PLASMA POLYMERIZATION OF HYDROCARBON IN AFTER-GLOW OF ARGON

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ABSTRACT

Glow discharge and plasma polymerization phenomena were studied for hydrocarbon which was introduced into the after glow of inductive and capacitive coupling 13.56MHz glow discharge of argon. White radiation zone was observed in the after glow and it was assumed to be an interaction zone between argon and hydrocarbon caused on Penning effect.

1. INTRODUCTION

Among numerious methods for thin film fabrication, the plasma deposition method is given attention from various fields of engineering[1,2,3]. The reason may be caused on the distinctive features of the plasma deposition method. For example, properties of the film are widely varied by selecting the operational parameters of discharge[4] and the structure of apparatus which includes the discharge electrode system is selected voluntarily depending on the demand[1]. However, there is not an universal theoretical standard for the plasma deposition mechanisms in various types of reactor because of complicated phenomena. It is known that the chemical reaction in a glow discharge will be reflected by behaviors of charged particles in the discharge[4,5]. But, there are very few studies concerned on the discharge phenomena of reactive gases like as organic vapour compared to inert and inorganic gases. Recently, there are several efforts to clarify the relation between the discharge phenomena and the polymerization mechanisms[4-8].

For a radio frequency discharge in the frequency range of MHz order, two types of coupling methods between the power generator and the discharge are usually used, namely an inductive coupling and a capacitive coupling. In the case of capacitive coupling, the growth rate is usually a function of discharge power level, but in the case of inductive coupling, the growth rate is independent on the discharge power level in a cirtain power level range[8]. The reason of this difference is not clearly explained in previous papers. In this study, both coupling discharge systems were used. Glow discharge and plasma polymerization phenomena were observed when hydrocarbon vapour was introduced into the after glow (or tail flame) of argon discharge.

2. EXPERIMENTALS

A schematic diagram of experimental apparatus is shown in Fig. 1. The numbers in this figure indicate the dimensions of each part in the unit of mm. The vessel was consisted of two parts, A and B. The gases were introduced from the inlets of a and b and evacuated from the outlet of c. Mcleord vacuum gage was connected to d. The radio frequency power generator was consisted of a generator of 13.56MHz (SAMUCO) and an impedance matching circuit. The discharge power level was measured by a wattmeter (Bird 43). The discharge power was supplied to a reactor by using an inductive or a capacitive coupling. The structures and the dimentions of the electrode systems are also shown in the figure. As a driving discharge, argon plasma was used. The hydrocarbon monomer used was ethane principally, but, styrene was also used. The properties of plasma polymerized films were studied by an infrared measurement using a spectrometer (JASCO IR-G). The films for the infrared spectroscopy were formed on NaCl crystal which was put on the stand setted in the coaxial center of region B.

3. RESULTS

In the case of inductive coupling, red plasma of argon was observed and radiation region as well as intensity were shown to be dependent on the discharge operational parameter. When a power level of generator was increased to a certain power level, the discharge initiated. Then, radiation intensity and region decreased with decreasing power level and the discharge stopped at a certain lowest power level. But when the power level was increased from the lowest power level, the radiation region and intensity increased again. Usually, radiation region was also observed at the up-stream of solenoid. When the flow rate of argon was changed in this experimental range, significant change of discharge was not observed. But, radiation region expanded in the vessel with decreasing pressure.

In the case of capacitive coupling, almost same discharge behaviour was observed at the operational parameter except the region around the electrodes. At the lower pressure range than 0.1torr, relatively large dark space was formed around the electrode, but it decreased with increasing pressure. At the higher pressure than 1.0 torr, the distinctive radiation was observed around the electrodes. At higher discharge power level, blue striped strings of radiation were appeared along the glass wall of reactor.

When ethane gas was introduced into the after glow of argon discharge in inductive coupling and capacitive coupling, white radiation zone was observed around the inlet b of ethane gas as shown in Fig. 2. The radiation zone moved to the up-stream of argon flow with increasing flow rate of ethane or with decreasing flow rate of argon. This radiation zone was observed at small flow rate of ethane like as a few cm^3STP/min and at higher flow rate of argon than 40 cm^3STP/min. At smaller flow rate of argon, the pressure of reactor decreased because the rate of evacuation was kept to be constant, and the glow of discharge distributed into the reactor. The radiation zone became to be indistinguishable.

