

Chapter
Chapter



2

Experiment

Ultra high vacuum (UHV) reaction chamber plays a vital role to study the interactions of atomic species with solid surfaces. The reason is that an UHV chamber can ensure the least number of collisions among the gaseous species. This system also keeps the sample clean during the experiments. Two important sections of this experimental set up are the generation of atomic beam and interaction of this beam with samples. If radical atoms are generated in the same reaction chamber (for example, generation of hydrogen atoms by a hot W filament) some unwanted species may form. This may affect the sample by heating or by contaminating the surface. Furthermore, the pressure of the reaction chamber may increase very much during the atomic beam generation. It causes serious background effect in signals detected by a QMS. Another point is that, investigations of surface reactions, induced by incident atoms from an abstraction point of view, require simultaneous measurement of desorbing species by a QMS. In this circumstance, pressure rising in the reaction chamber severely affects the data quality. To avoid these effects, atomic species should be generated in separate chamber isolated from the reaction chamber. To produce a well collimated atomic beam, three differentially pumping chambers connected with collimating apertures are employed.

2.1 Atomic beam chamber

Considering the above remarks, atomic beam generation chamber and reaction chamber are separated from each other via small aperture with a 3mm diameter to assure differential pumping. The beam chamber system is consists of three differentially pumped chambers for beam generation, beam chopper and buffer, connected through three 3mm apertures. The H, D or O beam is generated by means of gas plasma using a inductively

coupled radio frequency (RF, 13.56 MHz) plasma applying a power of 200 W. H₂ and D₂ gases are seeded with Ar gas (1:1 ratio) to produce atomic H and D beams. During the plasma generation, energy dissociates the H₂ or D₂ gases into atomic state.¹ A small amount of H₂O (D₂O) is introduced in the H₂/Ar (D₂/Ar) gas to enhance the plasma density.² The average kinetic energy of H atoms generated by this technique is ~0.05 eV, equivalent to the room temperature.³ In case of atomic O generation, pure O₂ gas is used. The chamber for beam generation is evacuated by an oil diffusion pump (2000 l/s) backed by a rotary pump. The beam is chopped by a vacuum tight pulse motor. This chamber is evacuated by an oil diffusion pump (800 l/s) backed by a rotary pump. The third chamber is a buffer chamber, evacuated by a turbo molecular pump (150 l/s) backed by a rotary pump. The distance from the RF plasma nozzle to the sample in the reaction chamber is 81 cm long.^{4,5,6,7,8}

2.2 Reaction chamber

The reaction chamber is equipped with a Quadruple Mass Spectrometer (QMS, Marlin, ABB Extrel), an Auger Electron Spectrometer (AES, ULVAC-PHI, INC, ULA-020), an Ar⁺ gun (ULVAC-PHI, INC, FIC-5), and a precisely controlled (x,y,z) sample manipulator. The sample was supported with molybdenum (Mo) plates on a ceramic base. The diameter of the beam is 3mm which is small enough to avoid an influence of unwanted desorption from the Mo holder. The QMS detects different gases simultaneously in the angle-integrated mode. Surface cleanliness is checked by AES. If the AES shows presence of contaminants (oxygen and/or carbon) Ar⁺ ion gun is used to sputter them. The reaction chamber is evacuated by a turbo-molecular pump (500 l/s) backed by a rotary pump and a liquid N₂ cooled Ti sublimation pump (800 l/s). The chamber is baked at 150 °C for 8 hours. At the end of baking, filaments of QMS, AES, Ar⁺ gun, ion gauze and sample are flashed to acquire a pressure

below 5.0×10^{-11} Torr. The top view of the full reaction system is shown in Fig. 2.1.

