Development of a three-electrode-lens drift tube for time-of-flight mass spectrometry

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A three-electrode-lens drift tube for time-of-flight mass spectrometry (TOF-MS) has been developed for utilizing a detector to observe photon-stimulated desorption (PSD). In spite of a small detection area, the detector has a high detection efficiency and durability to reactive gas atmosphere at high pressure. The TOF-MS performance of the drift tube was examined for PSD using single-bunch-mode synchrotron radiation on a dichlorosilane (SiH_2Cl_2)-saturated Si(001) surface. The measured acceleration and focusing-voltage dependences of the time of flight, intensity and full width at half-maximum for the peak of H^+ and Cl^+ PSD ions are discussed in terms of the numerical calculations of ion trajectories and focusing characteristic of the drift tube.

Keywords: time-of-flight mass spectrometry; drift tubes; lens; PSD; Si(001); dichlorosilane.

1. Introduction

Synchrotron-radiation-assisted processes have attracted much interest for developing low-temperature processes which are applicable to fabricating nano-scale semiconductor devices. The main purpose of synchrotron radiation irradiation during processes such as chemical vapour deposition (CVD) of silicon is to remove surface adsorbates at low temperature by photon-stimulated desorption (PSD) instead of thermal desorption (Takakuwa *et al.*, 1996). The detailed removal efficiency of irradiation has so far been explored by measuring the PSD yield of positive ions using time-of-flight mass spectrometry (TOF-MS) (Ueno *et al.*, 1996) and quadrupole mass spectrometry (QMS) (Takakuwa *et al.*, 1989). The ion detection efficiency of TOF-MS is much higher than that of QMS, because a microchannel plate (MCP) with a larger detection area above 25 mm diameter is available as a detector for the TOF-MS measurement. However, the MCP detector has crucial disadvantages: the deterioration of gain and the increase of dark current under reactive gas atmosphere for CVD or etching.

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In this study, a drift tube with a focusing effect has been investigated for employing a secondary electron multiplier detector such as Ceratron (Murata Mfg. Co. Ltd), which is made from a ceramics semiconductor and can operate with a rapid raising time of <2.0 ns, a high gain of >10^7, up to ~10^{-4} torr of reactive gases, and has a high detection efficiency in TOF-MS but has a small detection area of a few mm in diameter. The drift tube is composed of three cylindrical electrodes which can work as an electrostatic lens. The performance of the drift tube is measured for PSD using single-bunch-mode synchrotron radiation on a dichlorosilane (SiH_2Cl_2)-saturated Si(001) surface and is discussed on the basis of the numerical calculations of ion trajectories and focusing characteristic of the drift tube.

2. Experimental

The PSD experiments were performed on beamline BL-11D at the Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Japan. A block diagram of the TOF-MS measurement system is presented in Fig. 1(*a*). In order to obtain a large desorption amount, we used non-monochromated synchrotron radiation light, so-called white synchrotron radiation, the beam spot size of which was 1.5 mm in diameter, with an intensity maximum ~100 eV from a 2.5 GeV positron storage ring under single-bunch-mode operation. The repetition cycle and width of the white synchrotron radiation light for PSD were 624 ns and 100 ps, respectively. The surface-analysis apparatus used was equipped with facilities for TOF-MS, reflection high-energy electron diffraction (RHEED), UV photoelectron spectroscopy (UPS), QMS and gas inlet (Takakuwa *et al.*, 1996). The base pressure of the apparatus was below ~2×10^{-10} torr. The
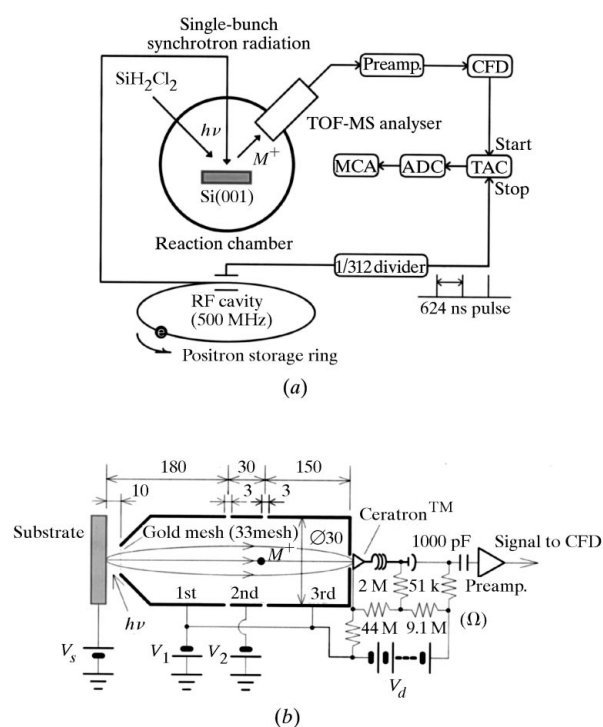

