Report on Visit to SungKyunKwan University by International Training Program

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Since I participated in the Long-term Placement Program of International Training Program (ITP), I'd like to report on research activities under the guidance of Prof. Han in the Center for Advance Plasma Surface Technology (CAPST) of SungKyunKwan University.

・Research

The research group of Prof. Han works on formation and control of properties and application of thin films using magnetron sputtering and plasma-enhanced chemical vapor deposition (PECVD). Because I am working on control of structures and properties of a carbon nanomaterial synthesized by PECVD, I conducted a research on the growth of carbon films and control of its properties using magnetron sputtering in order to not only utilize my knowledge and experiences but also acquire new ones.

The conceptual diagrams of sputtering evaporation sources for magnetron sputtering are shown in Fig. 1. As shown in Fig. 1(a), in the case of a conventional sputtering source, the strength of a magnetic field generated by an outer pole is almost same as that by inner one, which lead to form a closed equilibrium magnetic field between the outer and inner poles. Accordingly, because a plasma is generated almost only close to a target, diffusion to a substrate hardly occur, which is a desired situation for semiconductor manufacturing needing a suppression as much as possible of ion irradiation. On the other hand, for an unbalanced magnetron (UBM) sputtering in Fig. 1(b), a part of the magnetic lines from the outer pole stretches to a substrate due to a non-equilibrium magnetic field formed by intentionally losing the balance of the magnetic field between the poles. As a result, a part of the plasma confined around the target is easier to diffuse close to the substrate along the magnetic lines, which lead to increase the amount of irradiated argon (Ar) ion across the substrate during film formation. Therefore, UBM sputtering attracts attention recently due to promising densification and better adhesion caused by the ion assist effect.

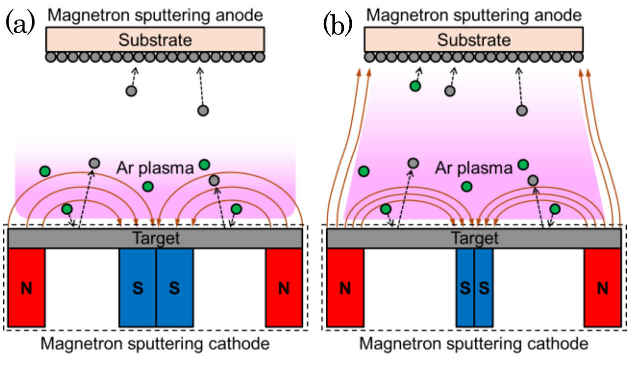

Fig. 1 (a) Conventional magnetron sputtering and (b) UBM sputtering

Features of film formation by UBM sputtering are easy to be applied to synthesis of carbon filmsa such as diamond-like carbon (DLC). Control of the process and properties can realize various characteristics of the films such as high hardness, low friction coefficient, high surface smoothness, chemical stability, permeability for visible and infrared light, and controllability of electrical resistance, which lead to applications in a wide range of areas such as cutting tools, molds, antiwear protection coatings for sliding machines, electronic devices, and optical components. However, the deposition rate during magnetron sputtering has not been enough to be put into practical use in addition to insufficient control of the properties of films. Particularly, formation techniques of conductive DLC films such as nitrogen and metal doping and control of the electrical properties are necessary in recent years. So, in this study, we aimed to fabricate conductive DLC films using UBM sputtering and control that. Concretely, we investigated dependence of the properties on input DC power and effects of Fe doping which is low-cost and reported to improve the csystallinity and photoconductivity.

Closed magnetic field UBM (CFUBM) sputtering system as shown in Fig. 2 was used to form carbon films [1].

