Report on Visit to Ruhr-University Bochum by International Training Program

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As a long-term placement program of ITP (International Training Program), I had studied in the Prof. Keudell research group in RUB (Ruhr-University Bochum) of Germany for two months, from January 27, 2012 up to March 26, 2012. This is a report of my stay.

Research

(a) Research theme

The research theme on my Ph.D. course is “Studies on basic process of photoresist surface reactions during plasma etching processes”, and I have been studying modifications of photoresist caused by irradiations of mass-separated ion beam, and plasma beam which is a beam of active species such as ions, radicals extracted plasma to clarify the mechanism of modification of photoresist.

The research group of Prof. Keudell established a system for measurements of *in-situ* FTIR (Fourier transform infrared spectroscopy) and QCM (Quartz crystal microbalance) to achieve real-time measurement during the plasma processes. It is one of the characteristics of the research group. I applied the dispatch to Prof. Keudell research group because I thought I could get well-understanding of reactions between photoresist and plasma by using this system.

Therefore, I set "Real-time observation of the modifications of photoresist during irradiations of Ar ion beam and oxygen atom beam" as the research theme in the Prof. Keudell research group. I exposed active species produced in plasma as a particle beam to the photoresist, and observed the changes of photoresist structure and thickness with FTIR and QCM. However I usually use reactive gases like fluorocarbon gases and HBr for my research in Japan, I used only Ar gas to investigate most fundamental modification process because the dispatch term is limited to only two months. Then, I irradiated oxygen atom beam to the modified photoresist which was exposed with Ar ion beam and pristine photoresist, and compared these results to investigate accurate parameter of ashing process of photoresist with oxygen atom. This research is closely related to my research theme in Japan as I mentioned and it makes my research in Japan expand widely and deeply.

In this report, I focused on the real-time observation of modification process of photoresist caused by Ar ion beam because of the space limitations.

(b) Experiment

At the beginning of experiment, I did experiment with a student who used a molecular beam system in Prof. Keudell group. He investigated changes of characteristics of PET (Polyethylene terephthalate) film like hydrophilic property, chemical binding. I learned fundamental usage of this molecular beam system, such as how to evacuate the chamber, expose ions, and measure FTIR and so on.

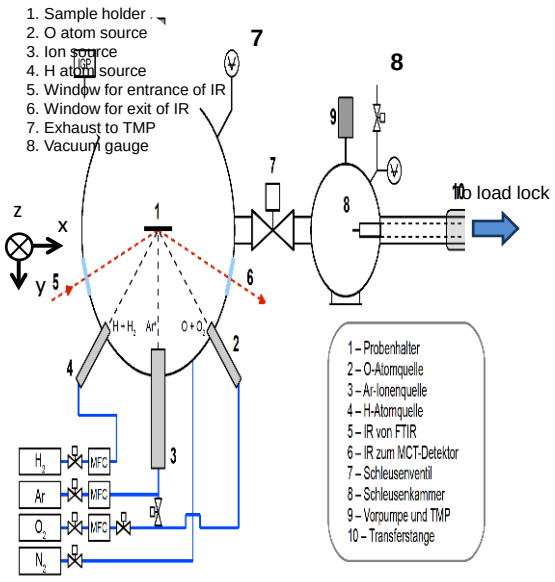

Fig 1. Schematic of experimental set-up (Top-view)

The schematic of experimental set-up I used in RUB is shown in Fig. 1. At the ion source, ions are generated in ECR (Electron cyclotron resonance) plasma, and these are accelerated to any energy by biased acceleration electrode and extraction electrode. At the atom source, induced gas is dissociated to atom by electron emitted from the heated filament, and atoms are exposed to the target through capillary. [1] We used OCS (Optical cavity substrate) to enhance the signal of infrared absorption when we did real-time FTIR measurement. [2] In this research, I used silicon substrate as OCS, which is coated with photoresist on the top and with 200 nm aluminum on the backside.

