A Comparison of Ions with Neutrals Emitted from Semiconductors Bombarded by MeV Si Ions

Yoshihiko Nakata, Satoshi Ninomiya^{*}, Takaaki Aoki^{*}, Hidetsugu Tsuchida^{*}, Jiro Matsuo^{*} and Akio Itoh^{*}

> Department of Nuclear Engineering, Kyoto University, Sakyo, Kyoto, Japan Fax: 81-75-753-3571, e-mail: yukai@nucleng.kyoto-u.ac.jp ^{*}Quantum Science and Engineering Center, Kyoto University, Uji, Kyoto, Japan Fax: 81-774-38-3978, e-mail: matsuo@nucleng.kyoto-u.ac.jp

We have measured both secondary ionized and neutral particles emitted from semiconductors under MeV-energy ion bombardment. Mass and axial emission energy distributions of the secondary particles were investigated. The secondary ions were measured with a linear- and reflective-type time-of-flight mass spectrometer, whereas the secondary neutral particles were photo-ionized by an ArF excimer laser and measured with a reflective-type time-of-flight mass spectrometer. Different results were obtained with sputtered neutrals as compared with sputtered ions. The Sb/In ratio of photo-ionized neutral particles emitted from the InSb target was one order of magnitude larger than that of simultaneously emitted ions. The axial emission energy distributions of In and Sb ions were nearly equal, whereas the mean emission energy distribution of neutral Sb atoms emitted from a GaSb target showed the same tendency as neutral Ga atoms emitted from the same sample. These results indicate the unique feature of neutral emissions from the InSb target compared to the emissions from the GaSb target.

Key words: Sputtering, Secondary Ions, Secondary Neutrals, Semiconducting material, Axial Emission Energy

1. INTRODUCTION

Particle emission from a solid target bombarded by energetic ions is generally well known and has been widely studied for various materials. Mass and emission energy distributions of secondary particles are of great importance for elucidating the dynamics of the particle emission. We have investigated the kinetics of secondary ion emission from insulators, metals and semiconductors in an MeV-energy range, where electronic energy loss is dominant, and proposed a material-dependent sputtering mechanism [1]. However, the emission mechanism of neutral particles, which occupy as much as 90% or more of secondary particles in most materials, is still unknown because it is not clear whether the emission mechanism of secondary ions could also be indicative for that of neutral particles. So far, in the MeV energy regime, few experiments have been carried out on mass and emission energy spectra of neutral particles, although there are many reports on the mass and emission energy distributions of neutral particles in the keV-energy range [2,3]. Therefore, recently the investigation of secondary neutral particles has been our concern, and total sputtering yields have been measured for insulator and metal targets at incident energies in the MeV-energy range using the quartz crystal microbalance technique [4]. Besides that, in a previous work [5] we have measured emission energy distributions of neutral and ionized particles emitted from semiconductors using the post-ionization technique, and obtained different results for neutrals and ions. In the present work, aiming for further understanding of the sputtering mechanism in the high energy region, we have measured mass and axial emission energy distributions of neutral and ionized particles emitted from InSb and GaSb targets under 3.0 MeV Si ion bombardment.

2. EXPERIMENTAL

A 3.0 MeV Si ion beam provided using Kyoto University's 1.7 MV tandem Cockcroft-Walton accelerator was incident on InSb and GaSb targets at an angle of 45 degrees to the sample surface after being collimated to a diameter of 2 mm. A schematic diagram of the experimental setup used to measure the secondary particles is shown in Fig. 1. Several methods were employed for measuring secondary ionized and neutral particles separately, as described in detail elsewhere [5]. Secondary ions were emitted from the targets under the bombardment of the Si ion beam chopped to a width of 50 ns in every 130 µs. Secondary ion mass spectroscopy was carried out using the reflective time-of-flight (TOF) technique, whereas the emission energy distribution of the emitted ions was measured with the linear TOF technique. For measurements of both mass and emission energy distributions of secondary neutral particles, the reflective TOF technique was used and the projectile was chopped to a width of 1 µs in every 10 ms. Emitted neutrals were photo-ionized by a UV pulsed laser (ArF: 193 nm, pulse duration: 8 ns) which was focused by a lens and directed in parallel to the sample



Fig. 1. Experimental setup.

surface. It is important to measure secondary neutrals separately from secondary ions. In the present experiments, emitted ions were accelerated to 1.6 keV in the extraction field and were not reflected in the reflector because the voltage at the back of the reflector was set at about 1.5 kV. On the other hand, secondary neutrals were photo-ionized at a distance of 2-10 mm above the surface, and so accelerated to around 1.4 keV. Thus, only photo-ionized neutral particles were reflected in the reflector and detected by the secondary electron multiplier.

