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

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This report is about a research project organized by International Training Program I was attending from 1st, Oct 2010 to 30th, Nov 2010 in Ruhr-university Bochum.

Introduction of Ruhr-university Bochum

Ruhr-University Bochum is located on the southern hills of central Ruhr area Bochum, was founded in 1962 and is the first new public university in Germany after World War II. The University of Bochum was one of the first universities in Germany to introduce international Bachelor and Master degrees, which replaced the traditional German Diploma and Master. Ruhr University is financed and administered by the state of North Rhine-Westphalia. Currently, 32,723 students (2008) are enrolled, and the university employs some 5,000 staff (369 of which are professors), making it the ninth largest university in Germany (2003).

Research theme

This time I visit Prof. Keudell's group in Graduate school of Physics, which is interested in plasma chemistry and application of micro plasma jet. My theme during project is "Growth mechanism of a-C:H(O) Functional Plasma Polymers by macroscopic kinetics", using new parameter to analyze the activation species in film deposition process.

It is a good opportunity for me to understand the reaction occurred in complex plasma using for GaN etching, which is my PhD theme.

Research background

a-C:H(O) functional plasma polymers gain increasing interest in applications where the stability of the coatings during storage. Although acrylic acid is often used as monomer for plasma polymerization, mixtures of hydrocarbons with carbon dioxide might show some advantages [1,2]. Experimental series using hydrocarbon monomers show a complex behavior of the deposition rate as a function of the energy input, where often a drop in deposition rate is reported at higher plasma energies. This work aims at understanding the nature of this behavior based on the various deposition/growth mechanisms.

Hence, Dr. Dirk Hegemann (Fig.1 right side) from EMPA (Swiss) approach macroscopic kinetics to understand the growth mechanism.
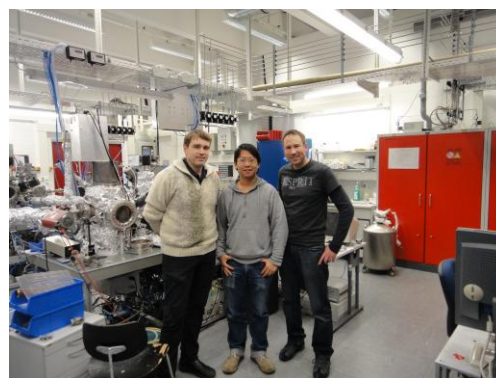

Figure 1 Laboratory with Prof. Benedikt (left side) and Dr. Hegemann (right side).

According to the competitive ablation and polymerization (CAP) principle, plasma polymerization comprises the following steps: (1) gas feed in, (2) gas phase, (3) surface processes, and (4) escape from the system (effluent gases). While gas phase processes initiated by electron impact excitations or collisional energy transfer are considered to be of chemical nature (i.e. the chemical reaction pathway), both plasma chemical and physical effects may play a role in surface processes.

In this approach, the deposition rate is measured as a function of the macroscopic reaction parameter power input per unit of gas flow, W/F. With a careful selection of experimental series, this method allows to distinguish the relative influence of both chemical and physical processes on the growth mechanism.

The experimental setup was shown as Fig.3, a double inductively coupled plasma

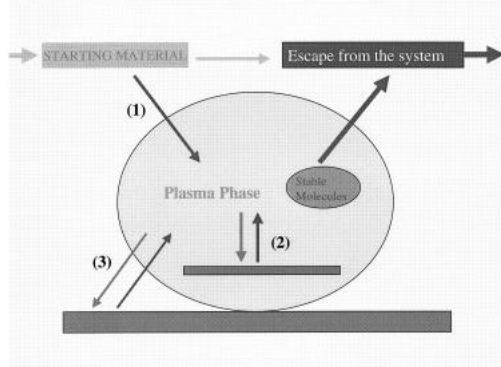(ICP) chemical vapor deposition (CVD)

Figure 2 competitive ablation and polymerization (CAP) principle.

equipment was used. Main electrode is at the top and bias electrode at the bottom of chamber. In order to measure the film thickness, the in-situ elliposometry was carried out. A Fourier transform infrared spectroscopy (FTIR) was used for investigate the detail information of polymers.
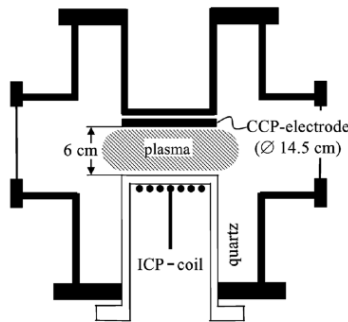

Figure 3 Sketch map of ICP CVD experiment.

