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The Effect of Incident Cluster Ion Size on Secondary Ion Yields Produced from Si

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Secondary ions emitted from a Si target have been investigated under large Ar cluster ion bombardment. Incident ion beams with energies from 10 to 30 keV were used and the mean size of the Ar cluster ion beam was about 1000 atoms per cluster. Secondary Si_n^+(n=1-11) ions were measured from Si under Ar cluster ion bombardment, while only atomic ions were measured under Ar monomer ion bombardment. In this study, we succeeded to accurately measure the incident size dependence of secondary ion spectra for Si under large Ar cluster ion bombardment using a time-of-flight technique combined a primary-ion beam deflector and a secondary-ion deflector. When the total incident ion energy was kept constant, the yields of secondary cluster ions such as Si_6^+ relative to those of Si^+ increased with size. On the other hand, when the incident Ar cluster size was kept constant, the yields of secondary cluster ions relative to those of Si^+ decreased with energy. The effect of incident cluster size on secondary ion yields is discussed.

Key words: Cluster ion beam, Secondary ion, TOF, Si

1. INTRODUCTION

Secondary ion mass spectrometry (SIMS) has been widely used in semiconductor analysis. With semiconductor devices getting smaller, depth resolution in the nanometer range is becoming increasingly important for SIMS. Recently the study of SIMS using cluster ions (Cluster-SIMS) has developed rapidly and this technique is expected to achieve both excellent sensitivity and depth resolution. When Au cluster and C_{60} ions are incident on solids, it has been confirmed that both sputtering yields and secondary ion yields increase considerably [1,2]. These effects are assumed to originate from the high-density energy deposition into a small region of the solid by the cluster ion bombardment, but the mechanisms of high sputtering and secondary ion yields are still not fully understood. It is also very important for cluster ion beam techniques to reveal incident cluster size effects on the interactions with solids to optimize surface modification processes such as atomic-scale surface smoothing and thin film formation [3-5].

We have proposed to use large cluster ions that are much larger than the molecular ions as primary ions for Cluster-SIMS [6-8]. In this study, we report on secondary ions emitted from Si under large Ar cluster ion bombardment, and the effect of incident cluster size on secondary ion yields will be discussed.

2. EXPERIMENTAL

Gas cluster ion beam (GCIB) techniques with current densities of a few μAs/cm^2 have been developed at Kyoto University. The gas cluster ion formation and ionization techniques have been described elsewhere [9,10]. In this study, the average size of Ar cluster beams was about 500 atoms/cluster. Figure 1 shows the gas cluster SIMS equipment, and it comprises a source chamber, an ionizing chamber and an analytical chamber with a mass spectrometer and an XYZ sample manipulator. Neutral Ar clusters are formed by supersonic expansion of high-pressure gas (6.7×10^5 Pa) through a nozzle (0.1 mm diameter) and are then introduced into the ionizing chamber. Electrons ejected from a hot filament are accelerated toward the neutral Ar clusters and ionize neutral clusters. Ionized Ar clusters are extracted towards the target with an accelerating voltage up to 30 kV. Magnets installed between the ionizing and analytical chambers remove small cluster and monomer ions included in the cluster ion beams. On the other hand, it is also possible that only Ar monomer ions are incident on the target, when atoms in an argon atmosphere are ionized by electron impacts and accelerated towards the target. When Ar monomer ions were incident, the nozzle to produce neutral clusters and magnets to remove monomer ions were not used. In this study, the maximum current densities of Ar cluster and Ar monomer beams were 10 μA/cm^2. The primary ion beam was incident on the Si target at an angle of 45° with respect to the surface normal. The base and working pressure in the analytical chamber were 2×10^{-6} and 5×10^{-5} Pa, respectively.

