Infrared spectroscopic study of control of plasma induced surface reactions during plasma chemical vapor deposition with ether molecules as source molecules

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An amorphous carbon film is a promising material, because of its unique properties such as chemical and mechanical hardness, surface smoothing, bio-compatibility, and so on. Then, amorphous carbon film has been used to coating materials for various fields. Moreover, coating medical tools becomes popular. Carbon-coating of stent is a promising technique. In stent coating process, amorphous carbon is oxidized by the oxygen plasma exposure, in order to exhibit hydrophilic properties. This method contains two steps: amorphous carbon film deposition and oxygen plasma exposure. It is good for industry to deposit oxidized amorphous carbon film by one step.

Plasma enhanced chemical vapor deposition (PECVD) is a promising method for film deposition. One of the merits is that it has a lot of process parameters. One of the parameters is source materials of PECVD. Ether molecules has a potential as source materials of CVD method, because they have an -O-C-O- structure in a molecule. The structure is bonded with alkyl groups, such as ethyl, propyl and so on. It indicates that O/C of atomic density ratios in the deposited film should be changed with kinds of ether molecules. Moreover, ether molecules are hazardless and easy to handle. One of the reasons is that ether molecules except for di-methyl-ether molecules are liquid at room temperature. Then, the chamber system including source feeding system can be simplified. However, PECVD process has very complicated. To obtain the film with desirable properties, the PECVD process should be controlled. Then, it is necessary to observe PECVD process.

MIR-IRAS (Multiple-Internal-Reflection Infrared Absorption Spectroscopy), as shown in Fig. 1², is a powerful tool for in-situ and real-time observation of film deposition process during PECVD. The plasma excitation is accomplished with RF (13.56 MHz) power of 30W in ether pressure of 50 mTorr.

Fig. 2 shows the IR absorption spectra of deposited film for 60 min with di-ethyl-ether and di-n-butyl-ether, which are denoted as \( ((C_2H_5)_2-O-C-O-(C_2H_5)_2) \), \( ((C_2H_3)_2-O-C-O-(C_2H_3)_2) \), respectively. IR absorption spectra are calculated, in a comparison with the IR spectrum of the Si prism without carbon film deposition. Three peaks are observed in both spectra; the first one is the strong peak, located at 1700 cm\(^{-1}\), which is attributed to the C=O bonding. The second one is the peak located between 2800 and 3000 cm\(^{-1}\), which is attributed to the C-H stretching vibration. The third one is the peak between 3200 and 3600 cm\(^{-1}\), which is attributed to the second harmonic C=O and/or OH components. Each peak intensity is different between the two spectra. The spectrum of the film deposited with di-ethyl-ether has large relative intensity of the C=O peak, compared with the C-H peak; on the other hand, the spectrum of the film deposited with di-butyl-ether does not have strong intensity of C=O peak. These facts show that the film deposited with di-ethyl-ether relatively contains relatively higher C=O density than the film deposited with di-butyl-ether. It is suggested that C=O density in the film can be controlled with the source molecules. The O/C ratio, the atomic number ratio of O to C, in a di-ethyl-ether molecule is 2/5and that in a di-butyl-ether is 2/9. This study would show ether molecules are smart source molecules of the amorphous carbon film deposition.

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References