Plasma Polymerization of Acetylene in RF Box-type Gas Discharge Reactor under Plug Flow Condition

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Plasma polymerization of acetylene/argon mixture in RF continuous and pulse discharge was carried out under a plug flow condition in a box-type reactor with well defined kinetic residence time beginning from first milliseconds. The polymerization was supposed to be caused on secondary gas phase products in the film formation beginning from about 30-40 msec of the gas residence time under the experimental condition. However post-discharge chemical reactions had very small effect on the film growth rate.

Introduction

Plasma polymerization is well known to be a deposition technique which forms thin crosslinked organic films. During the deposition process initial monomers undergo dissociation in the gas phase, then transferred to a solid surface and form a film. The mechanism of plasma polymerization is known to be a stepwise mechanism of initiation and recombination without any evidence of chain propagation reactions[1,2]. The gas phase chain polymerization reactions are negligible in gas discharge. However, some cases of chain propagation reaction can be probably found for the reactions of silane[3], fluorocarbon[4, 5], and methylmethacrylate(MMA)[6]. Hence, it is usually difficult to deposit polymer films with preserved monomer structure enhancing the gas phase plasma processes.

Surface processes are quite different. Speidel observed vacuum deposition of hydrocarbon films in e-beam columns of electron microscopes as an essential surface phenomenon[7]. Those systems were described in terms of surface chain polymerization reactions. Saksonsky also measured the maximum life time of surface active sites experimentally to be about 300 sec[8]. This time range is essentially different from that of pulse discharges studied by Bell *et.al.*9] and Yasuda *et.al.*[10] to reveal post discharge chemical reactions leading to the deposition of additional mass. The characteristic times of those experiments were in the order of 0.1-1 msec which is typical for the charge particles decay due to the ambipolar diffusion. This time range is very interesting for the pulse discharge operation. However, it hardly can give a chance to separate the role of post discharge chemical reactions. Plasma initiated vapor phase grafting onto the polymers was carried out in a typical minutes-hours time ranges.

Inorganic surface can hardly be activated to initiate surface grafting under the low monomer vapor pressure condition. In such a situation, plasma polymerization with enhanced surface chemical stages or grafting processes can be utilized. The possibility of

such enhancement depends on the magnitude of relative contribution of post discharge mass deposition. Here we attempted to reveal and estimate quantitatively under the well defined kinetic condition some post discharge deposition phenomena in the worst case of very light monomer, acetylene, in order to exclude the uncertainties originated from the kinetic non-ideally of plasma polymerization reactors and the long time adsorption-desorption equilibrium transitions typical for heavy monomer vapors.

Experimental

Plasma polymerization was carried out in a short residence time box-type reactor capacitively coupled to RF matching box and 13.56 MHz solid state generator controlled with a signal pulse generator[11]. The reactor has a rectangular channel limited by two temperature stabilized copper electrodes and three Teflon walls, one of which serves as a gas distributing shower with numerous small orifices(Fig. 1). The output cross section of the reactor was closed with a floating mesh to prevent outward spreading of plasma. The cross- section of gas flow was 1.5×6.0 cm^2. The length of the plasma zone on the gas flow direction was 10 cm. Plasma emission was measured by a monochromator. Experimental conditions were: pressure range 0.5-0.8 Torr, flow rate 20- 40 cc/min, discharge power 20-30 W, real gas residence time in a plasma region in a range of 5-70 msec depending on the gas flow rate, sampling position and discharge duration. About 0-5 msec residence time corresponds for a plasma- sheath input area. The discharge power was continuous or 100 % square modulated. Under pulse discharge condition the ON time was varied from 0.01 to 10 sec, and the OFF time was 0.05 to 100 sec.

Film thickness during deposition was monitored with a quartz crystal microbalance mounted on the semiconductor cooler-heater inserted in a temperature stabilized lower grounded electrode of the reactor. The films were also deposited on n-type silicon wafers(100 orientation, phosphorus doped, resistivity 3-6 Ohm·cm) located on the lower electrode. Distribution of film thickness after the deposition was measured with an automatic ellipsometer. The surface roughness of the film was observed by atomic force microscope(AFM). Film composition and structure were characterized by IR spectroscopy and X-ray photoelectron spectroscopy(XPS).