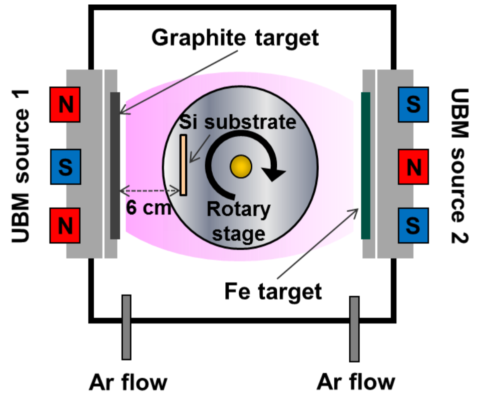

Fig. 2 CFUBM sputtering system [1]

In this system, two UBM sputtering sources are set facing each other across a rotary stage, which is a configuration that enhances a confinement of Ar plasma by forming a closed magnetic field between the UBM sputtering sources. This configuration is expected to increase the ion flux incident on a substrate, which leads to enhance the ion assist effect. First of all, as a fundamental estimation of UBM sputtering source, the current flowing through the outer pole was changed from 1 to 3 A with that through the inner pole fixed to be 1 A, and then the magnetic field distribution on a target was measured using a Gauss meter. In addition, discharge current-discharge voltage, I_d-V_d, characteristics for the each current were estimated with changing the input DC power supplied to a graphite target (UBM source 1) by controlling current under the conditions with the Ar gas flow rate of 55 sccm and pressure of 3×10-3 Torr. Furthermore, the ion current was measured using a copper plate as an index of ion flux incident on a substrate.

When formation of carbon films was carried out under the above conditions, the substrate temperature was measured with a thermocouple during film formation. Then, the deposition rates were calculated with the thickness measured by Alpha-Step. Through these estimations, the heights of carbon films fabricated under the each input power were constant and the resistivity was measured. Conducting Fe doping, for the above condition with the input power of 30 W/cm^2, UBM source 2 where a Fe target was installed was driven with rotating a substrate on the rotary stage at the same time. To control the deposition rate of Fe films, a pulsed power with the frequencies ranged from 5 to 50 kHz and duty ratios ranged from -20 to -50% was applied, which was adjusted to be 0.001 W/cm^2. As a result,

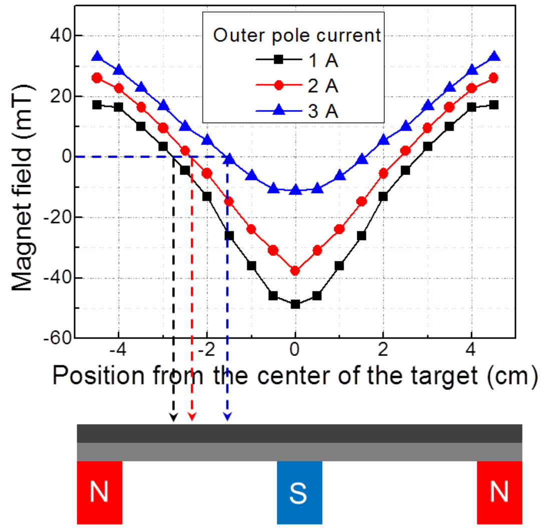

Fig. 3 Distribution of a magnetic field on a target

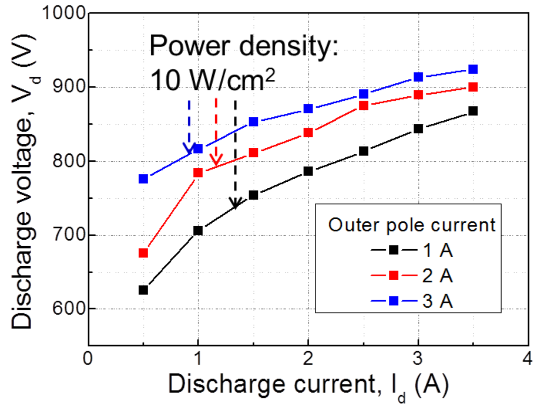

Fig. 4 I_d-V_d characteristics for each inner pole current

the carbon films containing 0.47 and 1.1% Fe atoms were synthesized and their resistivity was also measured.

