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基盤科学研究系 先端エネルギー工学専攻
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Synthesis of Carbon Films with Applying Negative DC Bias Voltages in Surface Wave excited Plasma CVD Apparatus

－ 表面波プロセスプラズマを用いた負の直流バイアス電圧印加によるカーボン系薄膜合成 －

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Key Words : Carbon Film, Surface Wave exited Plasma, Plasma CVD, Negative DC Bias Method

1. Introduction

Some advantages such as low gas temperature, large-area deposition, and atomic scale processing control are expected at low gas pressure chemical vapor deposition (CVD) process. However, factors such as high ion energy and low radical density limit the quality of deposit. To reduce the ion bombard energy, the sheath potential have been controlled with applying positive DC or RF bias voltage [1-2]. But in case of ring dielectric line typed surface wave plasma (RDL-SWP) apparatus, these bias method result in an arc-like discharging and an unstable plasma. To overcome these problems, J. Kim *et al* developed a new bias method. The space potential of bulk plasma was controlled with applying negative bias voltages to the metal plate inserted in surface wave generating region [3]. Using this bias method, a very high quality nanocrystalline diamond film of RMS 12.4 nm was deposited at the condition of 650℃ substrate temperature, –70V DC bias voltage, and 30 mTorr gas pressure. Moreover, a diamond film was deposited at the lower substrate temperature of 430℃ and lower DC bias voltage of –190V in the previous experiments. According to these results, it is considered that there are some relations between DC bias voltages and substrate temperatures on carbon film deposition. In this study, it is purposed to investigate the relations between DC bias voltages and substrate temperatures and the dependences of CO gas concentrations and substrate temperatures on carbon film deposition.

2. Experimental details

2.1 SWP Apparatus and Plasma parameters

RDL-SWP apparatus, which had been developed by Sumitomo Metal Co. in Japan, was employed as plasma enhanced CVD apparatus in this study. The apparatus was modified to control the space potential of bulk plasma as shown in Fig.1. And the plasma parameters with respect to negative bias voltages were measured by single probe method.

2.2 Carbon Films Deposition

A n-type mirror-polished Si(100) was used as substrate. The substrate was just cleaned in methanol and placed on the heater grounded electrically. Gas mixture of 95%H_2-5%CO was injected as source gas and the gas pressure was preserved as 30 ± 2 mTorr. And carbon films were deposited under the condition of the substrate temperature 500±5℃ and 590±5℃, varying DC bias voltages from －80V to －170V. To investigate the dependences of CO concentrations, CO concentration in gas mixture was changed 3%, 4%, and 5%. The deposited films were analyzed by Ar+ laser Raman spectroscopy, UV Raman spectroscopy, X-ray diffraction and field emission scanning electron microscopy (FE-SEM).

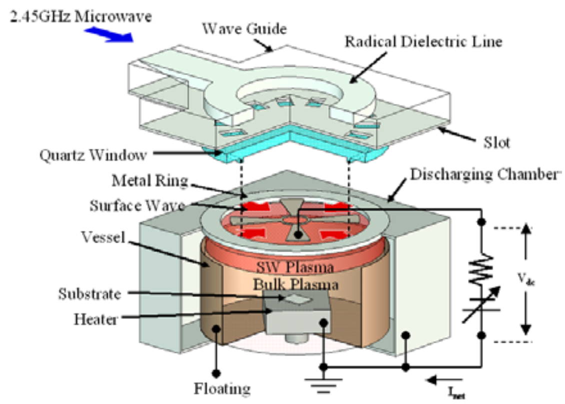
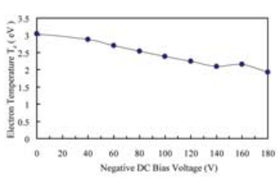


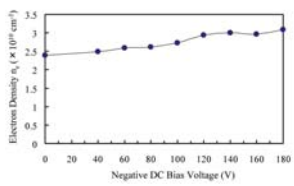
Fig. 1 Schematic illustration of the modified SWP apparatus

3. Result

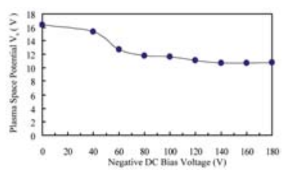
Fig. 2 shows the measurement results of plasma parameters by single probe method. With increasing the negative DC bias voltage, the electron temperature was decreased from 3.0eV to 1.9eV, but the electron density was increased from $2.3\times10^{10}cm^{-3}$ to $3.0\times10^{10}cm^{-3}$. The space potential of bulk plasma was decreased from 16.3V and saturated at ~11V at the condition of negative bias voltage lower than –80V.