Figure 1
(*a*) Block diagram of the TOF-MS measurement system for PSD using single-bunch-mode synchrotron radiation. (*b*) Schematic illustration of the TOF-MS analyser and its electronic circuits. V_S, V_1, V_2 and V_d are the applied voltages to the sample, first and third electrodes, second electrode and detector, respectively. Lengths in mm.

time of flight for PSD ions was measured by a time-to-amplitude converter (TAC), an analog-to-digital converter (ADC) and a multichannel analyser (MCA). The signal after 1/312 division of 500 MHz RF and the ion signal from a constant fractional discriminator (CFD) following a TOF-MS analyser were used as a start and a stop pulse of the TAC, respectively, to reduce dead time. The TOF-MS measurement of PSD ions was carried out at room temperature under $\sim 10^{-10}$ torr.

Fig. 1(b) shows details of the TOF-MS analyser and its electronic circuits. The drift tube is composed of three electrodes and is enclosed by an electrostatic shield tube (not shown). The inner diameter, the gap width between electrodes and the distance between two gaps of the drift tube are 30, 3 and 30 mm, respectively. The distance between an objective and imaging position for the lens performance of the drift tube is designed to be 360 mm so as to reduce the penetration effect of the electric field between each electrode. The detector of the Ceratron was installed at the imaging position with an inlet slit of diameter 10 mm. The focusing characteristic of the drift tube which was calculated on the basis of numerical tables (Harding & Read, 1976) is represented with non-dimensional parameters of $V3/V1$ and $V2/V1$ in Fig. 2. It is noted that there are two focusing conditions of $V2/V1$ for each $V3/V1$. In the present case, the drift tube was operated as a lens without any acceleration and deceleration of ions through it ($V3/V1 = 1.0$); then the calculated values of $V2/V1$ are 0.27 and 3.1.

Samples used were B-doped p-type Si(001) wafers. The surface was cleaned by flash heating at 1523 K and prolonged annealing at 1173 K for 600 s. The SiH_2Cl_2-saturated Si(001) surface was prepared by exposing a clean Si(001) 2 × 1 surface to SiH_2Cl_2 of 99% purity at $\sim 1 \times 10^{-6}$ torr for 600 s at room temperature. The SiH_2Cl_2-saturated Si(001) surface was clarified to be covered by monochloride and monohydride with almost the same coverage of ~ 0.5 monolayer (Sakamoto et al., 1996).

3. Results and discussion

Fig. 3(a) shows the V_1 dependence of the TOF spectrum for the SiH_2Cl_2-saturated Si(001) surface. The origin for the measured

time of flight is determined from the prompt peak due to the reflected synchrotron radiation light by a sample surface, part of which is seen around $t = 0$ ns in Fig. 3(a) (Ueno et al., 1996). The potential on the face of the Ceratron was set at the same voltage as V_1. V_2 is fixed at -0.7 kV, which satisfies the theoretical focusing condition for the case of $V_1 = -2.6$ kV as calculated from $V2/V1 = 0.27 = (V_2 + V_S)/(V_1 + V_S)$ and $V_S = +10$ V. In the TOF spectrum at $V_2 = -2.6$ kV, one sharp peak and another broad peak with a shoulder at the long-time side appear at ~ 50 and ~ 257 ns, respectively. The time of flight for the sharp peak becomes longer with decreasing V_1, proving clearly that the sharp peak is due to positive ions. On the other hand, the broad peak shows complicated behaviour with V_1. This suggests that the time of flight for the broad peak is longer than 624 ns and thereby is folded with some repetitions of 624 ns in the TOF spectra of Fig. 3(a). For the lens geometry in Fig. 1(b), the time of flight for H^+ and Cl^+ ions, which are possible PSD ion species from the SiH_2Cl_2-saturated Si(001) surface, can be calculated on the basis