After learning how to use the particle beam system fundamentally, I measured ion beam distribution with faraday cup. Figure 2 shows X position dependence of ion current density. The directions are defined as shown in Fig.1. The measurement area of FTIR is an ellipse which has major axis of 20 mm, minor axis of 10 mm approximately. I assumed the ion current distribution was almost uniform in the measurement area of FTIR under the condition of 400 eV acceleration voltage, which is set as a basal condition of this research. I could not measure the ion current density at the higher X position more than 25 mm, but we confirmed X=23.5 mm position was a center of beam spot with another method.

However I use photoresist of 200 nm thickness in Japan, I had to make a thin photoresist of approximately 50 nm thickness to get a enhanced signal of IR absorption with OCS at RUB. I created a condition for spin coating of thin photoresist on OCS in parallel with measurement of ion beam distribution. Firstly I tried to increase spin speed but it was not enough to make thin film. Then I diluted photoresist liquid to decrease its viscosity, it worked well and I could make a 50 nm photoresist on the OCS.

I measured changes of bindings of photoresist coating on OCS with real-time FTIR during Ar ion beam exposure. Variations of C-Hx bindings of photoresist during the process are shown in Fig..3. Experimental conditions were followings: an acceleration voltage and an extraction voltage were 400 eV and 0 eV respectively, and pressure during process was kept at 3.9×10^{-2} Pa. As shown in Fig.3 (a), C-H_x bindings decreased in the photoresist with increasing of beam exposure time. Figure 3 (b) shows variations of each peak height during the process. At the beginning of Ar ion beam exposure, the large peak immediately appeared at 2915.8 cm^{-1}, and the speed of change became slow once. With keeping ion beam exposure, the photoresist modification reached at steady state, and the speed of change

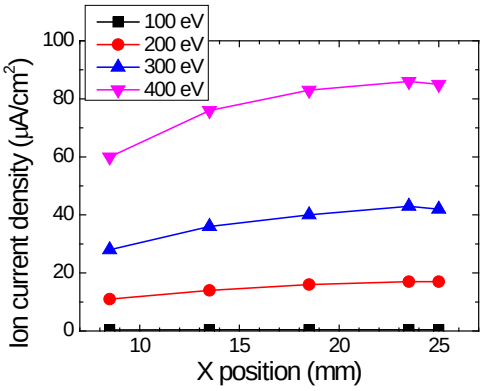

Fig 2. X position dependence of Ion current density

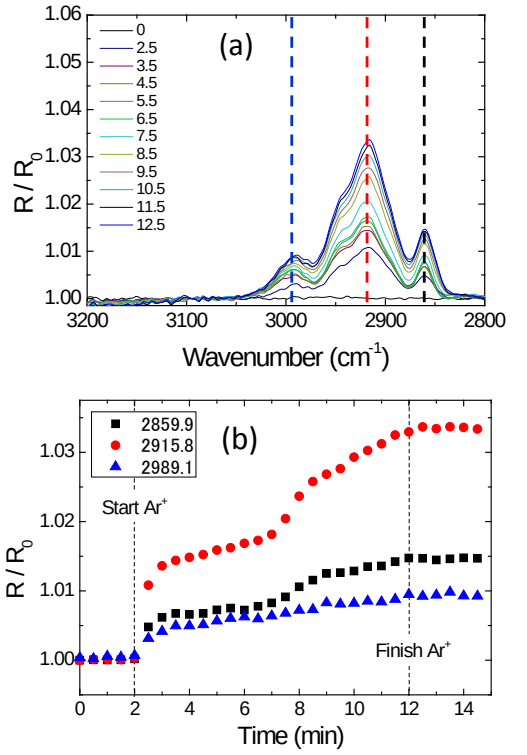

Fig. 3. Beam exposure time dependence of C-H_x
(a)Spectra of IR absorption (b) Peak height changes