Figure 3 shows the dependence of the magnetic field distributions on a graphite target on the current flowing through the outer pole. It is found from the shift of the point where the magnetic field dropped to 0 toward the inner pole that the balance of the magnetic field was altered and a non-equilibrium magnetic field was formed. The I_d-V_d characteristics at this time are also shown in Fig. 4. As an example, comparing the each value of I_d and V_d when the input power was 10 W/cm^2, I_d decreases with increasing the current flowing through the inner pole. This is considered to be caused by a weaken confinement effect due to a weaken closed magnetic field around the target, which leads to decrease the plasma density around the target. This result indicates that there are formation of a non-equilibrium magnetic field around the target and expansion of a plasma

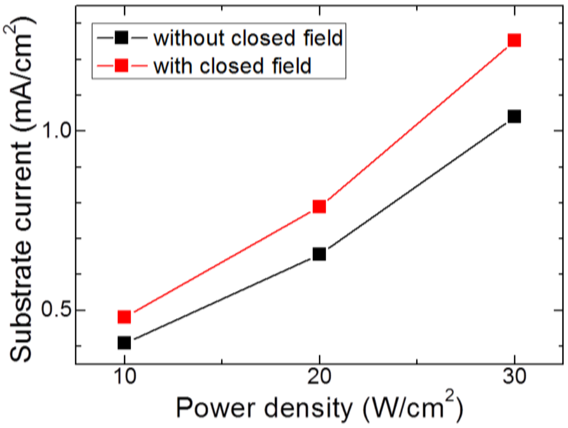

Fig. 5　基板電流の投入電力依存性

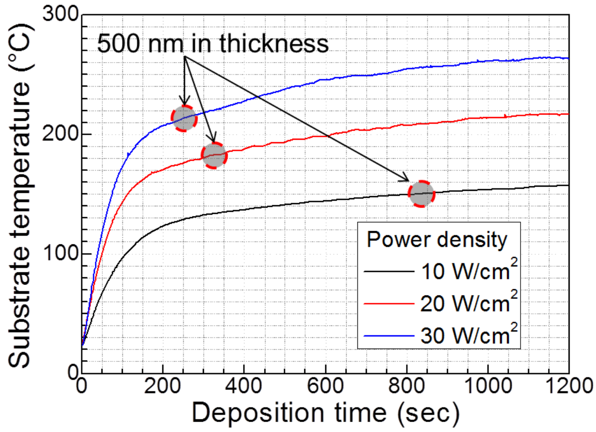

Fig. 6　Time dependence of substrate temperature

region to the substrate during UBM sputtering.

Next, a result of the measurement of the ion current flowing through a copper plate is shown in Fig. 5. To confirm the effects of a closed magnetic field, the ion current in the cases of open and closed magnetic fields which UBM source 2 was driven or not were measured. For the both cases, the ion current increases with increasing the input power. This means the increase in the plasma density around a substrate with increasing the input power. The ion current for the closed magnetic field was bigger than that for the open magnetic field. This result suggests a plasma confinement effect due to a closed magnetic field increase the plasma density around a substrate, which leads to an increase in the ion flux.

Figure 6 shows the deposition time dependence for each input power on the substrate temperature. In each case, the temperature tends to increase rapidly during the first 150 seconds of deposition, and then, increase moderately and saturate. Additionally, the bigger the input power, the higher the substrate temperature. This result is caused by an increase in the fluxes of sputtered particle and ion incident on a substrate, which corresponds to the result of the ion current measurements. Here, figure 7 shows Thornton zone model which expresses a relationship between film growth temperature and crystalline structures. Deriving the values of T/T_m from the substrate temperature T at the time when the thickness was 500 nm as shown in Fig. 6 and melting temperature T_m = 3642˚C, the value changed to 0.043, 0.053, and 0.062 with increasing the input power. Applying these values to Thornton zone model which is represented as a red part in Fig. 7, it can be said that substrate temperature hardly

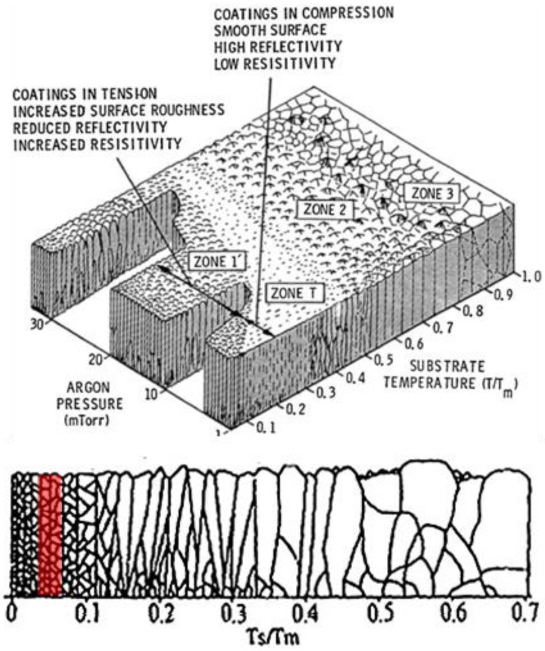

Fig. 7　Thornton zone model

affects the crystalline structure.