Secondary ions were measured with a linear time-of-flight (TOF) technique. Below we describe the process to accurately measure the incident size dependence of the secondary ion spectra with large Ar

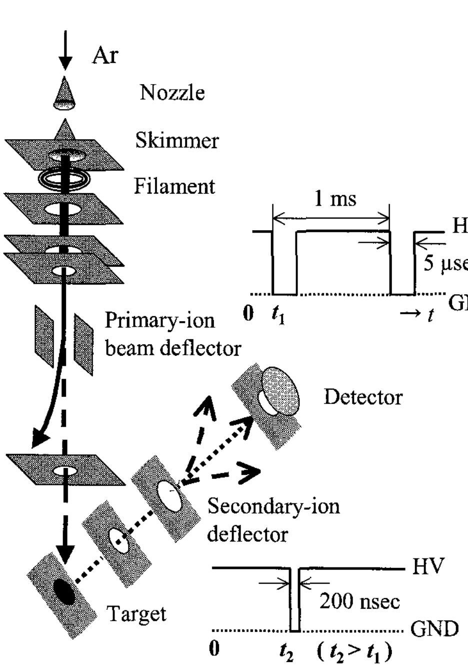

Fig. 1. Experimental setup.

cluster ion irradiation. First, the primary ion beam is chopped to a width of 5 μs by applying a high-voltage pulse (above 500V) between parallel electrodes (15mm effective deflector length). If 20keV Ar cluster ion beam is chopped, clusters up to Ar_{18000} pass through the deflector theoretically. Before the pulsed ion beam impacts on the Si target, the pulse width spreads beyond 100 μs because of the size difference of incident cluster ions. In other words, small and swift clusters reach the target earlier than large and slow clusters. Therefore, the cluster size dependence of secondary ion emission can be measured by installing additional deflector between the target and a secondary-ion detector, which is controlled to pass the secondary ions only for a certain time interval depending on the flight time of primary cluster ions. The secondary-ion deflector consists of two electrically insulated sets of thin wires mounted parallel to each other. This electrode is so-called the interleaved comb ion (mass) deflection gate, which has been proved to have high availability for TOF mass spectrometry by Weinkauf *et al.* [11] and Vlasak *et al.* [12]. When parallel plates are used as the secondary-ion deflector, secondary ions such as 2keV Si^+ or Si_{10}^+ pass the deflector for several tens of ns to 200 ns. The transmission rate of secondary ions depends strongly on their mass. In case of the interleaved comb deflector, secondary ions pass it in ten nano seconds because of short deflector length. In this study, the interleaved comb ion deflector with its wire diameter of 0.35 mm and the distance between wires of 0.85 mm was equipped, which allows to chop secondary ions to a width of 200 ns every 1ms by applying a relatively low-voltage pulse (below 500V) between wires. We can selectively measure secondary ions produced by different size of cluster ions changing the time interval (delay time ; t_2-t_1) between the primary-ion beam chopping and the secondary-ion chopping. The pulse repetition rate of primary-ion and secondary-ion

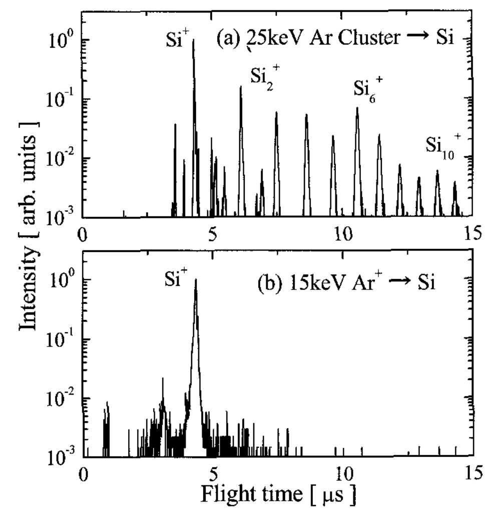

Fig. 2. Examples of TOF spectra of secondary ions for Si under (a) 25keV Ar cluster and (b) 15keV Ar monomer ion bombardment.

chopping was 1000 Hz and each TOF measurement was taken for 200 s. Secondary ions were accelerated to a kinetic energy of 2 keV and detected with a channel electron multiplier set on the axis of the surface normal. Timing of the secondary-ion chopping and detection was respectively used as a start and a stop signal for the TOF measurement.