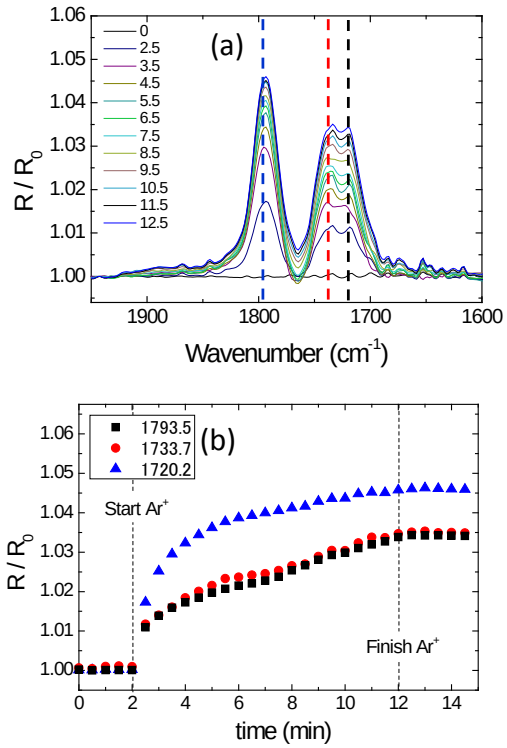

Fig. 4. Beam exposure time dependence of C=O
(a)Spectra of IR absorption (b)Peak height changes

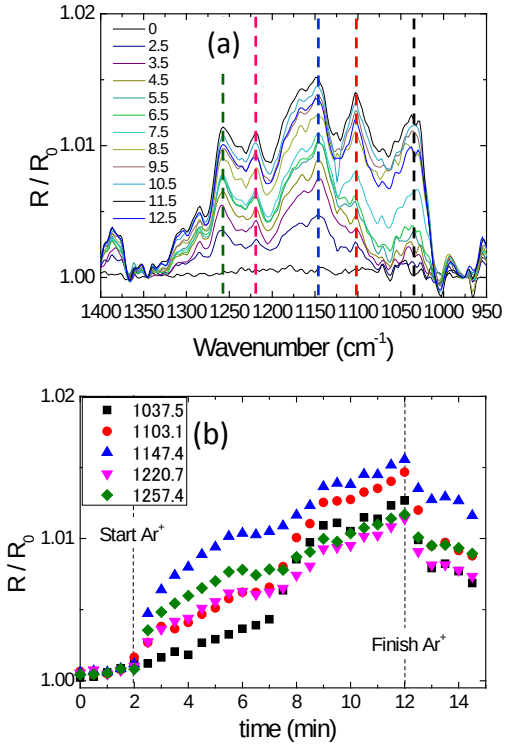

Fig. 5. Beam exposure time dependence of C-O
(a) Spectra of IR absorption (b) Peak height changes

became larger than that at intermediate state. We can see the same tendency in the peak at 2859.9 cm^{-1} even though this change was smaller than that of peak at 2915.8 cm^{-1}. The changes of C=O bindings and C-O bindings are shown in Fig.4 and Fig.5, respectively. C=O bindings immediately decreased at the beginning of the beam exposure, and then reached at steady state. On the other hand, C-O bindings mostly changed according to exposure time, but it seemed that there was a time region in which change was small as seen in the C-H_x bindings.

In this experiment, I employed ECR plasma to produce ion beam. So the photoresist was exposed to irradiations from not only ions but also ultraviolet light and it should be taken into consideration the photoresist can be also modified by ultraviolet light. There is a report in that C=O bindings in the photoresist material can be decreased by ultraviolet light exposure. [3] Similar with this case, it is supposed C=O bindings were decreased by ultraviolet light mainly, and the modification of caused by ultraviolet light seemed to reach at steadt at 2 minutes exposure (corresponds to 4 minutes after the start of measurement).