Results and Discussion

The plasma polymerized film was uniformly deposited but powder particles were not detected at the condition. The process of film deposition was stable and reproducible. Figure 2 demonstrates the distributions of thickness of the deposited film along the gas flow direction. The discharge power was pulsed as 0.1 sec ON and 0.9 sec OFF, and the number of pulses was 100 with the total discharge duration of 10 seconds. Here 1 cm position along the gas flow corresponds for 10 msec of the real gas residence time. The film deposition rate is established from the first milliseconds of the residence time. It means that the light highly reactive products of C_2H_2 decomposition and/or excitation take essential part at the initial stage of film formation.

The deposition rate is increasing remarkably near the distance of 3-4 cm as shown in Fig. 2, where the real film thickness was obtain by subtracting the deposited thickness by Ar discharge. It is to be interpreted as a participation of secondary neutral

products synthesized in the gas phase after about 30-40 msec.

The deposited film thickness was theoretically calculated using the model of gas phase propagation. The activation, propagation and adsorption of monomer are

$$Mg + e = 2Rg + e \quad (1)$$

$$Rgn + Mg = Rg(n+1) \quad (2)$$

$$S + Rgn = Rsn \quad (3)$$

where Mg and Rg: monomer and radical in gas phase, e and S: electron and surface of solid, n: number of reacted monomer. If mass of adsorbed radical increase linearly as following,

$$m(tp) = m(0) + ctp \quad (4)$$

where c is constant, the thickness distribution can be calculated to be the second function of distance x from the gas inlet. The result shows good co- relation with the experimental result. Discharge time dependence of film thickness was also calculated and show the good co-relation with the result as shown in Fig. 3. However these calculated results must be confirmed by the evaluated physical parameters.

The kinetics of polymer film growth depending on the condition was measured as shown in Fig. 4. This experiment was reproduced experimental results published by Inagaki and Yasuda[12] for acetylene, where the most striking result was the long time growth of polymer film after the discharge power was switched OFF, or both the acetylene flow was stopped and discharge power was switched OFF. We controlled the deposition kinetics while the discharge power, acetylene flow or both power and flow were switched ON and OFF under the plug flow condition.

One can see that the deposition is turn to ablation while the acetylene flow is stopped and Ar discharge was affecting the surface. It is consistent with the Activation Chemisoption Model of plasma polymerization[13] based on the destructive activation of the surface by neutralizing positive ions. While the discharge was switched OFF the deposition rate immediately drops to zero and the film thickness remains constant. When both the discharge power and the acetylene flow were stopped we did not find any thickness variation as well in contrast to the results reported in the reference of [12].

Figure 5, a and b show the optical emission spectra collected across the gas flow at the central plasma region above the quartz crystal monitor. Nor atomic, neither molecular hydrogen emission was detected. The maximum spectral intensity of the C_2H_2/Ar discharge is about 100 times lower in respect to the Ar discharge obtained immediately after the C_2H_2 flow was stopped. Such a dramatic change of intensity originates from the variation of plasma parameters while the organic molecular additive exceed the level of about 0.1- 1 %[14].

XPS spectrum together with the single C1s XPS peak of the 200 nm thick film corresponding to the time period in Fig. 6. The spectra clearly shows that the deposited film does not include any fluorine contamination. This fact means there is no contamination from the reactor wall of poly-tetrafluoro- ethylene.

conclusion

Plasma polymerization of acetylene was carried out with acetylene/argon mixture in a box-type RF kinetic reactor under plug flow condition. Well defined gas flow and pulse discharge operation provide the possibility for the deposition of perfect ultrathin ultrasmooth hydrocarbon films and for studying the film growth kinetics in the first milliseconds of the real residence time.

The characteristic time of secondary gas phase products formation increasing the deposition rate is about 30-40 msec. Acetylene gas itself does not demonstrate any post discharge surface processes longer than at least 0.1 second at the gas kinetic residence times of about 50msec. However, it is probable that some neutral chemically active precipitating gas phase products give the mass increase within less than 50 msec after the discharge is interrupted under the experimental condition. It means that acetylene doesn't undergo chain propagation reactions on the plasma activated surface. Probably it is typical for any low adsorbable stable molecules.

Much longer time delay of mass deposition could be, in principle, observed under the condition of very long or indefinite residence time typical for the bell-jar reactors. The first reason is their very long time of gas exchange: up to about ten minutes. Another reason could be the sedimentation of electrically charged dust particles synthesized in a gas phase on the surface after the discharge was interrupted. However, both features reflect the imperfections of the experimental system or artifacts, rather than the real kinetics of plasma process itself.