For the infrared measurement, the organic films were formed by the discharge of inductive coupling on the surface of NaCl crystal set on the stand in region B. The films were polymerized at different flow rates of argon, but the discharge power level of 25-30 watts and the flow rate of 2-3 cm^3STP/min of ethane were constant for all experiments of sample preparation. Infrared spectra of the films were shown in Fig. 3. In comparison with the infrared spectra of PPE films formed by the reactor of capacitive coupling[11], relatively large absorption peaks were observed at wave number of 3400 cm^{-1} and 1650 cm^{-1} for all samples of this experiments. The absorption at 3400 cm^{-1} is assigned to O-H stretch[11]. The absorption at 1650 cm^{-1} will be assigned to C=C stretch because the peaks of C=C stretch are observed at 1640 cm^{-1} and 1670 cm^{-1} [11]. The largest absorption peak was observed at 2900 cm^{-1} which was assigned to C-H stretch[10,11]. The absorption at 2900 cm^{-1} is proportional to optical density of the film[10]. The ratio of absorption at certain wave number to that at 2900 cm^{-1} will show the relative absorption intensity per thickness[4]. Resultant values of the ratio are plotted as a function of argon flow rate which was used for the plasma polymerization as shown in Fig. 4.

4. DISCUSSION

In the case of inductive coupling, magnetic field is almost constant in the tube of solenoid, but it decreases with increasing distance (r) from the solenoid as a function of $1/r^3$ at outside of solenoid. In the other hand, induced electric field in cross section of glass tube is proportional to the radius of a circle of electric lines of force. Therefore, maximum induced electric field will be obtained on the inner surface of glass tube in solenoid. In a static magnetic field, charged particles will show spiral motion caused by the interaction between magnetic field and charged particles with thermal motion. But in an alternating magnetic field charged particles will be affected by the induced electric field.

In the case of capacitive coupling, electric field decreased with increasing distance from electrodes as same function of distance as in the inductive coupling except the electric field between the electrodes. Observed behavior of discharge was almost same as that of inductive coupling. Blue striped strings of discharge at high power level may be attributed to the low frequency type discharge because blue discharge of argon is observed at high electric field like as negative glow[12]. The dark space at lower pressure and the relatively high radiation region at higher pressure observed around the electrodes may be also referred to the higher hield.

The white radiation zone in an after glow of argon may be attributed to Penning effect of mixed gases[7,12]. By introducing ethane into argon, most ethane molecules will be carried out to the down stream of argon, but some of ethane molecules will diffused to the up stream. The diffusion length increase with increasing flow rate of ethane or decreasing flow rate of argon. Then, the graded density distribution of ethane will be formed in the flow of argon. According to the theory of Penning effect in mixed gases of X and Y, for example, if the metastable activation energy of X is larger than the ionization energy of Y, the discharge voltage of X will become smaller than that of X[12]. Usually the discharge voltage becomes the function of mixed rate of two gases because there are several kinds of decomposed monomer which have different ionization energy and their densities are also function of mixed rate of two gases[7]. In some case, the minimum discharge voltage will be obtained at a certain rate of mixing[7]. Therefore, the observed radiation zone may be attributed to Penning effect at certain rate of mixing in the graded density of ethane in the flow of argon. Metastable activation energy of argon is 11.5 eV and 11.7 eV[7,12]. From above discussion, the ionization energy of ethane must be smaller than 11.5 eV. This value may be almost same as that of benzen (9.2 eV)[7] and ethylene (10.5 eV)[13].

The C=C structure may be introduced into the film in the process of polymerization, because the structure was not existed in original monomer. The relative absorption per thickness at 1650 cm^{-1} increased with increasing argon flow rate. In addition to usual Penning ionization, the existence of dissociative Penning ionization may be introduced, too[7].

$$Ar^* + C_2H_6 \longrightarrow Ar + C_2H_6^+ + e \qquad (1)$$

$$Ar^* + C_2H_6 \longrightarrow Ar + C_2H_4^+ + H_2 + e \qquad (2)$$

where * means the metastable state. Eq. 1 shows usual Penning ionization. Eq. 2 shows an example of dissociative Penning ionization. By the dissociation in a discharge, acetylene may be formed at the final stage[14].

By introducing styrene vapour into the after glow of argon, almost same discharge phenomena were observed as they were descrived in above discussions.

The different discharge power level dependences on the growth rate between the inductive coupling and the capacitive coupling cannot be explained by the discharge phenomena in this study. But, the possible reasons of the difference may be refer to the difference of physical structures of electrode and reactor, the positions of electrodes and substrate and the situation of mixed gases.