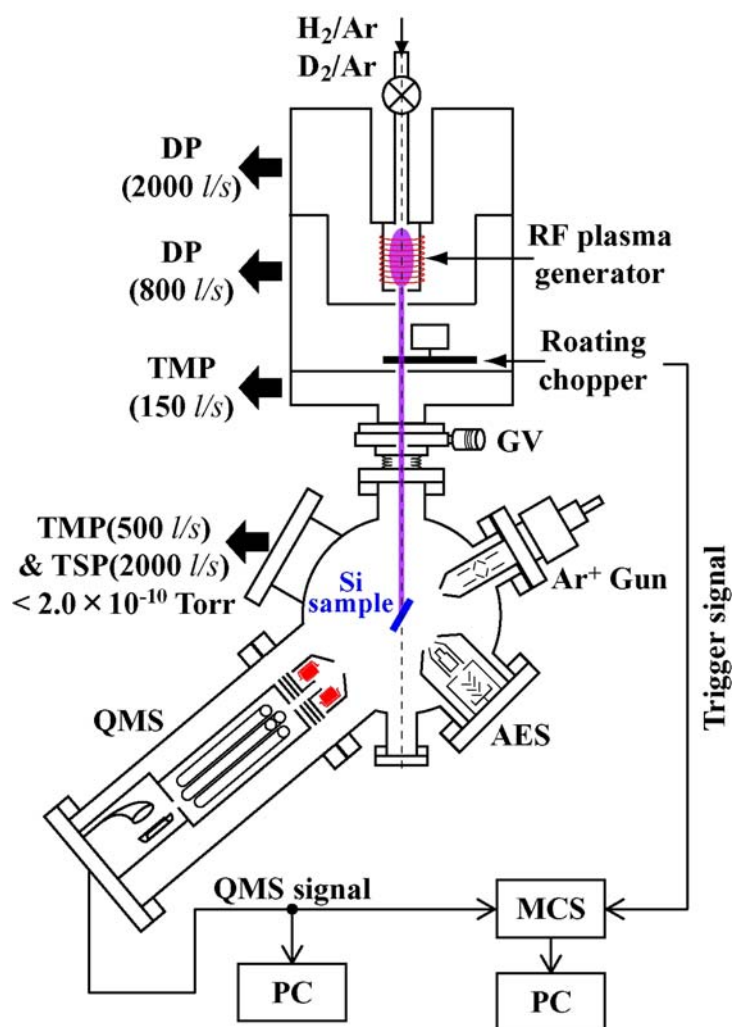


Fig. 2.1. Top view of the ultra high vacuum reaction system

2.3 Sample preparation

Commercially available Si(100) and Si(110) surfaces have been used to study the abstraction reaction. The sample is cut into a $15 \times 24 \times 0.3 \text{ mm}^3$ size and is mounted on the sample holder. The sample is cleaned by means of resistive heating. The flashing temperature is about 1000°C for a minute and annealed at 600°C for 10 minutes. After cooling to room temperature with a rate of 0.5 K/s , cleanliness is checked by AES. Both the C(KLL) and O(KLL) intensities are generally less than 1% of Si(LVV) intensity. An AES spectrum of clean Si(100) surface after cleaning process is shown in Fig.2.2.

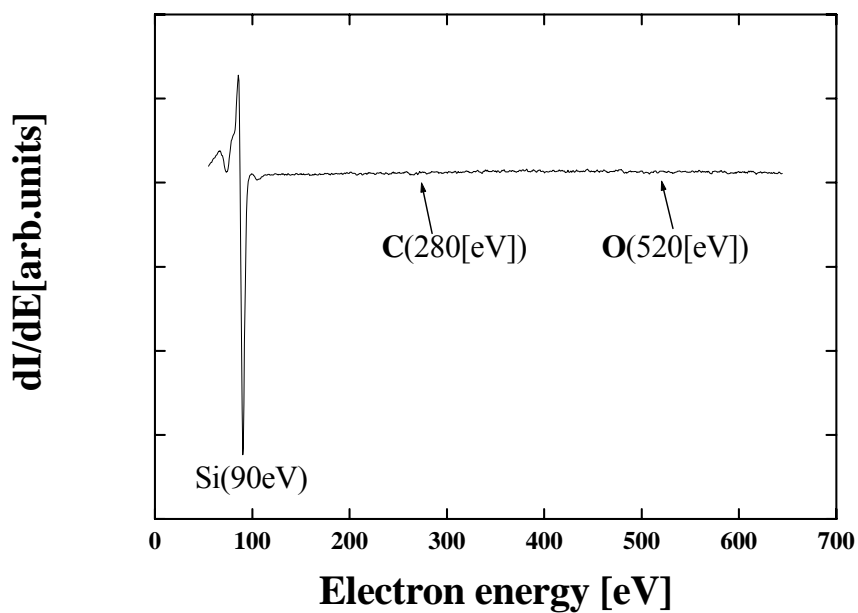


Fig. 2.2. AES spectrum of clean Si(100) surface taken at RT. No peak due to existence of surface O and/or C is present.

2.4 Surface temperature calibration

Surface temperature shows a strong influence on abstraction reactions. To keep the surface temperature constant during surface reactions and to increase the surface temperature in a constant rate during the thermal desorption (TD) experiments, direct resistive heating technique is used. DC current is supplied to the sample from a current source (EX-750H2) controlled by a personal computer. Using this device and specially designed software, temperature of the sample is either automatically or manually controlled over the range of 373 K to 1375 K. During TD experiments and cooling the samples, the ramp rate is 3.14 and -0.5 K/s, respectively. A general relation of resistance (R, Ohm) and temperature (T, °C) of the sample is $R = a \times T^b$, where a and b are the constants. Surface temperature (T_s) is measured by an IR pyrometer (KTL-P1) and a R vs. T curve is obtained. From the calibration of the R vs. T curve as shown Fig.2.3, the constants a and b are determined. They are set into temperature calibration program run by a C++ programming. Finally, correctness of surface temperature is checked by referencing the established β_1 and β_2 TD peak maxima.