To measure the axial emission energies of secondary neutral particles, the flight time dependence of the neutral particle intensity S(t) has to be obtained. The velocity of the neutral particle v is calculated from the length r from the surface to the laser volume, and the flight time t from the ion pulse to the laser irradiation event. S(t) is obtained by changing the delay time between the laser irradiation event and the ion pulse. Since the signal obtained by the present method is the density $\rho(t)$, not the flux I(t), which is equal to $\rho(t)v(t)$, the velocity distribution f(v) is calculated from the flight time distribution as described in [6]

 $f(v) = t^2/r I(t) \propto S(t) / v$ (1),

where t^2/r is extracted from | dv/dt |. The emission energy distribution f(E) is obtained by

 $f(E) = \frac{dv}{dE} f(v) \propto S(t) / v \quad (2).$

In these experiments an ion pulse of 1 μ s was used for the measurements of neutral emission energies, although eq. (2) holds when the ion pulse duration is infinitely short.

3. RESULTS AND DISCUSSION

The mass spectra of secondary ionized and neutral particles emitted from InSb [5] and GaSb targets under bombardment of 3.0 MeV Si ions are shown in Fig. 2. Abundance of isotopes of gallium, indium and antimony are 60.1% (⁶⁹Ga) and 39.9% (⁷¹Ga), 95.7% (¹¹⁵In) and 4.3% (¹¹³In), and 57.4% (¹²¹Sb) and 42.6% (¹²³Sb), respectively. These isotopes were found in the mass spectra in Fig. 2. As for secondary ions emitted from the InSb, In⁺ was mainly observed and cluster ions like In₂Sb⁺ were also detected, as previously reported [1]. The intensity of Sb⁺ is two orders of magnitude lower than that of In⁺ and this may be



Fig. 2. Mass spectra of secondary ions and neutrals emitted from InSb (upper) and GaSb (lower) targets bombarded by 3.0 MeV Si ions



Fig. 3. Flight time distributions of neutral particles emitted from the InSb (upper) and GaSb (lower) targets under the bombardment of 3.0 MeV Si ion.



Fig. 4. Emission energy distributions of ions (upper) and neutrals (lower) sputtered from the InSb and GaSb targets.

attributed to the higher ionization potential of the Sb atom compared to that of the In atom. Similarly, most of the detected photo-ionized neutral particles ejected from the InSb target were In atoms, and particles such as In₂ and In₂Sb were also detected. The relative yields between photo-ionized In and Sb atoms are quite different from that of In and Sb ions. The Sb/In ratio of integrated neutral is one order of magnitude larger than that of ions. On the other hand, as for the GaSb target, Ga⁺ was mainly detected and the intensity of Ga⁺ was two orders of magnitude higher than the Sb⁺ intensity. Ga and Sb atoms were found in the mass spectrum of neutral particles from GaSb and the relative yields between Ga and Sb atoms are same as those of ions. No cluster was detected for GaSb, although indium and antimony dimmers were observed for InSb.

The flight time dependence of neutral-intensities was obtained from the TOF distributions with changing delay times of laser irradiation from the ion pulse. The flight time distributions of neutral In and Sb atoms emitted from the InSb target and those of Ga and Sb atoms from GaSb are shown in Fig. 3. It is noted that each distribution is normalized to the maximum value. Figure 3 indicates that the time distributions of In and Sb atoms are quite different, despite the nearly equal mass of these atoms. The maximum intensity of Sb atoms was observed about 1 µs later than that of In atoms. That is, the mean velocity of Sb atoms is much lower than that of In atoms, which implies some different emission processes of the neutral In and Sb atoms sputtered from the InSb target. For the post-ionization technique, cluster fragmentation should

be taken into consideration [7]. As found in the previous work [5], the flight time distribution of neutral Sb atoms was similar to that of neutral InSb molecules. Therefore, it is possible that the detected Sb atoms originate from neutral InSb molecules which are fragmented by laser irradiation after leaving the surface. Indium ions are also produced through photo-dissociation and photo-ionization of emitted InSb molecules by laser irradiation. But this effect is masked by the intense In signals originally from emitted neutral In atoms because an indium atom is easily ionized by just one photon. As a result, the observed velocity of neutral Sb atoms was lower than that of neutral In atoms. On the other hand, the flight time distribution of neutral Ga atoms was similar to that of neutral Sb atoms as shown in Fig 3. In addition, the neutral Sb distribution for InSb is different from that for GaSb, thus it is obvious that neutral Sb atoms from the InSb target were emitted from the surface through a different process compared to the emission from the GaSb target.

