Plasma Generation in Organic Solvent for Amorphous Carbon Film Deposition

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The plasma was generated in organic solvents (ethanol and n-hexane mixture) in order to coating inside the narrow tubes. From measurements of discharge current, plasma is easily generated in ethanol, but the generation of plasma has difficulty in n-hexane. The ratio of mixture of 1:1 is suitable to film deposition, since ethanol is used for plasma generation and hexane is used for source of the films. FTIR spectra exhibited the deposited films are typically polymer-like amorphous carbon (PLC) films.

Key words: plasma, organic solvent, discharge current, amorphous carbon,

An amorphous carbon film is one of the promising coating materials for medical application, as the films are already commercially used in various field \([1]\). The films are comprised of mainly carbon and hydrogen atoms. The films have a lot of useful properties, such as chemical inertness, mechanical hardness, surface smoothing and bio-compatibility. Furthermore, a lot of reports have been proposed that the surface can be easily modified to increase the bio-compatibilities \([2, 3]\). However, there are difficulties to coat inside the narrow tube. For example, Fujiyama, \(et\ al.\) proposed the 2nd harmonic ECR plasma to coat inside the tube \([4, 5]\). Kosaka \(et\ al.\) proposed surface-wave plasma \([6]\). Baba \(et\ al.\) proposed a PBII (plasma beam ion immersion) method \([7]\). These techniques need very complicated and high-cost experimental apparatus. Moreover, electrochemical processes can hardly be used in a deposition of insulators, although the experimental setup is very cheap. Then, other simple techniques are needed for low-cost production.

One of the candidates is so-called solution plasma. In the past, the discharge in liquid was also utilized in electrical discharge machining, such as weld \([8]\). Now the plasma in liquid is utilized for water clarification, fabrication of nano-particles, sterilization, and so on \([9-11]\). The plasma has various advantages; it was can be generated in a small area, at low cost. Moreover, the processing can be done in safety at low temperature, since there are a lot of kinds of solvents. Then, a choice of the solvent was important, as well as a choice of the configuration of electrodes. In this study, we will show the plasma generation in n-hexane with coaxial type electrodes and for coating the fine tube.

The plasma generation in liquid will have more possibility in the future. For example, the anaerobic bacterium will be able to be treated with the plasma in solvents, because this processing can be done without the exposure to air.

2. EXPERIMENTS

The experimental setup was shown in Fig. 1. The electrode structure was the coaxial type. The core electrode was Ti wire with a diameter of approximately 0.8 mm. The outer electrode was made of brass. Glass tube was set between the core electrode and the outer electrode. The inner and outer diameters of the glass tube are 4 and 6 mm, respectively. Glass tubes were used for the substrate so that the deposited film can be easily removed from the glass substrate. The high voltage was generated by low-frequency (11 kHz) sine wave power supply (TE-OZ5W-NU: Tamaoki Inc. for electric measurements, and LHV-13AC: Loggy electric. Inc. for film deposition). The supplied voltage and discharge current can be monitored with oscilloscope (Tektronics). Voltage was measured with high voltage probe (P6015A). Current was measured with current probe (TCP312). Ethanol/n-hexane mix solution was used as organic solvents. Ethanol was used as a bubble source for generation of plasma. n-hexane, which is a relatively small straight-chain molecule and has a relatively low boiling point, was used as a source molecule of amorphous carbon films.

The deposited films were analyzed with a conventional FTIR measurement. In the FTIR
measurement, a KBr pellet method was adopted. Pellets were made from KBr powder and the deposit on Glass tube.

2. RESULTS AND DISCUSSION

The voltage-time and current-time behaviors of high core line were measured with the oscilloscope. The waves are shown in Fig. 2 (a)–(e). The voltage and current waves were plotted as a function of the mixture ratio of the solvent (ethanol: n-hexane). High voltage in the form of sine wave was supplied to the core line electrode in every case. The current between both electrodes was large in the form of spikes, when the sine wave of the supplied voltage came to 0V. Except for each several spikes at approximately 0V, current was in the form of a sine wave. Each phase of the current leads by approximately \( \pi/4 \), compared with the voltage curve.

