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Effect of residual oxygen in Si(1 1 1)-7 × 7 surface on Si^+ and Si^{2+} sputter yields

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Abstract

Effect of the residual oxygen impurity on the secondary ion yields in the sputtering from the Si(1 1 1)-7 × 7 surface bombarded by the 11 keV Ar^0 neutral beam has been studied with use of a time-of-flight technique. Even if the oxygen concentration is much less than the detection limit of the present Auger electron spectrometer, not only Si^+ and Si^{2+} ions but also SiO^+ and SiO_2^+ ions have been significantly detected. As the oxygen ion yield, estimated from SiO^+ and SiO_2^+ signals, increases, the Si^+ yield is enhanced, whereas the Si^{2+} yield is reduced. The enhancement of the Si^+ yield may be ascribed to the large electron affinity of O in comparison to that of Si, while the decrease in the Si^{2+} yield could be explained in terms of the inter-atomic Auger transition between O and one of the precursors for Si^{2+} (viz. an excited Si^+ with a 2p hole, Si^{+*}), which efficiently interferes with the production of Si^{2+}.

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1. Introduction

Secondary ion mass spectroscopy (SIMS) is known as one of powerful techniques for the micro-composition analysis of surface. However, the charge states of the sputtered particles depend strongly on their ambient environment at the surface [1,2]. For example, almost of all sputtered particles from a clean surface are neutral, whereas singly charged ions are efficiently produced from oxidized surfaces [1,3]. This effect of surface oxidation is often used to enhance the secondary ion yields in the conventional SIMS measurement and is convenient for a qualitative analysis. However, the quantitative analysis becomes a formidable task if the detailed mechanisms about the ionization processes are not well understood.

One of the important issues during the ionization process is the production and neutralization of multiply charged ions. The earlier study on the formation process of the doubly charged ion Si^{2+} from a clean Si(1 1 1) surface bombarded with an incident neutral Ar^0 beam [4] points out that the Si^{2+} sputtering yield is anomalously large. It is known that such doubly charged ions are created by intra-atomic Auger transition after the creation of a hole in an inner shell, in particular, Si 2p hole, by the electron promotion mechanism in an energetic atomic collision inside collision cascade [5,6]. However, the effect of the residual oxygen impurity on the production of Si^{2+} has not yet been studied.

In the present study, we have investigated the secondary ion yields from a clean Si(1 1 1)-7 × 7 surface bombarded with a pulsed Ar^0 beam and have clarified the effect of the oxygen impurity on secondary ions yields.

2. Experiment

The mass and charge of particles sputtered from a Si surface have been measured by means of a time-of-flight (TOF) technique under a base pressure of 7×10^{-9} Pa. The experimental setup mainly consists of a pulsed neutral

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Ar^0 beam source, a sample manipulator with a heater, a TOF tube and measuring system, and a LEED-Auger optics for the surface characterization. The details of experimental setup are presented elsewhere [4].

The Si sample used was the n-type Si(1 1 1) wafers of 3 Ω cm in resistivity and cut into a size of $5 \times 10\ mm^2$. A "clean" Si surface was prepared by several repetitive cycles of 7 keV Ar^0 sputtering and subsequent annealing at ~1100 K. This sputtering and annealing cycle was in turn used to control the oxygen impurity concentration at the surface and in the subsurface layers. Before the TOF measurements, the cleanness of the Si surface was evaluated by LEED and AES techniques. The clear Si(1 1 1)-7 × 7 LEED pattern was confirmed and the residual impurities viz. C and O, were below the detection limit of the AES measurement (~0.01 monolayer). However, Si oxide ion species were observed with the present TOF technique, as mentioned later. These Si oxides arise from the small residual oxygen in the subsurface layers.

The Si(1 1 1)-7 × 7 surface as-prepared was irradiated by 11 keV Ar^0 pulsed beam. The pulse width was 3 μs and the angle of incidence was 45°. The secondary ions ejected in the surface normal direction were detected with the TOF tube. In order to separate the ion species, bias voltages of +60 V and −60 V relative to the sample were applied to the TOF tube. The bias voltage of +60 V is sufficiently large to repel almost all the secondary ions, so that only secondary neutral species may be collected by the detector through the TOF tube. On the other hand, the acceleration of positively charged ions by a bias voltage of −60 V was sufficient to separate the positive ion species in the TOF tube. The sputter yield of each ion species, thus, can be obtained by subtracting the TOF spectrum recorded at the bias voltage of +60 V from that at −60 V.