The resistivity of the carbon films formed under the input power of 10, 20, and 30 W/cm^2 was 6.4, 0.35, and 0.083 Ωcm, respectively. From the results as described above, it is unlikely that there are effects of temperature on the properties. Therefore, it is considered that the number of sp2 bond or size of sp2 cluster in carbon films increased due to increases in the ion flux and energy with increasing the input power. On the other hand, the resistivity of Fe doped carbon films with 0.47 and 1.1% Fe atoms were 0.002 and 0.001 Ωcm. This result would be attributed to electron transfer between sp2 clusters assisted by Fe particles. In addition, it is possible for Fe doping to occur in the sp2 clusters.

In this study, effects of the behavior of particles and temperature during CFUBM sputtering on carbon film formation and its effects on the electrical properties were clarified. Finally, it has been confirmed that an ion assist effect was enhanced using UBM and closed magnetic field. Additionally, it was indicated that energies of sputtered particles and ions rather than an increase in temperature due to particle bombardments mainly affected the crystalline structure and electrical properties of carbon films. It was also found that Fe doping could improve the electric conductivity. However, it is necessary to prove the above effects by material evaluations because evaluation of the crystalline structures of carbon films has been insufficient. Accordingly, in the future, the structures of carbon films have to be analyzed by morphological observations with scanning electron microscopy (SEM) and transmission electron microscopy (TEM), analysis of crystalline structures with Raman spectroscopy and X-ray diffraction (XRD), and analysis of chemical compositions with X-ray photoelectron spectroscopy (XPS), which will clarify a correlation between the structures and electrical properties of carbon films.

At the end, the knowledge and experience obtained from this study are expected to contribute strongly to future works on precise control of structures of the carbon nanomaterial. Concretely, they include the results obtained from this study related to an importance of ion assist effect on film properties, consideration of temperature effects with Thornton zone model, and effectiveness of metal doping such as Fe doping.

・Life

Despite a little summer heat had remained when I started to live in Korea at the end of September, it started rapidly getting cold since the beginning of November and went down to as cold as during deep of winter in Japan. I fell sick for a while because of not keeping up with the change in climate. However, I felt even that a life in the guest house was better than that in Japan due to the Ondol which is a Korean traditional underfloor heating. Regarding the food, there are basically a lot of spicy food as I could had imagined and some of them made me feel pain in stomachache after eating, but almost all seasoning may make it easy for Japanese to enjoy. Additionally, I was happy prices were generally a little lower than that in Japan. Sometimes I went shopping to a supermarket, but often used the nearest convenience store because the supermarket was a little far from the guest house. Sometimes, we went to eat some popular Korean foods such as Jjigae and Samgyeopsal together with Korean students who were in the Prof. Han's Laboratory and enjoyed eating Korean foods fully.

Fortunately, I had an opportunity to participate in the laboratory one-day trip and see around traditional temples. In addition, I was given a chance to eat flesh seafood at markets near a fishing port and deepened exchanges with the professor and students while drinking. On weekends, we occasionally went to the Soul city by train. We walked around the city and ate Korean foods with a Japanese student who stayed in the same period. Furthermore, the short trip provided a good opportunity to experience Korean customs through going to see world heritages.

Finally, I want to thank the professors for their help and support for my participation in this program. In addition, I really appreciate to Korean students for their support. I would like to take use of the experience obtained this time within the future work and life and go on to be an engineer or researcher who will be active internationally.

[1] S. I. Kim, *et al.*, J. Korean Phys. Soc. **55** 1865 (2009).

Fig. 8　Changdeokgung Palace Complex