Figure 3
(a) V_1 (ion acceleration voltage) dependence of the TOF spectrum for the SiH_2Cl_2-saturated Si(001) surface. (b) V_1 dependence of the time of flight for PSD ions of $^1H^+$ and $^{35}Cl^+$ obtained from (a).
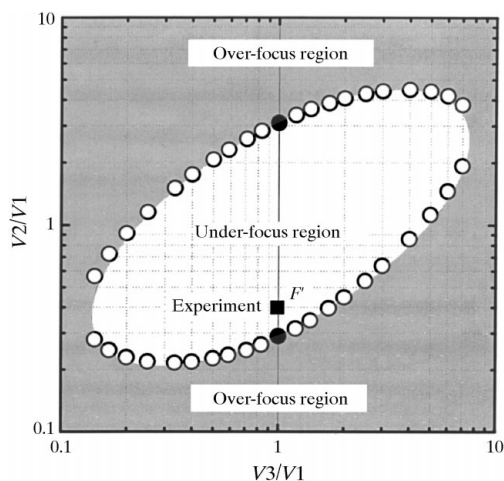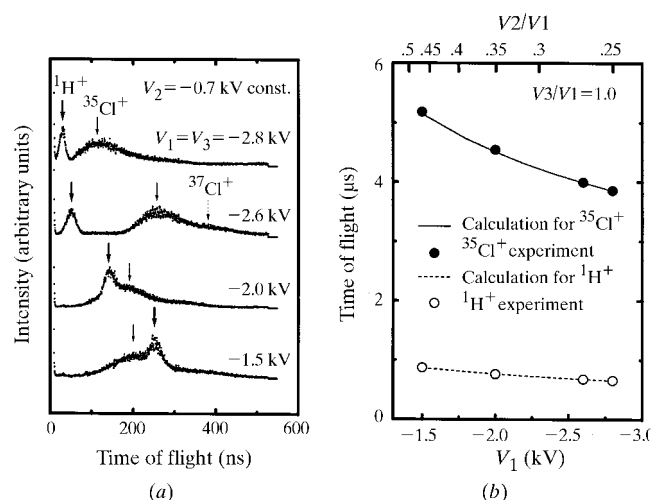
Figure 2
Focusing characteristic of the three-electrode-lens drift tube represented by non-dimensional parameters of $V2/V1$ and $V3/V1$; theoretical data (open circles) and a measured value (solid square with F'). $V1$, $V2$ and $V3$ are the kinetic energies of drifting ions through the first, second and third electrodes, respectively.
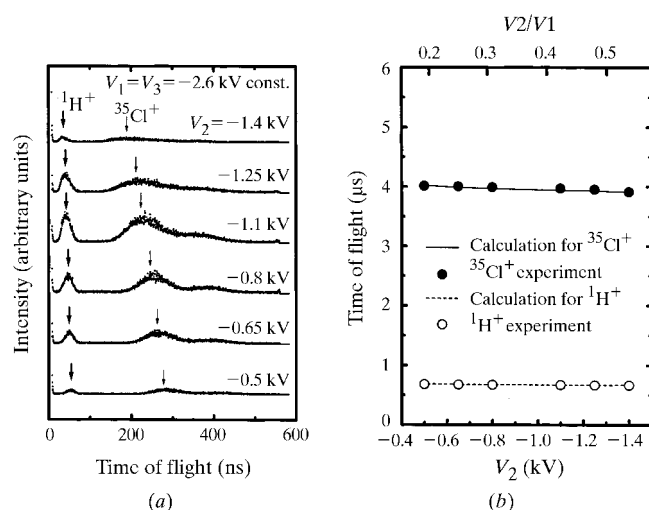
Figure 4
(a) V_2 (lens focusing voltage) dependence of the TOF spectrum for the SiH_2Cl_2-saturated Si(001) surface. (b) V_2 dependence of the time of flight for PSD ions of $^1H^+$ and $^{35}Cl^+$ obtained from (a).
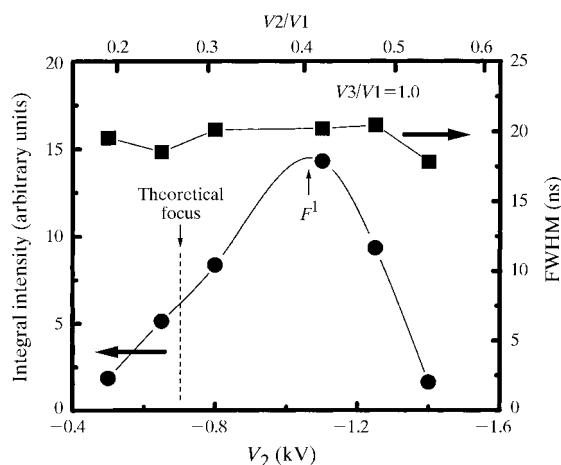
Figure 5
V_2 (lens focusing voltage) dependence of the intensity and FWHM of the peak for $^1H^+$ PSD ions obtained from Fig. 4(a).

of the calculation of each ion trajectory using an approximated potential in the three-electrode lens (El-Kareh & Sturans, 1971) and a predictor–corrector procedure by the fourth-order Adams–Bashforth–Moulton method (Johnson & Riess, 1982). In the calculation, the initial desorption energy of a few eV is ignored because it is much smaller than V_1. The angular distribution of desorbed ions along the chemical bonds is also ignored due to the large ion collection effect of V_1. The time of flight for H^+ ions is calculated to be 0.675 μs, which is in good agreement with ∼50 + 624 ns. Hence the sharp peak can be attributed to H^+ ions. The time of flight for $^{35}Cl^+$ ions is estimated to be 4.0 μs, consistent with ∼257 + 624 × 6 ns for the broad peak.

