SiO_2 Etching Induced by Soft X-ray from Figure-8 Undulator

Osamu MAIDA[1)], Norihiro KOHMA[1)], Takeshi KANASHIMA[1)], Hideo WADA[1)], Masashi AGATA[1)]
Shinji YUDATE[1)], Masanori OKUYAMA[1)] and Haruhiko OHASHI[2)]

1) Department of Physical Science, Graduate School of Engineering Science, Osaka University,
2) Japan Synchrotron Radiation Research Institute

1. Introduction

Recently, ultralarge-scale integrated circuits (ULSIs) have been developed extensively, and the size of one element has been reduced very much. However, it is difficult to more integrate LSI using conventional LSI process. Therefore, a new process has been desired in electronics manufacturing. Strong soft X-rays from undulator in a storage ring is expected to solve these requirements. Because, atoms could be excited very much by high energy photon, and extraordinary chemical reactivity is caused by remarkable dissociation and multi-ion production, consequently. Moreover, chemical reaction can be controlled by matching emitted photon energy from undulator to a bond dissociation energy. Therefore, CVD, surface modification, ablation and etching technique used strong soft X-rays are paid to great attention. In this work, we have made setting of BL27SU Soft X-ray CVD station and investigated soft X-ray (0.5 - 5.0 keV) induced etching of SiO_2 film, as the preliminary experiment. SR induced etching of SiO_2 film has been studied in various research organizations [1, 2, 3] to apply it to semiconductor process and to make clear its surface reaction.

2. Experimental

2-1 Instrument Details

Radiation from the figure-8 undulator set in the storage ring was used as a light source. The undulator light is reflected by 2.2˚ using an Au-coated Si mirror located 35 m far from the center of the undulator magnets. Soft X-ray CVD station consists of some chambers, analysis instruments, gas supply and toxic gas treatment system. The base pressures of the reaction and analysis chamber were 5.0 x 10^{-7} Pa and 5.0 x 10^{-8} Pa respectively. O_2, N_2 and Ar gas supply system is installed for gas phase reaction or ion sputtering. Three differential pumping chambers are set to irradiate SR light to sample and reaction gas without window directly. Using this system, reaction gas could be introduced at pressure 0.1 Torr in reaction chamber.

It is essential that the analysis chamber with analytical instruments is directly connected to the reaction chamber. Therefore, Auger electron spectrometer (AES), Reflected high energy electron diffraction (RHEED) and Quadrupole mass spectrometer (QMS) were installed for *in situ* measurement of the interesting sample reacted with SR. Moreover, installation of the X-ray photoelectron spectrometer (XPS) is in planning stage.

2-2 Experimental Details

Undulator radiation was incident normal to the sample surfaces. The beam spot on the target was an ellipse with major and minor diameters of 4 and 1.5 mm. Electrons beam current in the storage ring is between 40 and 70 mA and all results are shown after normalization for a current of 70 mA. Samples were thermally grown SiO_2 films on n-type (200-500 Ω·cm) Si(100) wafers. The thickness of the oxide layer for the evaporation rate measurement and mass spectroscopic measurements was 1 μm. Thinner films (22 nm) were used for AES measurements in order to prevent charge up. To clarify the difference of the film in SR irradiated and non-irradiated region, a honeycombed structure stainless mask was put on samples. The etching rate was evaluated by using a stylus step profiler to measure the evaporated depth at the center of the irradiated region.

2-3 Results and Discussion

Figure 1 shows the two-dimensional image of the sample surface that was SR irradiated for a

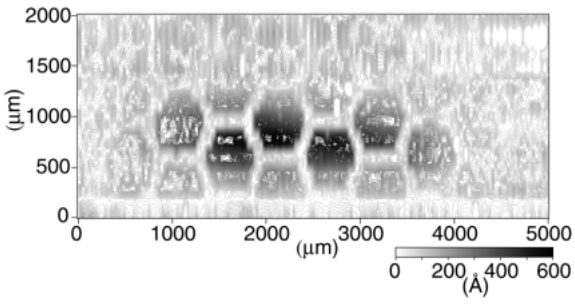

Fig. 1: Thickness profile of the SiO_2 film that was irradiated for a dose of about 9,400 mA·min at 825˚C.

