Report on Visit to University of Texas at Dallas by International Training Program

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1. First of all

The tie-up of Toshiba and Samsung in the System LSI area was announced on the newspaper, "Nippon Keizai Shinbun", and surprised the industry on December 24, 2010. This imply that Semiconductor industry is facing the problem of NRE (Non-Recurring Engineering), which cannot earn the production cost, and it is assumed that world wise industry restructuring will be conducted. In the research industry, cost of equipment is getting more and more complicated and increasing. So before the industry, corporation and roll allotment beyond board is preceded.

In this internationalization, Japan seems to be late compared to the others countries. In spite of most of the cutting edge conference and paper are written with English, English level of Japan is still low. The number of students who study abroad is low, too. Japan have to take a view on abroad and focus on the other countries movement and the position of Japan in international world to lead the industry with the stock of money and skills until now. To see the affairs of the oversea, I thought that to feel it there would be the best way, that's why I desired this training program.

2. About the University which I stayed

I went to the University of Texas at Dallas (UTD) witch main campus is located in Richardson, Texas, America. I worked on this experiment in International Center for Advanced Materials Processing (ICAMP).

UTD is established as one of the science institute of Texas Instruments (TI), which is famous as worldwide development and producing Semiconductor Company. UTD will be 40 years old from adopting students in 2009, and 20 years old from adopting the undergraduate students. However UTD is evaluated Tier-1, as one of the best college in 2011, by US news and world report, and recognized as a high powered research college in the USA. Especially development of these years is outstanding. Experiment budget in 2010 is 85,000,000\$, which increased 60% for 4 years. It is assumed to be one of the cutting edge experiment college.

- 3. Experiment
- (1) Measurements

In the UTD, I researched about "Formulation of a Global Model for 2ClpX (C_8H_9Cl) Plasma Coupling Gas Phase & Wall Surface Reaction Kinetics", which is counted on to apply medical parylene coating.

In ordinary palyrene is widely applied to medical, electronics, car, airplane industry and so on. Because it has outstanding properties, very thin, high water proof, high chemical proof, gas imperviableness, high insulation properties and high burning resistance, compared to the other polymer layers, epoxy, and silicon urethane^[1].

Parylene coating is forwarded with inserting the reactive monomer gas, in the chamber heated from 650 deg. to 700 deg., to the vacuumed chamber, which is room temperature. Applying the parylene character which is polymerize on the surface of the room–temperature wall, deposition of the thin formal film is available without pin hall free and depending on the structure of the surface ^[2].

However, high chemical bonding and sticking bonding are needed for the application which needs very thin film, like medical application. So these



Fig. 1 Parylene C

days, plasma film deposition which can deposit the thin film which has chemical bonding and sticking bonding are focused on. In this experiment, parylene C, which has high speck compared to the other paraxylene plastic, is focused (Fig. 1).

2-Chloro-p-xylene (2ClpX: C_8H_9Cl) plasma is used to deposit Parylene C (Fig. 2). With producing the plasma, radical, by providing the high power to the electrode, film is deposited on the substrate set on the bottom electrode. At that time, it is known that excellent adhesion film is available with supplying high power, and better functionality is available with supplying low power. In this way plasma condition affect the film characteristics. So we have to know the reactions inside the plasma to control the film condition.

So the objective of this research is "Formulation of a Global Model for C_8H_9Cl Plasma Coupling Gas Phase & Wall Surface Reaction Kinetics". With calculating the generic mass balance at the steady state, important inner parameter, the densities of neutral and charged species and electrons and the temperature of electrons can be measured and so no, can be measured ^[4].

The generic mass balance at the steady state for a species i (neutral or charged) in the gas phase is the balance of the mass flow at the inlet, the mass flow at the outlet, production in the gas phase and production on the surface, which is formulated as

$$0 = \frac{Q_{f,i}}{Vk_BT_0} - \frac{S_p}{V}n_i + \sum_{j=1}^{n_{r,gas}} R_{i,j}^{gas} + \sum_{k=1}^{n_{r,surf}} R_{i,k}^{surf}$$
(1)

The generic mass balance at the steady state for a



Fig. 2 2-Chloro-p-xylene (C₈H₉Cl)

species m (neutral or charged) on the surface is the balance of Production on the surface, which is formulated as

$$0 = \sum_{k=1}^{n_{r,surf}} R_{m,k^{surf}} \quad (2)$$

The generic power balance at the steady state for a species i (neutral or charged) is the balance of power absorbed by the electrons and ions, energy loss for the electron impact reaction, energies of the escaping to the walls and potential energy of the gas, which is formulated as

$$0 = \frac{P_{abs}}{V} + \sum_{j=1}^{n_{r,gas}} R_{e,j}^{gas} \varepsilon_{loss,j} + \sum_{k=1}^{n_{r,surf}} R_{c,k}^{surf} (\varepsilon_{ion,w} + \varepsilon_{ion,w})$$
$$+ \frac{S_p}{V} \frac{3}{2} \left(n_e k_B T_e + \sum_{c=1}^{n_c} n_{+,c} k_B T_{ion} \right)$$
(3)

From these equations, rate constant becomes the function depending on individual each particle. But most of them don't have the references. So it is needed to calculate the main reaction's rate constant to build the model.

The Gaseous Electronics Conference RF Reference Cell (GEC Cell) was used for the experiment (Fig. 3)^[5].