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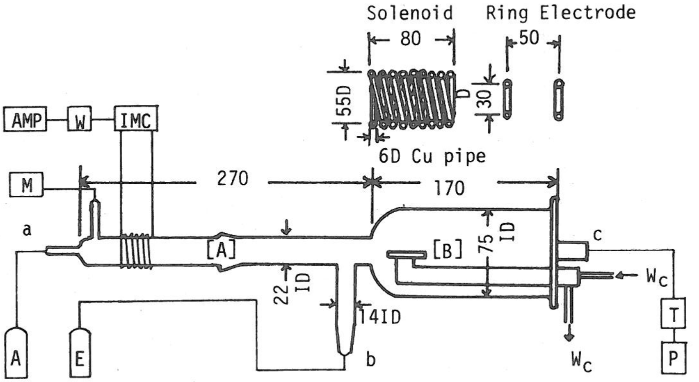

AMP: RF Generator
W: Wattmeter
IMC: Impedance Matching Circuit
A: Argon Reservoir
E: Hydrocarbon Reservoir
M: Macleord Vacuum Gage
T: Liquid N_2 Trap
P: Mechanical Pump
W_C: Circulating Water

Fig. 1. Schematic Diagram of Apparatus and Two Types of Electrodes

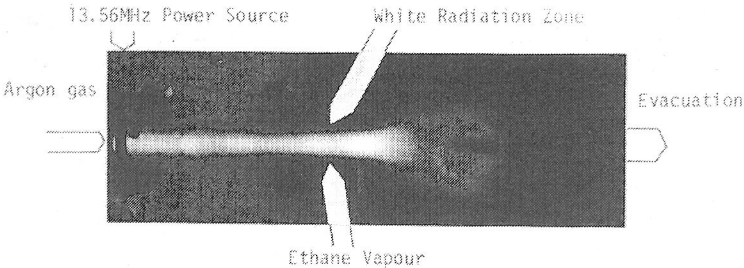

Fig. 2. Photograph of White Radiation Zone

Discharge Condition
Argon 160 cm^3STP/min
Ethane 2-3 cm^3STP/min
Pressure 1.0 torr
Power Level 30 Watts

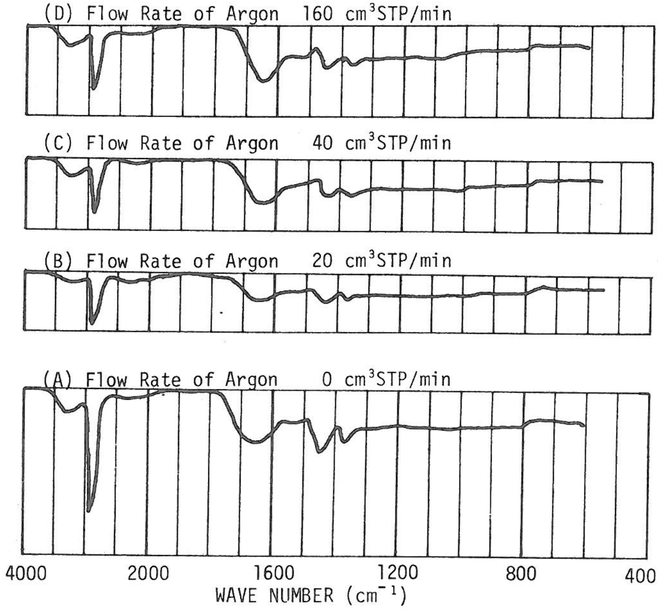

Fig. 3. Infrared Spectra of Plasma Polymerized Ethane Film formed at various flow rate of Argon.
Flow rate of Ethane: 2-3 cm^3STP/min
Discharge Power Level: 25-30 Watts
Inductive Coupling

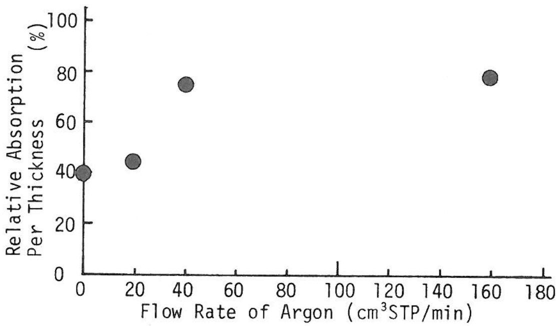

Fig. 4. Relative Absorption Per Thickness Dependence on Flow Rate of Argon