In order to further investigate the macroscopic approach to plasma polymerization, both gas phase and surface processes have to be considered [3,4]. Electron density determines the production of active species, i.e. the chemical reactivity of plasma, and the ion flux towards the substrate. Mainly, it was found that the electron density of the polymer-forming gas mixtures used in this study is proportional to the power input.

Ion bombardment, i.e. both ion flux and ion energies, only depends on power input W for a fixed pressure. From these values, the characteristic energy density ε (in [eV/nm3]) deposited during the plasma polymerization process can be obtained by

$$\varepsilon = \frac{\Gamma_i E_i}{R},$$

where Γ_i is the ion flux incident on the substrate; Ei, the average energy of ions incident on the substrate (in [eV]); and R, the deposition rate (in [nm/s]) depending on the actual process conditions. R might be replaced by Rm, the mass deposition rate, to obtain the energy dissipated per mass of the plasma polymer coating or can be given per deposited (carbon) atom. Hence, higher deposition rates yield lower energy densities during the film growth.

Using macroscopic kinetics, it is assumed that the rate constants are proportional to the power input, which is justified when the electron density is reasonably proportional to the power input. Thus, kinetic curves can be derived as a function of the specific energy input as reaction parameter. The increase in energy input is considered to merely accelerate the rate of reaction exponentially, while it does not alter the chemical reaction pathways. Assuming that the film growth is limited by the activation of the monomer in the gas phase, it could be shown that this approach is also applicable for plasma polymerization yielding a quasi-Arrhenius equation as long as the active plasma zone is the source of the film-forming species

$$\frac{R_m}{F} = G \exp\left(-\frac{E_a}{W/F}\right)$$

Thus expresses the deposited mass per area out of the plasma volume (in [g/cm^5]) as a function of the specific energy input W/F (in [J/cm^3]), while G is a reactor and process depending factor. The macroscopic parameter W/F represents the energy invested per particle within the active plasma zone and can easily be converted to [kJ/mol] or [eV] using the ideal gas law. Equation yields a linear increase within an Arrhenius-type plot, where the slope is equal to Ea, the apparent activation barrier. Following this approach, a change in the growth mechanism can easily be observed by deviations from this linear range. Regarding the active plasma zone of width d_{act} as the source for the film-forming species, while the gas particles travel a distance of d_{gas} towards the substrate, the actual energy consumed in the plasma volume that contributes to film deposition is given by

$$\left.\frac{W}{F}\right|_{dep} = \frac{W}{F}\frac{d_{act}}{d_{gas}}$$

According macroscopic kinetic, we analyze the polymers deposition process as Fig.4 shown. These results suggest that the main chemical reaction pathways leading to a-C:H:O deposition are similar to those relevant for the a-C:H film growth (i.e. the same reaction pathway for C_2H_4 dissociation). The reduced deposition rates per flow (R_m/F) for the linear range of the Arrhenius-type plot with increasing CO_2/C_2H_4 gas ratio probably stems from a partial oxidation of the C_xH_y intermediates within the gas phase leading to a lowered reactivity during film growth.

In order to obtain detail information of films, we measure the FTIR of several conditons. Figure.5 shown the film deposited in pure C_2H_4 plasma, OH, C=H,C=O,C-H,C-O peak could be observed. With increasing input power, the intensity of each peak was increasing.

In CO_2/C_2H_4 =8:8 sccm condition, the CH peak was relatively decreased and C=O increased remarkable (Fig.6). The energy dependence is similar to pure plasma condition that is each peak increasing with increasing input power.

When varing the gas flow ratio to CO_2/C_2H_4 =16:8 sccm. The CH peak decreased and C=O increased (Fig.7). It suggests that by increasing the CO2 gas flow rate, the C=O bounding was more than CH.
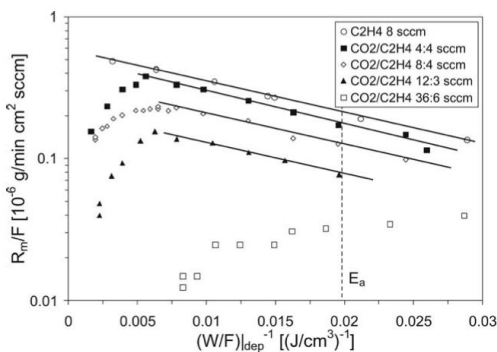
Figure 4 Mass deposition rates per gas flow depending on the inverse energy input.