The unique point of this chamber, Fourier Transform Infrared Spectroscopy (FT-IR) and Optical Emission Spectrometer (OES) are set to chamber directly to measure inner parameters. The wall is heated to 60 deg. C not to deposit palyrene. As a preparation before the experiment, cleaning was proceeded with O_2 plasma with the addition of small amounts of CF₄. To add small amount of CF₄ into O_2



Fig. 3 GEC cell equipment

plasma, CF film removal can be accelerated. After this cleaning treatment, film is deposited with ClpX plasma on the substrate set on the bottom electrode.

Under this film deposition condition, to search the main reaction process FT-IR and OES are used. When molecular are exposed to infrared radiation, it absorb infrared radiation related to waving energy between atomic which constitute of molecular. With measuring the amount of the absorption, FT-IR can measure components of chemical compound and determinate quality. FT-IR can mainly measure the dissociation reaction, and in this experiment we could measure HCl, methane, acetylene's strong peaks. OES can measure the element-specific spectrum from plasma with splitting spectrum by prism qualitatively and quantitatively. OES can mainly measure the excitation reaction and reactive reaction, and in this experiment we could measure Cl₂, H₂, HCl and CH's strong peak. Based on these results, list of main reaction is established from more than 30 references.

(2) About simulation

The code which is made through this research can be divided to 2 parts. First part is the process to calculate the rate constant from the cross section of the particles. The other is the process for fitting of rate constant into the equation.



Fig. 4 Energy dependency on the cross section

Rate constant can be calculated with the sum of the product of cross section and velocity of the particle ^[3].However cross section change depending on a particle's energy. This is caused by the quantum effect and different depend on the particle. Thus far, papers about cross sections of many particles were published. So rate constants which have the reference data of the particle's cross section can be calculated from the data of the cross section.

Usually particles velocity distribution depends on the temperature and has the Maxwell distribution (Fig. 5). So the equation can be formulated as

$$K(T) = \langle \sigma(v)v \rangle_{V} = \int \sigma(v)vf(v) d^{3}v$$
$$= \int_{0}^{\infty} \sigma(v)v4\pi v^{2} \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} exp\left(-\frac{mv^{2}}{2kT}\right) dv \quad (4)$$

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Fig. 5 Velocity distribution depending on the temperature

Energy is easiest to measure. From the relation between velocity and energy, temperature and energy the equation can be formulated as

$$K(T_e) = \left(\frac{m}{2\pi T_e q}\right)^{\frac{3}{2}} 8\pi \left(\frac{1}{m}\right)^{\frac{1}{2}} \int_0^\infty \sigma Eexp\left(-\frac{E}{T_e q}\right) d\nu$$
(5)

From this equation, the rate constant is calculated from the data of the cross section for each temperature. It is said that the rate constant can be approximated with the equation shown below^[4].

$$K(T_e) = aT_e^b exp\left(\frac{c}{T_e}\right) \qquad (6)$$

Fitting was done to minimize the difference between this equation and data. As a checking operation, it is confirmed to be able to get the pretty close value to the data of the reference from the calculation with the code. However to build a formulation of a Global Model for C_8H_9Cl Plasma Coupling Gas Phase & Wall Surface Reaction Kinetics, there are many cross sections which is unknown. So we have to do the experiment to calculate through the experiment.

As achievements of this experiment program which can calculate the rate constant from cross section. And calculation about some of rate constant of the main reactions based on FT-IR and OES data were succeeded.

4. Through the life in the laboratory in America

I had two impressive point through the life in the laboratory in America.

First of them, most of thing were gave over to proceed their experiments. I guess it depends on the laboratory, but meeting, weekly meeting, and paper study class and so on, are free- to-attend. If one's research is going well, he doesn't have to come to the university. It depends on his personal choice. However their position was if you drop the course it doesn't matter me. There was a good atmosphere like self-responsibility and students in USA seemed to study harder compared to Japanese ones. I could see freshman or sophomore to attend the research voluntary. In the university in USA you can join the laboratory and attend their research for study and he can even get the chair if he asks to professor of the lab. In this way, American student were high motivated compared to students in Japan and there's a system they can utilize their high motivation.

Second of them, I was surprised about the number of the much students from Korea and China, and the number of the less students from Japan. In the engineering building, where plasma science laboratory is located, I met a lot of students and I met more than 10 students from Korea or China but I could see only one student from Japan. Until now, Japan leaded the world based on the massive economy and skills. However it is assumed to increase that Japanese common scene isn't taken in because Japanese economy's impact is getting weaker and weaker in the international society. To get the leadership and vision in the society like that, Japanese students should go overseas and learn a lot to take in good thing.

5. Finally

I would like to say a word thanks to Prof. Hori, Prof. Sekine, Prof. Toyoda and ITP affiliate to give me a chance like this. And appreciate to Prof. Overzet, Prof. Goeckner and ICAMP affiliate who support me both of research and daily life.

Reference

[1] Parylene Japan Co. <u>http://www.parylene.co.jp/</u>
[2] KISCO Co. http://www.kisco-net.co.jp/dix/index.html
[3] Principles of Plasma Discharges and Materials Processing
Michael A. Liberman and Allan J. Lichatenberg

[4] G Kokkoris, A Goodyear, M Cooke and E Gogolides, J. Phys.D: Appl. Phys. 41, 195211 (2008)

[5] J. K. Olthoff, K. E. Greenberg, J. Res. Natl. Inst. Stand. Technol. 100, (1995) 327-339