The V_1 dependence of the measured time of flight for $^1H^+$ and $^{35}Cl^+$ ions is summarized in Fig. 3(b), in comparison with the calculations. The agreement between experiment and calculation is very good for both the PSD ion species in the whole V_1 region examined, indicating that the present calculation method is reasonable. According to the calculation, moreover, the shoulder of the broad peak is assigned to $^{37}Cl^+$ ions. The spectral intensity ratio between $^{35}Cl^+$ and $^{37}Cl^+$ is consistent with the isotope abundance ratio of 3:1 for chlorine.

Fig. 4(a) shows the V_2 dependence of the TOF spectrum taken at a fixed V_1 of −2.6 kV. The time of flight for both H^+ and Cl^+ ions changes slightly with V_2 as summarized in Fig. 4(b), and their intensities show a strong dependence on V_2 as summarized for the peak intensity of H^+ ions in Fig. 5. The gradual increase in the time of flight with decreasing V_2 in Fig. 4(b) results from the asymmetric geometry of the lens. In Fig. 5, the maximum in the peak intensity of $^1H^+$ ions is located at $V_2 = -1.0$ kV ($V2/V1 = 0.4$), which is larger than the theoretical $V2/V1$ of 0.27. The disagreement is caused by spherical aberration (Harding & Read, 1976). The focusing characteristic in Fig. 2 was theoretically calculated for the small divergence in the incidence angle of PSD ions at the inlet of the drift tube where the spherical aberration effect is negligible. In practice, however, the focusing efficiency of the drift tube can be maximized by adjusting V_2 as shown in Fig. 5.

On the other hand, the large divergence in the incidence angle of PSD ions, which is indicated by the significant spherical aberration effect in the focusing behaviour, is suspected to make the TOF spectral feature broad. This is because a PSD ion with a larger incidence angle travels a longer trajectory through the drift tube, resulting in its longer time of flight. Fig. 5 also shows the V_2 dependence of the measured full width at half-maximum (FWHM) of the peak for $^1H^+$ ions. In general, the FWHM broadens with the mass resolution, Δm. In the present case, it is hard to calculate theoretically the FWHM. When V_2 increases from −0.5 to −1.1 kV, the focusing effect reaches about 800% of the increase for the peak intensity. Then, the change in FWHM is within only 5%. Thus, Δm observed at the focusing condition is not so badly degraded contrary to the above suspicion. This means that the present drift tube with a lens function makes it possible to increase considerably the detection efficiency in the TOF-MS measurement without significant degradation of the mass resolution.

4. Conclusions

We have investigated the three-electrode-lens drift tube for the TOF-MS measurement. The performance of the drift tube was measured for PSD ions from the SiH_2Cl_2-saturated Si(001) surface and was discussed in terms of the numerical calculations of ion tragectories and focusing characteristic. It was concluded that the detection efficiency can be increased by the focusing effect of the drift tube without significant degradation of the mass resolution. Therefore, the drift tube composed of an electrostatic lens allows us to achieve a high detection efficiency when a detector with a small detection area but resistant to reactive gases is employed for observing *in situ* PSD ions under reactive gas atmosphere at high pressure.

References

El-Kareh, A. B. & Sturans, M. A. (1971). *J. Appl. Phys.* **42**, 4902–4907.
Harding, E. & Read, F. H. (1976). *Electron Static Lenses*. Amsterdam: Elsevier.
Johnson, L. W. & Riess, R. D. (1982). *Numerical Analysis*. Reading, MA: Addison-Wesley.
Sakamoto, H., Takakuwa, Y., Hori, T., Horie, T., Suemitsu, M. & Miyamoto, N. (1996). *Appl. Surf. Sci.* **107**, 68–74.
Takakuwa, Y., Enta, Y. & Miyamoto, N. (1996). *Optoelectron. Devices Technol.* **11**, 3–22.
Takakuwa, Y., Nogawa, M., Niwano, M., Katakura, H., Matsuyoshi, S., Ishida, H., Kato, H. & Miyamoto, N. (1989). *Jpn. J. Appl. Phys.* **28**, L1274–L1277.
Ueno, N., Kamiya, K., Harada, Y., Tinone, M. C. K., Sekitani, T. & Tanaka, K. (1996). *Optoelectron. Devices Technol.* **11**, 91–98.