown in Fig. 3. It is noteworthy that the peak at a mass of 152, corresponding to $Si_2O_6^-$ ion species, was barely observed with less than 10 counts of intensity. Furthermore, the peak at a mass of 212, corresponding to $Si_3O_8^-$ ion species, was not detected.