(A) Electron Temperature



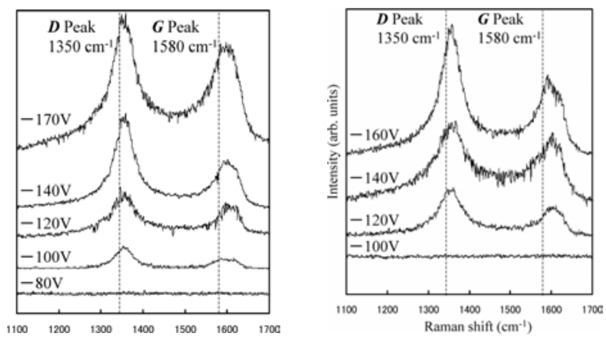
(B) Electron density



(C) Plasma space potential

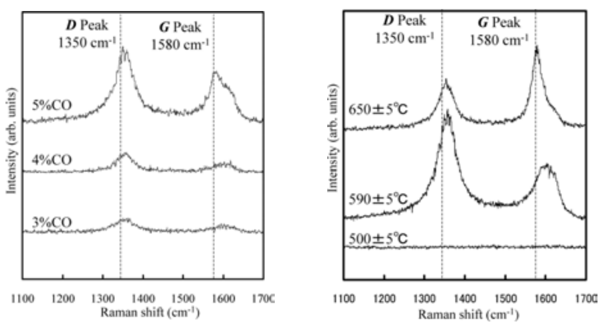
Fig. 2 Plasma parameters

Fig. 3 shows the Ar+ laser Raman spectra of carbon films deposited under the conditions of the substrate temperatures of 500±5℃ and 590±5℃ and DC bias voltages from −80V to −170V. And the Fig.4 shows the Ar+ laser Raman spectra of carbon films deposited under the condition of 3%,4%, and 5% CO concentrations (A) and the substrate temperatures of 650±5℃, 590±5℃, and 500±5℃(B) with applying −100V DC bias voltage. In case of natural diamond, the Raman spectrum exhibits a sharp peak at 1332 cm^{-1}, but no diamond peak is presented in Fig.3 and Fig. 4. However, the peaks called *D* peak and *G* peak attributed to sp^2-bonded C are presented at 1350cm^{-1} and 1580cm^{-1}, respectively. According to the results, the *D* and *G* peaks are intensified at the both conditions of substrate temperatures of 590±5℃ and 500±5℃ in Fig.3 (A)(B) with increasing the negative bias voltages. And as shown in Fig.4 (A), the *D* and *G* peaks were also intensified with increasing the CO concentrations. In Fig.4 (B), the *D* and *G* peaks were intensified with increasing the substrate temperature from 500±5℃ to 590±5℃, but the intensities of *D* and *G* peaks were inversed at the substrate temperature of 650±5℃.



(A) 590±5℃ (B) 500±5℃

Fig. 3. Ar+ laser Raman spectra
(Bais voltages vs Substrate temperature)

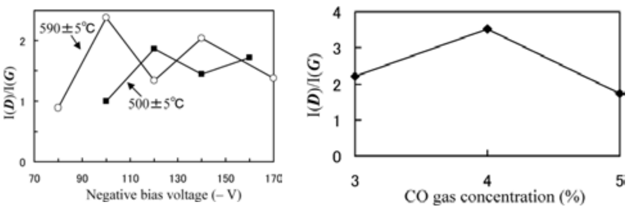


(A) CO concentration (B) Substrate temperature

Fig. 4. Ar+ laser Raman spectra

4. Discussion

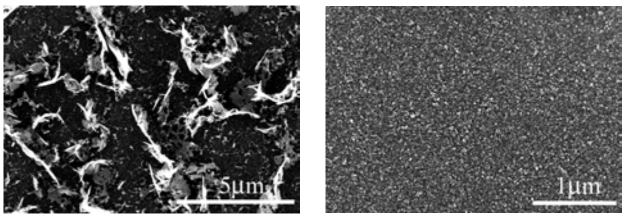
The *G* mode is actually stretching vibration mode of any pair of sp^2 sites, whether in C=C chain or in aromatic rings. However, the *D* mode is the breathing mode of sp^2 sites only in rings, not chain. Thus, the intensity ratio of *D* and *G* peak is proportional to the number of rings at the edge of the grain [4]. The ratios of the intensities of *D* and *G* peaks were calculated and plotted as shown in Fig.5. From these graph, it is considered that sp^2 domains are divide to small domain and the gain size get smaller at the beginning of negative bias appliance, but amorphisation is promoted at more lower bias voltage. And the change curves of the ratio of intensities of *D* and *G* peak are very similar at both substrate conditions of 500±5℃ and 590±5℃. But the ratio curve of lower substrate temperature similar is presented at higher bias voltage than the one of 590±5℃. And one more important thing is that these changes of film morphologies occurred in the region that the space potential is saturated. This indicates that the film morphology can be changed even not the sheath voltage changed. And dependences of CO gas concentrations are similar to the one of bias voltages.



(A) vs. negative bias voltage (B) vs. CO gas concentration

Fig. 5 Intensity ratio of *D* and *G* peak

In fig.4 (B), the intensities of *D* and *G* peaks were significantly inversed at the substrate temperature of 650±5℃. According to FE-SEM images, the increasing of the intensity of *G* peak is due to the wall-like structure of film morphology.



(A) 650±5℃, −100V (B) 590±5℃, −100V

Fig. 6 FE-SEM images

5. Conclusion

In this study, carbon films were synthesized on mirror-polished silicon (100) substrate under the conditions of different bias voltages, different substrate temperatures, and different CO gas concentrations at a low gas pressure of 30mTorr in RDL-SWP. According to the film analysis results, sp^2 domain and grain size get smaller at first with increasing the negative bias voltages. And simultaneously armorphisation is promoted. But these changes are affected by substrate temperature. In lower substrate temperature condition, the change is presented at lower bias voltage. These changes of film morphologies are may related to the plasma parameters. However, the detailed physics should be studied. And the dependences of CO gas concentrations are considered to be similar to the one of bias voltages. These dependences also are needs to be studied with more detailed experiments.

References

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