It is suggested that each solvent exhibited the dielectric feature. Each spike was not symmetry between positive and negative regions. Spikes were large, when positive high voltage was supplied to the core line electrode. The supplied electrons were accumulated in the solvents when negative high voltage was supplied at the core line electrode. The accumulated electrons were collected when positive was supplied to the core line electrode; the electron might be deprived from the solvent molecules, to generate ions in the solvent, when positive was supplied to the core line electrode. The ions were collected when positive was supplied to the core line electrode. The electrons might be accumulated in solvent more than the ions. Furthermore, the discharge might be occurred in the spike regions. Then, the discharge was not continuously occurred, but the discharge would be occurred when voltage comes to 0V. Then, these results suggest that square wave pulse was suitable to generate continuous plasma.

Furthermore, Fig. 2(a) shows that the current-wave amplitude except the spikes was large in ethanol. On the other hand, Fig. 2(e) shows the amplitude was small in n-hexane. Both intensity of the spikes and the sine-wave were decreased, as the ratio of n-hexane increases. These results suggested that the discharge would be easily occurred in the ethanol; the bubbles generated by heating ethanol would be used to the generation of solution plasma. Ethanol is a polar molecule, which would show a little conductive like water. Joule heating would be used to the generation of bubbles. On the other
hand, n-hexane is a nonpolar molecule and a good insulator. Bubbles could not be generated like in ethanol. Then, the discharge would partially be controlled by changing the mixture ratio of nonpolar molecules to polar molecules in the solvent.

We applied this solution plasma to the film coating inside the fine glass tube. The total deposition time is 60 min; the plasma generation time was divided to each 5 min because the solvent temperature was increased with the plasma generation. Then, the solvent was cooled after every plasma generation. Fig. 3 shows the photograph of the deposited film inside the tubes. The films were deposited by changing the mixture ratio of the solvent; label A, B, C, D, and E show the mixture ratio (ethanol: n-hexane) of 1:0, 3:1, 1:1, 1:3, and 0:1, respectively. The photograph of label A has a striped shape. It means that the uniform film was not deposited. The uniform film cannot be deposited in the photograph of label E, too. These results would be corresponded with the plasma generation. The plasma in n-hexane would be generated in a relatively small region, because the observed current is small, as shown in Fig. 2 (e). Then, the film also was partially deposited. The plasma in ethanol would be generated in a relatively large region, because the observed current is large. The plasma in ethanol has high power. Then, ethanol would be decomposed into carbon particle, which would be deposited in the tube. Here, the film of the label C is relatively uniform. When the plasma is generated in the solvent with the ratio of 1:1, the discharge area would be middle between that generated in ethanol and that generated in n-hexane. Then, solvent can be effectively decomposed.

The film obtained at the solvent ratio of 1:1 was analyzed with FTIR to clarify the bonding configuration, as shown in Fig. 4. The spectrum has three distinct peaks. Both of the peaks located at 2875 cm⁻¹ and at 2960 cm⁻¹ are attributed to the sp³-CH₃ group. And the peak at 2930 cm⁻¹ is attributed to the sp³-CH and or sp³-CH₂ group. The slight shoulder observed at 2850 cm⁻¹ can be assigned to the sp³-CH₂ group. The spectral shape is identified with the polymer-like carbon (PLC) film [12].

3. CONCLUSION

The plasma was generated in the mixture of ethanol and n-hexane for coating the inside of the tubes. The current-time feature between two electrodes was observed, in comparison with the supplied voltage in the form of sine wave. The large current can be generated in the high ratio of ethanol, while the generation of plasma has difficulty in n-hexane.

The uniform film cannot be deposited either in ethanol, or in n-hexane. The uniform film can be deposited when the mixture ratio of n-hexane to ethanol is 1. The film exhibited the feature of polymer-like amorphous carbon (PLC) film from FTIR analysis.

ACKNOWLEDGMENTS

This research was partially supported by a Grant-in-Aid for Scientific Research Nagasaki University (2007-2008) and Research for promoting technological seeds from JST (2008-2009) and.

REFERENCE


Fig. 3  Photograph of the deposited film inside the tube. Each film was deposited by changing the mixture ratio of ethanol to hexane. The ratios (ethanol: n-hexane) of A, B, C, D, and E are 1:0, 3:1, 1:1, 1:3, and 0:1, respectively.

Fig. 4  FTIR spectrum in the C-H stretching vibration region of the deposited film by using the plasma in the solvent of ethanol and n-hexane (ethanol: n-hexane = 1:1)

(Received December 31, 2009; Accepted April 1, 2010)