Report on Visit to Sungkyunkwan University by International Training Program

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This is a summarization report on my research visiting to Center for Advanced Plasma Surface Technology (CAPST), Sungkyunkwan University (SKKU), Korea, from 2nd, Jan. to 1st Mar. 2012, which is of the International Training Program (ITP) organized by Japan Society for the Promotion of Science.

I. Introduction to SKKU and CAPST

Sungkyunkwan University can be regarded as the oldest private university and used to be the imperial college of Korea since being found in 1398. SKKU has two campuses: the Humanities and Social Sciences campus located in central Seoul seems more well-known for its geographical advantage, while the Natural Sciences Campus 35km away south of Seoul and near to Suwon, where housed the headquarters of Samsung Electronics and Samsung SDI, has a more ideal collaboration condition for development of future scientists and engineers.

CAPST is just located in the latter campus, at 3F in Research Complex 1 Building in the southeast part of the campus. Supported by government ministry and cooperated with companies, CAPST has been contributing for advance in plasma application on novel materials processing, such as Tin-doped indium oxide (ITO) deposition using a planar magnetron sputtering system with facing targets, SiNx barrier film growth and functionalization using room temperature Plasma enhanced MOCVD, microcrystalline Si thin film fabrication by PECVD for thin film solar cell and so on. Combined with various plasma diagnosis studies, it can provide a state-of-the-art research platform for students and researchers to study, create and communicate, aiming at establish a bridge between plasma science and industrial application.

II. About my study and research

1. Research theme

My research in CAPST was carried out with the guidance from master student Mr. Joon S. Lee, it was a study on low temperature step-by-step synthesis of Silicon oxide (SiOx) film with anti-scratch and anti-fingerprint surface layer using PECVD. Considering that my future new project in Japan will be related to SiOx Atomic Layer Deposition (ALD), after a comprehensive introduction to CAPST experiment apparatus by its students, I expressed a wish to study on SiOx PECVD that was one of the strongest research fields in CAPST. Although I had just come into contact with this part, I hoped that these 2 months of training would be beneficial for my subsequent work.

2. Background

With a booming popularity of portable electronics and terminal displays in the recent few years, more flexible polymers have been attracting increasing research interest as the next generation touchscreen top layer material for future application in smart phones, tablets and flexible electronic devices. As the limitation of such materials, a thin barrier film proved necessary to have surface protected with high wear resistance and good optical transparency. SiOx film, with its mechanical, chemical and optical properties, is considered as promising candidate to achieve an anti-scratch coat. Another big issue is to realize a functional surface which grease such as fingerprint is hardly attached. To resolve this, the outermost surface of SiOx coat is expected to be ultra-oil-repelling type that can resist grease sticking to the surface.

PECVD is used extensively to deposit a wide range of industrially important coatings as well as SiOx thin films. By tuning the plasma processing parameters, the dissociation and recombination of precursor molecules in discharge area can be controlled to fabricate films with wear-resistance, anti- friction and specific optical and electrical effect. Moreover, further improvement of film synthesis process at low temperature (below the glass transition temperature) has been required for the temperature-sensitive polymers including polycarbonate (PC) and polymethyl methacrylate (PMMA) used as substrates.

Plasma surface functionalization treatment is widely applied for its significant availability in interface compatibility. Through energetic ion bombardment and reactive radicals bonding, surface can be remodeled or grafted to achieve new properties as hydrophobicity, hydrophilicity, antibacterium, dispersibility, adsorbability and various chemical function. Updated research results proved that HMDS/ H_2 plasma CVD enabled the substrate covered with ultra-hydrophobic SiOx film. However, this kind of film showed a poor adhesion to substrate that its fingerprint resistance would become invalid easily with utility. To have it improved, an intermediate layer was considered to add between substrate and functional layer.

In these two months of ITP research visiting, my main works included high deposition rate and large size SiOx film coating with high hardness and good transparency using PECVD at room temperature, and ultra-hydrophilicity functionalization post-treatment by O_2 plasma so as to enhance the adhesion of hydrophobicity top layer to the hard coat.

3. Experiment methods

The preparation procedure of sample can be divided into 3 steps: SiOx thin film deposition, surface hydrophilization and surface hydrophobization, and all of these processes were carried out in one PECVD chamber successively. As shown in the schematic diagram of chamber's inner structure (Fig.1), it owns three electrode as top showerhead, middle metal net and bottom sample stage. For this study, only middle and bottom electrodes are connected to RF matching network, and the distance between has been set properly.