Next, I measured thickness changes of photoresist with QCM, and calculated the etching yield of Ar ion to the photoresist from the result. In this study, etching yield is defined as the number of carbon atoms removed from the photoresist film per an incident Ar ion. The results are described in Fig.6. I coated Al-coated quatz crystal with photoresist for the measurement of microbalance. As shown in Fig.6, the etching of photoresist progressed with high etching yield at the beginning of beam exposure, and an etching yield dropped to almost zero immediately. It seemed to be the balance of mass between a decrease by etching and an increase by Ar ion implantation. Then, after the enough Ar ion implantation, the modification of photoresist reached at steady state and the etching yield became steady. This change was similar to the changes of C-H_x bindings (especially the peak at 2915.9 cm^{-1}), it seemed the C-H_x changes depend on the thickness of photoresist. However, the etched thickness of photoresist on the OCS after the 10 minutes irradiation of ion beam measured with surface profilometer was around 30 nm. It was around 10 nm larger than the result of microbalance. Surface profilometer measures the thickness directly. On the other hand,

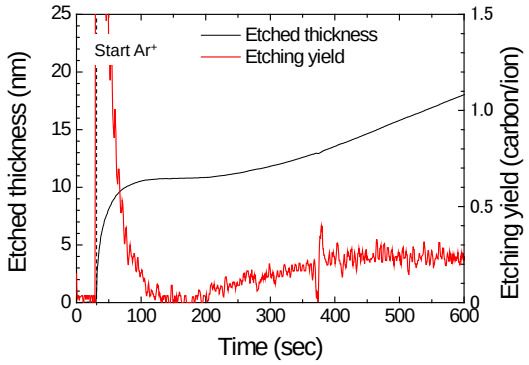

Fig. 6. Exposure time dependence of etched thickness and etching yield of photoresist

microbalance measures the mass variation and calculates the thickness from the measured mass variation on the assumption that the density of material is constant during the process. From the view point of measurement principle, the difference between them is thought to be caused by the shrinkage of photoresist.

From these results, I created a model for the etching of photoresist by Ar plasma. At the beginning, ultraviolet light cuts C=O bindings of photoresist film and makes dangling bond immediately. The etching yield is very high during this period. Then, Ar ion implantation becomes dominant and the shrinkage of photoresist occurs due to the recombination of dangling bond in the photoresist film. The thickness decreased for the cause of the shrinkage, but the etching yield is small because the decrease of thickness is not caused by removing of atoms from the photoresist during this period. Finally, the modification reaches at steady state through the enough shrinkage period, etching of photoresist progresses with a constant etching yield.

College life in RUB

After I arrived at Frankfurt airport, I moved to Bochum by DB (Deutshe Bundesbahn). It was 11 pm on January 27th, Friday when I arrived at the dormitory near the university. The dormitory I stayed at was one of institution of the Ruhr-University, it is called as Landesspracheninstitut in der Ruhr-Universität Bochum. This institution is sometimes used as guesthouse like us, but the main users are students who attend lectures for language exchange program. The institution is located on opposite side of university from the station; it takes 10 minutes to the university station by walk. In the dormitory, we could use common kitchen and wash machines, and there are all other things we need. I could stay there without feeling uncomfortable.

I usually had lunch at Menza, school cafeteria, dinner at the kitchen in the dormitory. There are many foods at Menza, Greece food, Argentina food and Asian food and so on. Menza is very convenient because we students can use here with discounted price. There is an Asian shop near the university station, I could buy some of Japanese food there such as Japanese rice, wasabi, and shoyu.

Summary

As mentioned above, every experience that I had during my stay in Germany through this program such as study of "Real-time observation of modification process of photoresist", discussions with students and professor in English, and life in a foreign country, will help me to promote my study in Japan and international understanding between Germany and Japan. This stay in Germany gave me an irreplaceable two months.

Finally, I deeply appropriate Prof. Keudell, Prof. Hori, Prof. Toyoda for giving me such a great opportunity, and all of people for assisting my stay.

References

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