When continuous primary ion beam was incident on the target and only the secondary-ion deflector was used, TOF mass spectra were also obtained. In this case, secondary ions produced by Ar cluster ions with an average size of 500 atoms were measured.

3. RESULTS AND DISCUSSION

Figure 2 shows an example of mass spectra of positively charged secondary ions for a Si target bombarded with 15 keV Ar cluster and monomer ions. In this measurement, continuous primary ion beam was incident and only the secondary-ion deflector was used for TOF mass spectrometry (TOF-MS). For Ar cluster ion incidence (Fig. 2 (a)), the mass spectrum is similar to the spectrum measured with a quadrupole mass spectrometer (QMS) [13]. It is considered to be an inevitable result because of continuous beam incidence. The dominant secondary ions were Si_n^+ ions up to n=11. As Si_n^+ ions above n=8 were not measured with the QMS under Ar cluster ion bombardment in our previous work, secondary-ion detection efficiency and mass resolution are more improved than before. On the other hand, a few oxidized and impure ions such as SiO^+, $(H_2O)_mH^+$ (m=1-3) were also detected with a small quantity. Among them, $(H_2O)_mH^+$ ions were not emitted from the Si surface, because other primary beams such as Ar monomer and O_2 cluster did not produce them at all. That is, $(H_2O)_mH^+$ ions are originated from primary Ar cluster ions. The mass spectrum for Ar monomer ion bombardment differed from that for Ar cluster, and Si_n^+ ions (n>1) were hardly detected. H^+ ions were surely measured under Ar monomer ion bombardment, while they were hardly detected for Ar cluster impact.

Figure 3 shows relative secondary-ion yields per incident ion as a function of accelerating voltage under

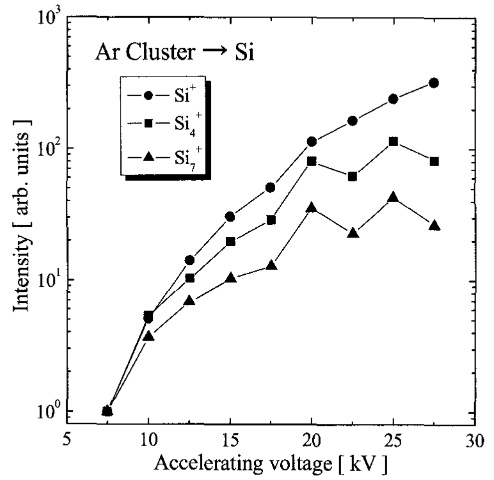

Fig. 3. Accelerating voltage dependence of relative secondary-ion yields per incident ion under Ar cluster ion bombardment.

the incidence of Ar cluster ions. Secondary-ion yields are normalized by the yields for 7.5keV Ar cluster incidence. In this measurement, continuous primary cluster ion beam was incident on Si and only the secondary-ion deflector was utilized for TOF-MS. It is found that the secondary-ion yields increased nonlinearly with increasing incident energy (accelerating voltage), and this nonlinear increase was also found in our previous data measured with the QMS [13]. Yields of secondary cluster ions such as Si_4^+ and Si_7^+ increased slightly with energy compared to that of Si^+.

In comparing secondary ions produced by Ar cluster and monomer ions, we should pay attention to the circumstances described below. For a beam accelerating voltage of 20 kV, the maximum energy deposited to surface by an Ar cluster or monomer ion is equal. However, an Ar cluster ion is composed of many Ar atoms. If an Ar cluster ion consists of 1000 atoms, the incident energy per Ar atom is only 20 eV. The projectile energy dependence of sputtering yields for Ar monomer ion at incident energies between several hundreds and a few tens of thousands of eV has been well understood both theoretically and experimentally [14]. Secondary ion yields for large cluster ion incidence, however, are difficult to compare those experimental data, because the mean size of primary Ar cluster ions used in this study is about 1000 atoms/cluster and the incident energy per atom is between a few eV and several hundreds of eV. Then, in our previous report, the yields of Si^+ emitted by Ar cluster ion irradiation were compared with the sputtering yields calculated by TRIM code [15], a semi-empirical formula [16] and molecular dynamics (MD) simulation [17]. The relative yields of Si^+ were much higher than those predicted from the TRIM results and were in good agreement with those by MD results for Ar_{1000}.