3. Results

Fig. 1 shows a typical TOF spectra of the secondary neutral species (curve with squares) and secondary ions (curve with circles) from a "clean" Si(1 1 1)-7 × 7 surface bombarded by 11 keV Ar^0 beam, and Fig. 2 shows the difference spectrum, which is obtained by subtracting the spectrum recorded at the bias voltage of +60 V from that recorded at −60 V, as already mentioned above. In these figures, vertical bars indicate the time-of-flight calculated for the indicated ion species, which are ejected with the zero kinetic energy and accelerated by the bias voltage of −60 V. As seen from the figures, the neutral species appear as the first peak of Fig. 1 at the time-of-flight around 10 μs, and five ion species are separately observed: peaks in the spectrum at the bias voltage of −60 V could be assigned to Si^{2+}, Si^+, SiO^+ and SiO_2^+ in the increasing order of the time-of-flight. However, the last peak around 60 μs could not be assigned, and it was neglected because this peak is small and was not always observed in the present study. The sputter yields of those ion species, $Y(Si^+)$, $Y(Si^{2+})$, $Y(SiO^+)$, and $Y(SiO_2^+)$, are estimated from an integrated

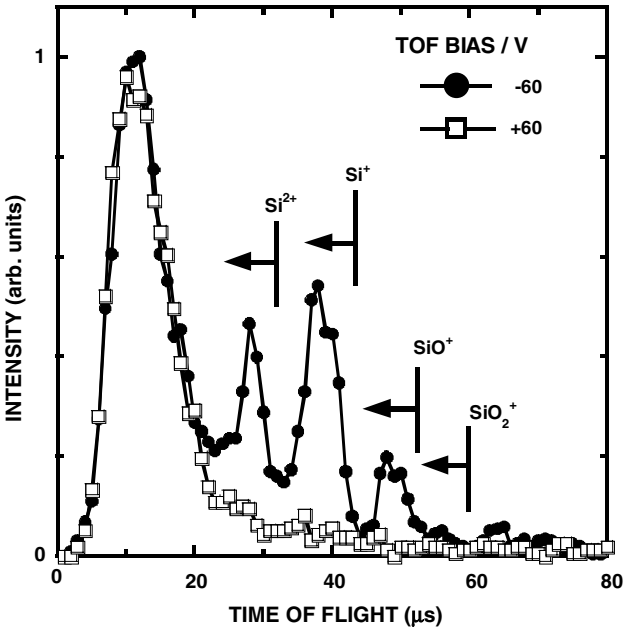

Fig. 1. Typical TOF spectra of particles sputtered from a Si(1 1 1) surface irradiated with a 11 keV Ar^0 beam. Bias voltages of −60 V (circles) and +60 V (squares) are applied to the TOF tube.

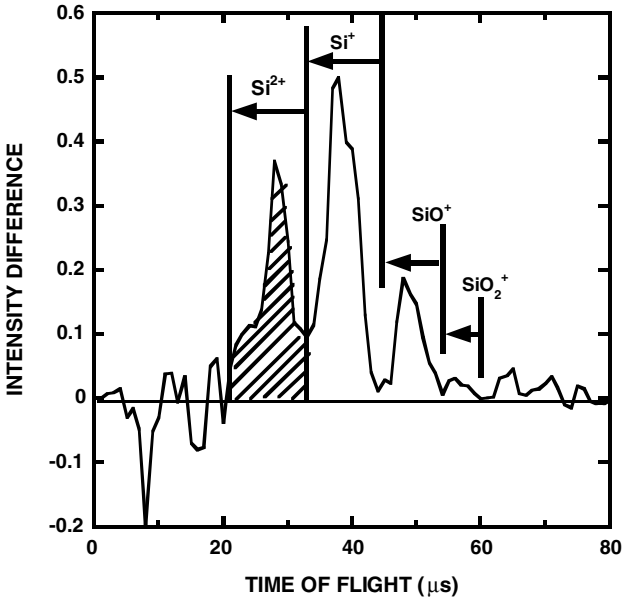

Fig. 2. Difference spectrum between time-of-flight spectra measured at bias voltage of −60 V and +60 V. The hatched area under the peak is regarded as the Si^{2+} sputter yield.

intensity between the adjacent vertical bars. For example, the Si^{2+} yield $Y(Si^{2+})$ is obtained from the hatched area under the peak as shown in Fig. 2.

Fractions of Si^+ and Si^{2+} ion yields to the total ion yield are plotted in Fig. 3 as a function of the yield of oxygen sputtered as the Si oxides, $Y(O) = Y(SiO^+) + 2Y(SiO_2^+)$. Since the concentrations of the impurity oxygen are less than the detection limit of the present AES spectrometer,