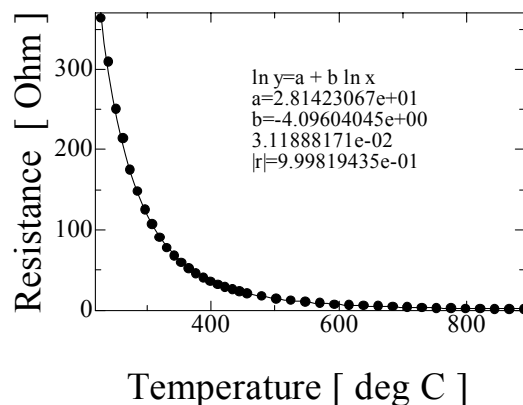


Fig. 2.3. Temperature calibration parameter (a and b) are determined from the best fitted curve drawn by Sma4Win software.

2.5 QMS calibration and pulsed-H beam profile

The QMS signal intensities obtained in TD or in abstraction reactions are proportional to the desorption rates of HD and D₂ molecules. To determine absolute desorption rates with a unity of ML/s, the sensitivity of the QMS, are calibrated by following manner.⁹

Desorption rates of HD and D₂, R_i ($i = \text{HD or D}_2$) are expressed as $R_i = K_i P_i$, where K_i is the constant and P_i is the count rate measured by the density sensitive QMS. The sensitivity K_{D_2} is determined using the integrated intensity of D₂ TD spectrum from 1ML D/Si(100)-2x1 surface as follows:

$$K_{D_2} = \frac{1}{2 \int_{t=0}^{t=\infty} P_{D_2}(t) dt}$$

In the interaction of H atoms with D/Si(100) surfaces, the D adatoms are desorbed as HD and D₂ molecules. Therefore, K_{HD} is determined from HD and D₂ desorption intensities measured in the reaction of H + D/Si(100) and post reaction thermal desorption (TD) as follows:

$$A_{(ABS+AID)} + T_{(TD)} = I (ML)$$

where,

$$A_{(ABS+AID)} = \int_0^{t_m} [K_{HD} P_{HD}(t) + 2K_{D_2} P_{D_2}(t)] dt$$

$$T_{(TD)} = \int_{t=0}^{t=\infty} [K_{HD} P_{HD}(t') + 2K_{D_2} P_{D_2}(t')] dt'$$

In case of H-induced D abstraction, t_m is the time when H exposure is stopped. The determined constants K_i are used to measure the desorption rates of HD and D₂ in the reaction between continuous H beam and D/Si surfaces in the next chapters.

To collect abstraction data for a short time range through a multi-channel scalar (MCS), QMS signal is fed into the MCS. The MCS is triggered with the rotating beam chopper equipped in the second chamber of the atomic beam generation system. (Fig. 2.1.) Depending on the experimental conditions, the rotation rate of the chopper is chosen. To reveal the transient behavior of desorbing D_2 molecules induced by the atomic H-beam on the Si(100) surfaces, the chopper with a 5% duty ratio is rotated at 0.5 Hz. Figure 2.4 shows the pulsed beam profile having a 0.1 sec on-cycles and 1.9 sec off-cycles. On the other hand, in order to reveal the kinetics of O induced D_2 and D_2O desorption, two choppers of two different duty ratios, (50% and 5%) with a rotation of 0.1 Hz were used. Figure 2.5 shows the chopper profile of 0.1 Hz rotation.

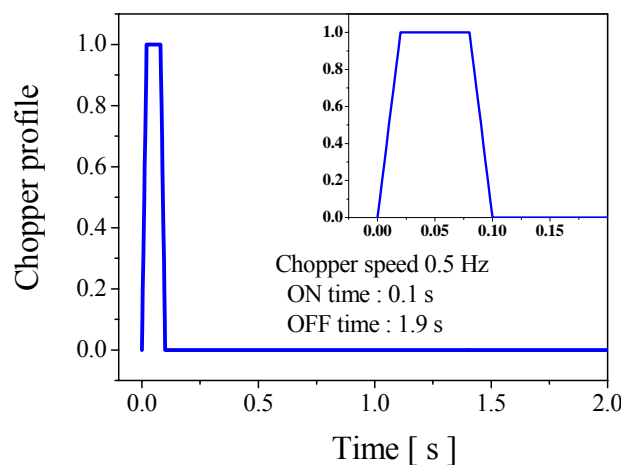


Fig. 2.4. Schematic illustration of rotating chopper of 0.5 Hz showing a 0.1s on- and 1.9s off-cycle.