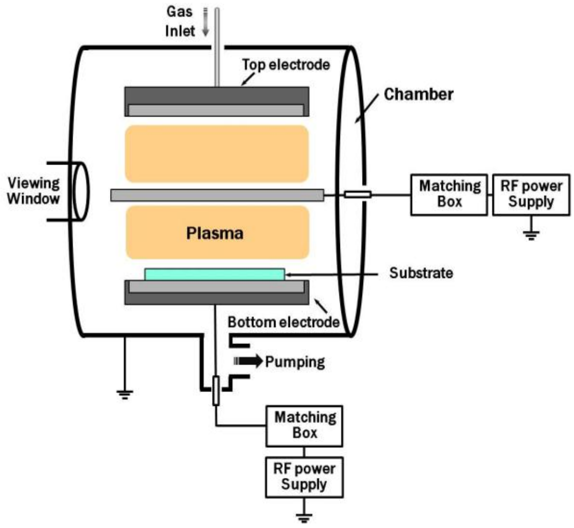

Figure 1. schematic diagram of PECVD chamber

To begin with, two glass substrates are cleaned by ethanol and dried by high speed N_2 flow, then one is put in the center of stage and the other is put near the right edge of the stage for a test to processing uniformity. The rotary pump assisted with booster pump can make the chamber pressure down to about 3.0×10^{-3} Torr as base pressure. OMCTS ($C_8H_{24}Si_4O_4$), as SiOx CVD precursor, can be heated by thermocouple but kept below 80^oC. O_2 is used to introduce OMCTS vapor into the CVD chamber from the top as a precursor carrier gas with variable flow from 0 sccm to 100 sccm. Middle and bottom electrode can be energized with RF power simultaneously up to 600W. Deposition is executed for several minutes then stop power and gas supply.

Surface hydrophilization, as the second step, is carried out by O_2 plasma treatment. In this step, O_2 is input to the chamber directly with 60 sccm, and the pressure rose to about 3.6×10^{-2} Torr as treatment pressure. Only bottom stage is supplied with RF power to generate plasma and surface self-bias.

The last step uses HMDS ($C_6H_{18}Si_2$) precursor with H_2 plasma to achieve a hydrophilic surface. Instead of

13.56MHz RF, middle electrode is changed to connect 100 kHz HF power source, bottom electrode is unused for this step. According to previous research results, H_2 flow is set at 100 sccm with pressure at about 8.8×10^{-2} Torr.

During plasma processing, discharge state and element distribution can be characterized by Optical Emission Spectrometer (OES) with a resolution of 0.1 nm operating in the region of 250 – 850 nm, and reaction ingredient can be quantitatively monitored by Quadrupole Mass Spectrometer (QMS).

SiOx thin film deposition rate can be measured by Alfa Step iQ Surface Profiler. Attenuated Total Reflection Fourier Transform Infrared (ATR FT-IR) spectrometer can used to reveal surficial changes chemical binding composition. The surface hardness of the SiOx film is measured by a pencil hardness test according to the standard ASTM D3363 method. The optical transmittance of the thin film is measured over the wavelength range from 400 to 3300 nm by UV-VIS spectrometer. Functionalized hydrophobicity and hydrophilicity can be test by Contact Angle Analyzer (CAA). And the post-treated surface morphology is learnt by Atomic Force Microscopy (AFM).

4. Research Results

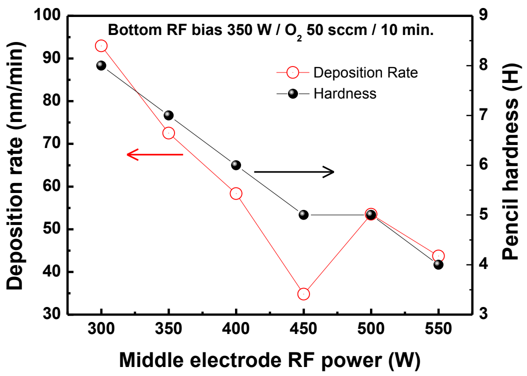

Figure 2. SiOx deposition rate and hardness as a function of middle electrode RF power with bottom RF bias set at 350 W and O_2 flow at 50 sccm for 10 min.

As the study and research plan for my ITP period, I learnt the operation of PECVD system and evaluation methods to thin film and coat properties. Through turning varied processing parameters as gas flow rate, precursor temperature and discharge powers, I managed to find the optimized condition for SiOx deposition with high growth rate and good hardness. As shown in the Fig.2, a series of test results indicated that deposition rate appeared a decreasing tendency with middle electrode RF power from 300 W to 550 W, and film hardness correspondingly decreased from 8H to 4H monotonously. Bottom RF bias power also played an important role in deposition as shown in Fig.3. As it was set at 350 W with middle power at 300 W, after 10 min. of processing, SiOx thin film can own good hardness as 8H at a deposition rate reaching as high as 92.96 nm/min. However, a further increasing of the bias power to 400 W or higher made the deposition rate as well as hardness plummet to low level, which might be attributed to etching effect of bias-induced energetic ions.