Figure 4 shows the axial emission energy distributions of neutral particles ejected from the InSb and GaSb targets, as calculated from their flight time distributions shown in Fig. 3. The emission energy distributions of secondary atomic ions from the InSb and GaSb targets are also shown in Fig. 4. The distributions have approximately the same trend, which agrees well with the Thompson-Sigmund distribution [8], as also observed in a previous work for other electro-conductive materials [9]. The energy distributions of Ga and Sb atoms emitted from the GaSb target are nearly equal, indicating that in this case Sb and Ga atoms are sputtered through the same process. There are some other features in Fig. 4. The tail of the In distribution falls off in a lower energy region than that of neutral atoms sputtered from the GaSb target, and in addition the mean emission energy of Sb atoms from the InSb target is much lower. As mentioned above, the fragmentations of neutral InSb molecules result in a lower velocity of neutral Sb atoms from the InSb target. On the other hand, no cluster-fragmentation was observed in the case of the GaSb target, and it is considered that the detected Sb atoms from GaSb are emitted from the surface as atoms. These results indicate that, at the MeV-ion impacts, molecules might be more easily released from InSb surface than from the same III-V the semiconductor target, GaSb. Further research is required to elucidate whether InSb molecules are more easily ejected from the InSb target and fragmented by laser irradiation than GaSb molecules from the GaSb target.

4. SUMMARY

Mass and axial emission energy distributions of secondary ionized and neutral particles sputtered from InSb and GaSb targets in the MeV-energy range were analyzed. The emission energy distributions of secondary atomic ions emitted from both targets could be well characterized by the Thompson-Sigmund distribution, whereas the distributions of secondary neutrals from InSb and GaSb targets were different. The mean emission energy of neutral Sb atoms from the InSb target was much lower than that of other neutral atoms. This difference must be caused by cluster fragmentation, as observed in a previous work [5]. It is concluded that InSb molecules are more easily sputtered and fragmented by laser irradiation, but this is not the case for the GaSb target.

ACKNOWLEDGEMENTS

This work was done with the Experimental System for Ion Beam Analysis at Kyoto University. We thank A. Itoh, K. Yoshida and K. Norizawa for their useful advice and technical support during the experiments. This work was partly supported by a Grant-in-Aid from Japan Society for the Promotion of Science (JSPS).

REFERRENCES

[1] S. Ninomiya and N. Imanishi, Vacuum, 73 (2004) 79.

[2] S.R. Coon, W.F. Calaway, J.W. Burnett, M.J. Pellin, D.M. Gruen, D.R. Spiegel, J.M. White, *Surf. Sci.* **259** (1991) 275.

[3] W. Husinsky, G. Betz and I. Girgis, J. Vac. Sci. Technol. A2 (1984) 698.

[4] S. Ninomiya, C. Imada, M. Nagai, Y. Nakata, T. Aoki, J. Matsuo, N. Imanishi, *Nucl. Instr. and Meth. B* 230 (2005) 483.

[5] Y. Nakata, S. Ninomiya, C. Imada, M. Nagai, T. Aoki, J. Matsuo, N. Imanishi, *Nucl. Instr. and Meth. B* 230 (2005) 489.

[6] Frank M. Zimmermann and W. Ho, *Surf. Sci. Rep.* **22** (1995) 127.

[7] W. Husinsky, G. Nicolussi and G. Betz, Nucl. Instr. and Meth. B 82 (1993) 323.

[8] M. W. Thompson, Philos. Mag. 18 (1968) 377.

[9] S. Ninomiya, N. Imanishi, J. Xue, S. Gomi, M. Imai Nucl. Instr. and Meth. B 193 (2002) 745.

(Received January 26, 2005; Accepted May 12, 2005)