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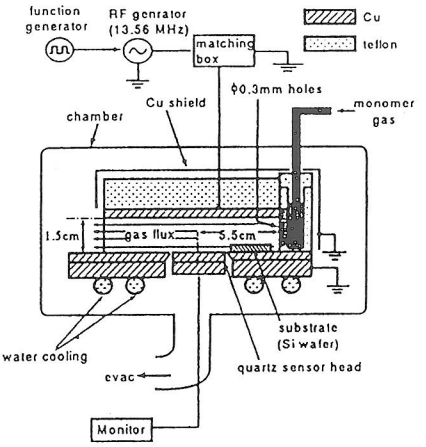

Fig. 1. Gas Discharge box-type RF reactor

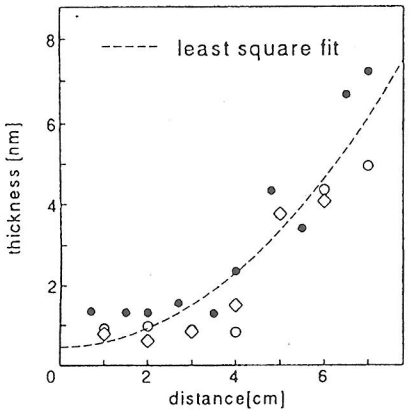

Fig. 2. Distribution of ultra thin thin film along the gas flow

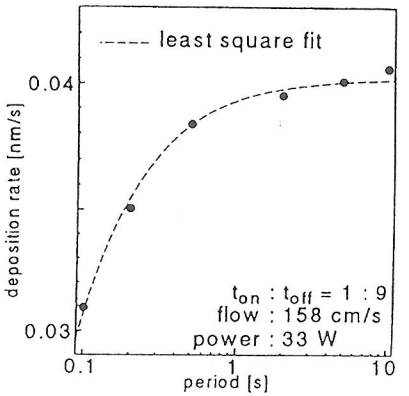

Fig. 3. Deposition rate depending on the discharge period

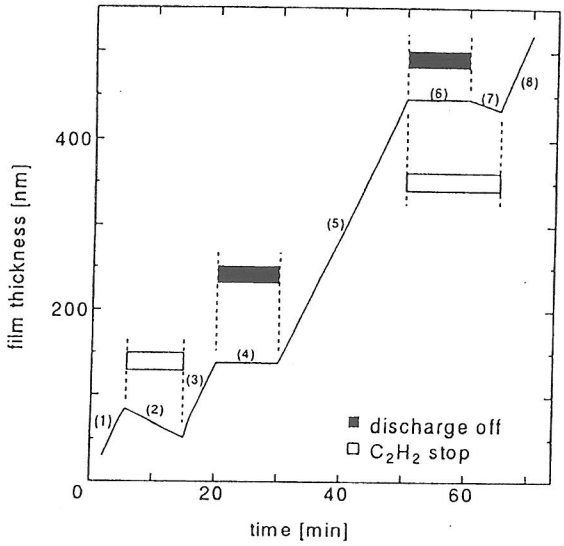

Fig. 4. The kinetics of film growth and ablation on the quartz crystal monitor while the discharge power and/or acetylene flow were switched ON and OFF.

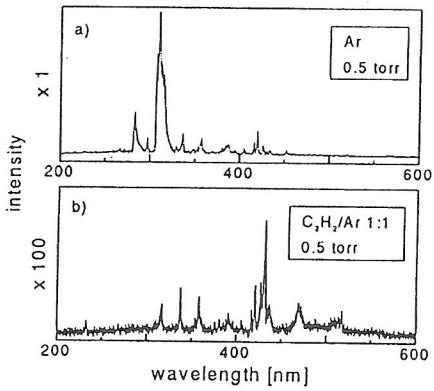

Fig. 5. Optical emission spectra of plasma

a) Ar discharge immedeately after acetylene flow was stopped

b) acetylene/Ar(1:1) discharge

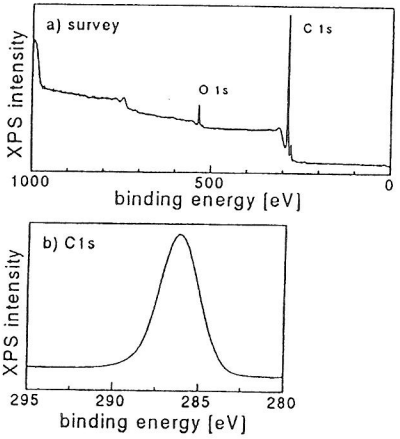

Fig. 6. XPS spectra of the organic film on the silicon substrate in acetylene/Ar discharge

a) survey, b) C1s signal