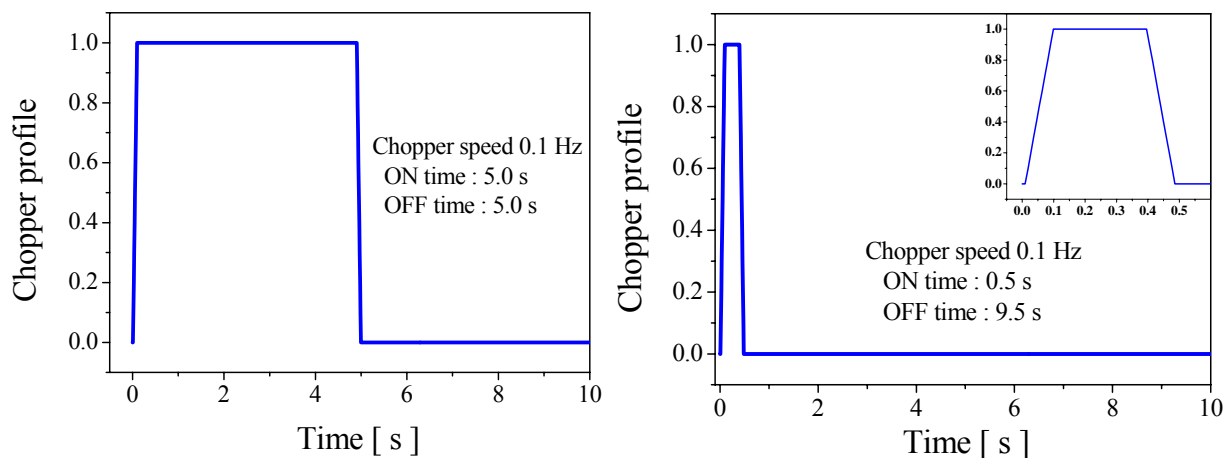


Fig. 2.5. Schematic illustration of rotating chopper of 0.1 Hz with 50% duty ratio (left) and 5% duty ratio (right).

2.6 FTIR setup

Infrared (IR) spectra of H-terminated Si(110) surfaces were obtained with an FTIR absorption spectrometer in an ultra high vacuum chamber equipped with an RHEED installed at Suemitsu's lab in Tohoku University. IR light was introduced to the chamber through a BaF₂ window, and was focused onto one of bevel-polished edges of the sample. The light then underwent about 70 times internal reflections until it emerged from the other end of the sample, and was finally focused onto an InSb IR detector. The resolution of the FTIR spectrometer was 2 cm⁻¹ after averaging 600 interferograms. IR spectrum measured for the clean Si(110) surface was used as a background. Deposition of H atoms onto the sample was done through thermal cracking of H₂ gas on a heated W filament.¹⁰ This spectrum is used to characterize surface species on H/Si(100) surfaces.

References

1. S. Iordanova and I. Koleva, *Spectrochimica Acta Part B* 62 (2007) 344.
2. S. Shimokawa, A. Namiki, T. Ano and Y. Sato, *J. Chem. Phys.* 112 (2000) 356.
3. F. Rahman, Ph.D. thesis, Kyushu Institute of technology, February, 2004.
4. F. Khanom, S. Shimokawa, S. Inanaga, A. Namiki, M.N. Gamo, T. Ando, *J. Chem. Phys.* 113 (2000) 3792.
5. E. Hayakawa, F. Khanom, T. Yoshifuku, S. Shimokawa, A. Namiki, T. Ando, *Phys. Rev. B* 65 (2001) 033405
6. F. Khanom, A. Aoki, F. Rahman, A. Namiki, *Surf. Sci.* 536 (2003) 191
7. S. Shimokawa, F. Khanom, T. Fujimoto, S. Inanaga, A. Namiki, T. Ando, *Appl. Surf. Sci.* 167 (2000) 94
8. H. Tsurumaki, K. Iwamura, T. Karato, S. Inanaga, and A. Namiki, *Phys. Rev. B.* 67 (2003) 155316
9. A. Kubo, Ph.D. Thesis, University of Tsukuba, January, 2003.
10. Y. Tsukidate, M. Suemitsu, *Jpn. J. Appl. Phys.* 40 (2001) 5206.