The effects of incident cluster-ion size on secondary ion spectra were investigated using both the primary-ion and secondary-ion chopping system described in the experimental section. Figure 4 shows secondary-ion spectra obtained under the incidence of 20keV Ar_{300}, Ar_{600} and Ar_{1000}. As far as we know, no one has reported

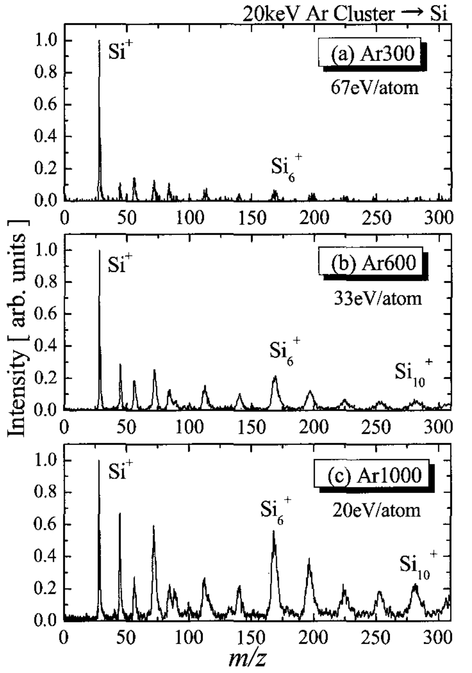

Fig. 4. Size dependence of secondary-ion spectra of Si obtained under the incidence of 20keV (a) Ar300, (b) Ar600 and (c) Ar1000.

that secondary-ion spectra were obtained at the incidence of specially fixed cluster size above 500 atoms. When 20keV Ar_{300} (67eV/atim) ions were incident on Si, Si^+ ions were mainly detected and Si cluster-ion yields such as Si_6^+ were extremely low(Fig. 4(a)). Surprisingly, yields of secondary cluster ions such as Si_6^+ ions relative to those of Si^+ increased rapidly with size, as can be seen from Fig. 4 (b) and (c). That is, the size dependence of Si^+ yields is surely different from the dependence of cluster ions such as Si_6^+ or Si_{10}^+.

In general, atomic ion induced sputtering is explained by the collision cascade theory [14]. According to the theory, sputtering and secondary ion yields decrease with decreasing incident energy, as atomic ions below 1 keV were incident. Yields of secondary cluster ions were reported to decrease with decreasing sputtering yields, when atomic ions were incident on metals [18,19]. In this study, however relative secondary cluster-ion yields increased with decreasing incident energy per atom, as shown in Fig. 4. The result contradicts with those results of atomic ion incidence. Therefore, Si cluster ions should not be emitted by collision cascade, because large Ar cluster incidence below a few tens of eV/atom hardly produce atomic collision cascade. On the other hand, Si clusters are mainly produced through thermal processes, when Si is irradiated by fs and ns laser [20,21] or Si is simply annealed [22]. The enhancement of relative secondary cluster-ion yields under large Ar cluster ion bombardment may be due to increased Si cluster emission probabilities through thermal processes such as laser irradiation. This assumption also agrees with the accelerating voltage dependence of relative secondary ion yields in Fig. 3, because the secondary cluster-ion yields increased slightly with increasing incident energy compared to Si^+ yields.

4. SUMMARY

Secondary ions emitted from Si were measured using a time-of-flight technique under large Ar cluster ion bombardment at accelerating voltages between 10 and 30 kV. Si_n^+ ions up to n=11 were detected, and secondary-ion detection efficiency and mass resolution are more improved than our previous work using QMS. The effect of incident cluster ion size on secondary ion spectra was measured using a primary-ion beam deflector (parallel plates) and a secondary-ion deflector (interleaved comb ion deflection gate). Yields of secondary cluster ions such as Si_6^+ relative to those of Si^+ became relatively high with increasing incident cluster size. It is considered that secondary cluster ions are not produced by collision cascade, and Si cluster formation process is similar to thermal processes.

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