We also planed to make farther research to understand the activation species in gas phase of plasma. But unfortunately, we don't have enough machines time to got reasonable result of that. Instead of that, I was invited to be a part of The 13th Workshop on the Exploration of Low Temperature Plasma Physics (WELTPP-13) held in Kerkrade, Netherlands. This workshop held in every November and most

of members are student. The atmosphere was so easy and every students are activity give me a profundity impression (Fig. 8).
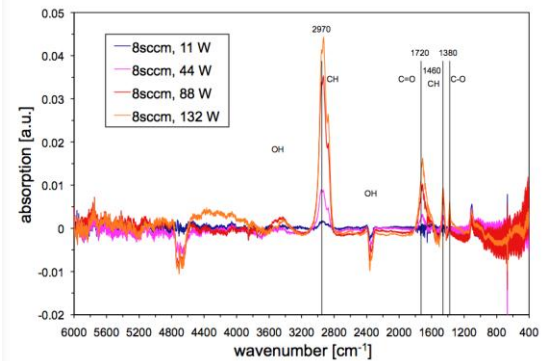
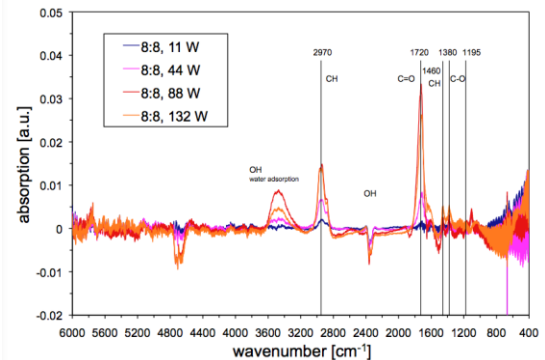Figure 5 FTIR spectrum of pure C_2H_4 plasma deposited polymers.

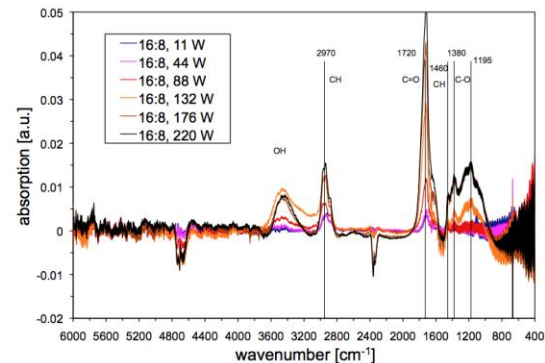Figure 6 FTIR spectrum of CO_2/C_2H_4=8:8 sccm plasma deposited polymers.

Figure 7 FTIR spectrum of CO_2/C_2H_4=16:8 sccm plasma deposited polymers.

About the life in Germany
In university, we had lunch in Meza everyday. There are too many menus that we can try different food longer than one month. If you could show your student ID, they also could give you discount, so every meal just cost you below 4 euro (including dessert and juice). For dinner, we bought food from supermarket near to the university, beer, sausage and pizza from many countries,

there is too much choice to decide what we eat in evening.

Figure 8 The night session during the workshop

In holiday, I travel to the most eastern city of Germany "Aachen". The Aachen Cathedral was erected on the orders of Charlemagne in 786 AD and was on completion the largest dome north of the Alps. (Fig.9)

Figure 9 Aachen Cathedral.

Because of this is my first time to Europe, I travelled every weekend to find different to Asia. Talked to people from different country, it was very helpful for me to practice my English and open my mind. This experience will also meaningful in my future work.

At last, I would like appreciate Prof. Keudell give me a chance to known the Germany style work, all staff and students they help me so much, without them I cant do anything. I also appreciate Prof. Hori, Prof. Sekine, Prof. Toyoda, secretary of ITP office, without their support I cant finish this project.

[1] B. Finke et.al., Plasma Process. Polym. 2009, 6, S70.
[2] E. Ko□rner et.al, Plasma Process. Polym. 2009, 6, 119.
[3] A. von Keudell et.al, Plasma Process. Polym. 2010, 7, 376.
[4] D. Hegemann et.al., Proc. 53rd SVC Ann. Tech. Conf., Orlando, FL, April 17-22, 2010.