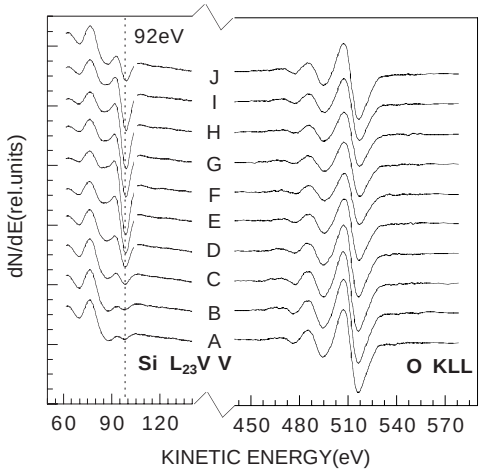

Fig. 2: Auger signal from irradiated with a dose of about 9,400 mA·min at 740˚C. (A to C: non irradiated region, D to J: irradiated region)

dose of about 9400 mA·min at 825˚C and 79.3 mm undulator gap length (L_g=79.3 mm). It is found that the intensity distribution of the beam with L_g=79.3 mm has its fundamental mode at slightly higher energy of *K*-shell absorption edge of Si (1,844 eV) [4]. SiO_2 evaporation only in the irradiated region shows that it is essential for this reaction to irradiate soft X-ray. The evaporation rate of SiO_2 film has strongly temperature dependence. The Arrhenius plot between 500 and 900˚C could be fitted by a straight line and the activation energy of this reaction was estimated to be 0.28 eV, which is lower than the 0.60 eV reported by H. Akazawa *et al.* in beam line 1C at the Photon Factory in the National Laboratories for High Energy Physics [3].

On the other hand, the evaporation rate also had photon energy dependence. Evaporation rates of samples irradiated at L_g =70.0 mm and 79.3 mm were estimated to be 11.6 Å / 70 mA·min and 3.8 Å / 70 mA·min, respectively. The reason for this difference is that the intensity distribution of the beam with L_g =70.0 mm has its 0.5th harmonic at the energy of *K*-shell absorption edge of O (543 eV) and 1.5th harmonic at the energy of *K*-shell absorption edge of Si (1844 eV). This result shows that *K*-shell electron excitation of oxygen accelerates this reaction effectively and agrees with the result by K. Shobatake *et al.*

Figure 2 shows the O *KLL* and Si $L_{23}VV$ Auger signals from SR irradiated sample for a dose of about 9400 mA·min at 740˚C and L_g=79.3 mm. AES spectrum from irradiated region (D to J) had Si (92 eV) $L_{23}VV$ signals. This signal is originated from oxygen-deficient defects and shows that the surface composition changed to SiO_x (x < 2) [5].

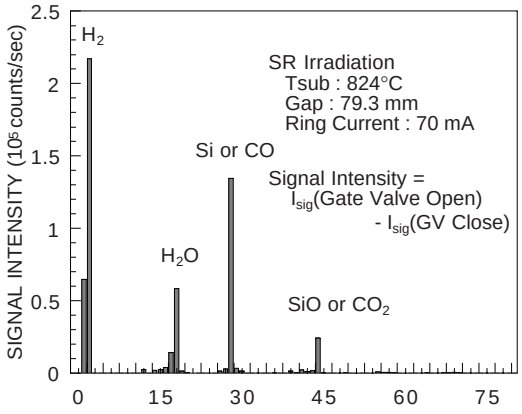

Fig. 3: Mass spectrum of desorped molecules at 825˚C.

Figure 3 shows the mass spectrum of desorped molecules at 825˚C. Some remarkable signals that are found at *m/e* = 18,28,44 are expected to be H_2O, Si and SiO respectively. On the other hand, we could not find *m/e* = 18 (O_2) and *m/e* = 60 (SiO_2) signals. In quadrupole mass spectroscopy, however, Si and CO are all possible sources of the *m/e* = 28 signal. Similarly, SiO and CO_2 are possible sources of the *m/e* = 44 signal. If the *m/e* = 28 signal was originated from Si, this result was very interesting. Unfortunately, we have not found which is the source of these signals yet.

3. Conclusions

We studied SiO_2 film etching induced by high energy photon (0.5~ 5.0 keV) in BL27SU. The evaporation rate of this reaction had strongly temperature and photon energy dependence. The activation energy of this reaction was estimated to be 0.28 eV. It was considered that oxygen *K*-shell electron exiting accelerates this reaction effectively. AES spectrum from irradiated region showed the surface composition changed to SiO_x (x < 2). In the mass spectroscopic measurement, some remarkable signals were found at *m/e* = 18,28,44.

References

[1] K. Shobatake *et al.*, Appl. Phys. Lett. **56** (1990) 2189.
[2] T. Urisu *et al.*, J. Appl. Phys. **70** (1991) 2958.
[3] H. Akazawa *et al.*, Phys. Rev. B **52** (1995) 12386.
[4] Synchrotron Radiation Calculation Program for Win32 V.1.1 Mar. 19,1996, by Hideo Kitamura and Takashi Tanaka
[5] B. Carriere and B. Lang, Surf. Sci. **64** (1977) 209.