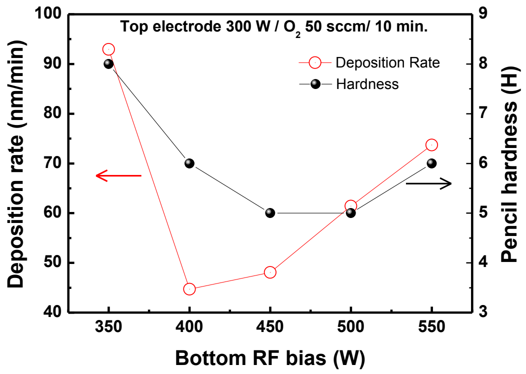

Figure 3. SiOx deposition rate and hardness as a function of bottom RF bias with middle electrode RF power set at 300 W and O_2 flow at 50 sccm for 10 min.

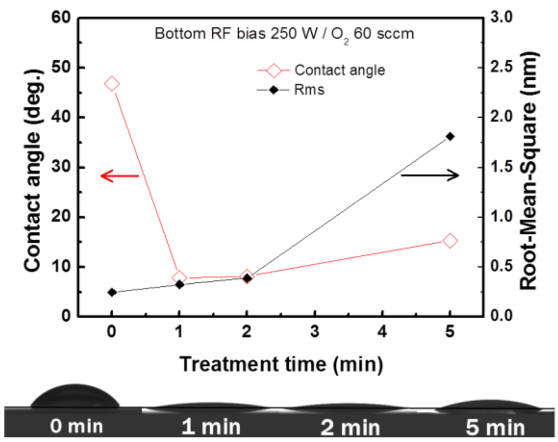

Figure 4. Contact angle and Rms value of O_2 plasma treated surface as a function of treatment time with bottom RF bias set at 350 W and O_2 flow at 60 sccm

O_2 plasma treatment preformed with a significant hydrophilization effect under different bottom bias powers. As shown in Fig.4, contact angle could be decreased to 7.8^{o} without noticeable change on Rms by only 1 min. of 250 W RF bias processing. The further slight rise with treatment time extended to 5 min. could be considered to have a relationship with increasing roughness. Moreover, subsequent results proved the hydrophilicity functionalization effective for adhesion improvement that there is no obvious drop of contact angle of new hydrophobic layer after surface rubbing which can remove physical absorption layer easily. However, compared with previous data, HDMS/H_2 plasma deposited hydrophobic coat shown a limited contact angle on hydrophilic layer, which is still under research.

III. About my life in CAPST

1. Laboratory activities

Many activities were held by CAPST members in this ITP period, some of them were for student education and others for fun. In my opinion, all of them help me make wonderful discoveries as well as be enlightened and inspired when I attended and enjoyed them.

A weekly study session was launched by Ph.D. student Mr. Kim to strengthen our understanding to vacuum technique and magnetron sputtering coating process. With a consciousness of knowledge lack to these fields, I joined into it and took charge of explanation on the content of vacuum system construction, maintenance, and troubleshooting, and participated in active paper-studying discussion. "Sometimes, to search for an answer in a paper, we need to read it over and over even to a hundred of times until we can really have a thorough grasp of its meaning", told Mr. Kim. He always show patience to my basic questions and give a completed solution.

I attended the seminar where a presentation about SIMS analysis on SiC was given by Dr. Larry Wang, Vice President and Scientific Fellow of SIMS Services at Evans Analytical Group (EAG). I consulted him with a few question about material boundary limit and application scope of SIMS analysis as my existing research is also related to depth profiling. He gave me some useful advices for my future SIMS utility.

On Feb. 8th, with CAPST students, I went to attend SEMICON Korea 2012 exhibition where numerous leading manufacturers within or outside of Korea got together. I saw a variety of novel and advanced apparatus for semiconductor and nano-tech research, which enriched my knowledge to new possibility of experiment methods. I learnt from New Power Plasma (NP corp.) about information of its high density plasma source devices, appreciated the operation of a part of ASM's device production line such as ALD and high speed detection for element quality, and ask about advantage of PE-CVD equipment with ULVAC corp. This trip had me to set a further goal and a stronger determination to make effort on my future research.

2. Culture experience

Korea is well-known by its unique-tasted food and characteristic landscape. I had always been trying sorts of Korea cuisine and taking a trip around the university if got chance. I like bibimbap the most, and among them the one named Jeyukudopubopu is my favorite. And I take a visit to the famous N Seoul Tower (Fig.5) on top of Namsan Park where the whole Seoul city can be overlooked.

Figure 5. N Seoul Tower

IV. Written in the last

This ITP visiting in SKKU was an important experience in my study, and will have more profound impact to my future. I would like to appreciate Prof. Han for this meaningful opportunity, and thank Prof. Hori, Prof. Toyoda and Ms. Era for your kind support and help on this project.