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PARAMETERS AND CONTROLLING OF PLASMA CHEMISTRY

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16. Abstract

The text deals with parameters in plasma polymerization reaction(conditions of the equipment, electricity, pressure, etc.) and shows how we can control the reaction using these parameters.

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PARAMETERS AND CONTROLLING OF PLASMA CHEMISTRY

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1. Introduction

The application of plasma in chemical reactions has been known /62 for a long time. As examples, we have the composition of organic and inorganic compounds [1, 2], polymers, thin films [3, 4], and surface treatment techniques [6], which includes etching and curing [5]. These examples are known as plasma chemistry. As plasma chemistry is used on a practical scale, the explanation of the mechanism of plasma chemistry reactions, the parameters of the reactions and the control of plasma chemistry is inevitably required. The parameters which play an important role in plasma chemistry and the optional control of these reactions make it possible to improve the efficiency of the reactions due to the possibility of stably continuing the reactions.

In reality, with thin plasma polymer films, duplication is difficult to achieve. There are many differences in experimental apparatuses and conditions. In addition, there are various sources of electricity for developing plasma and differences in the frequencies. When the conditions of the equipment used in the reactions are different, various factors are accumulated and many times duplication is negatively affected. Consequently, in this manuscript, the representative plasma reaction equipment, the surrounding equipment and their control are related by the use of unequal plasma $(T_e \gg T_g)$. As for the reaction parameters and their association, the most recent trend is presented in an example of a plasma polymer and plasma CVD (chemical vapor deposition).

2. Plasma Parameters

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*Numbers in the margin indicate pagination in the foreign text.

The principal experimental conditions, which are generally entered in the bibliography, are:

(1) the conditions of the reaction equipment,

(2) the variety of the source of the electricity used in development of plasma, the voltage, current, etc.,

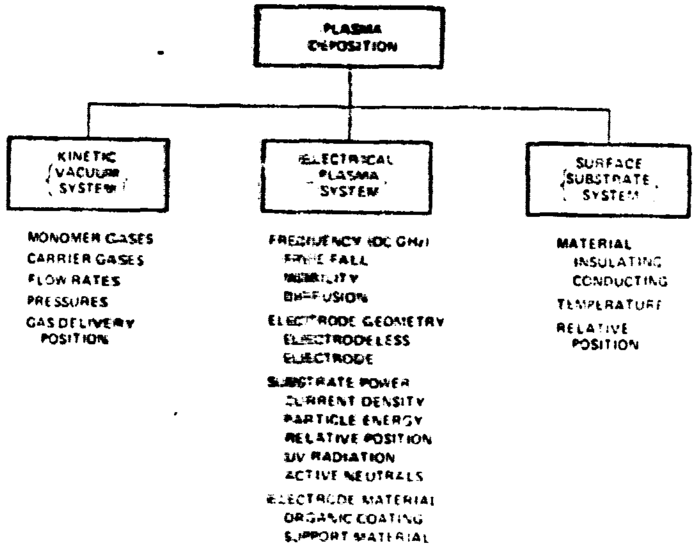
(3) the pressure within the reaction chamber,

(4) the monomer supplied, the type of gas, the amount supplied and

(5) the condition of the sample holders.

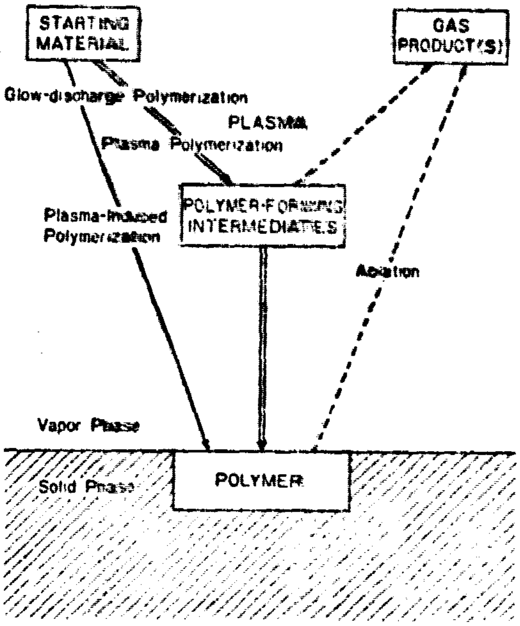
Hudis [8] has separated these in detail. For example, they are classified as shown in Table 1. The fact that there are many parameters only means that the experimental system is complex. The next possible consideration would be the simplicity of the process. Easy comparison is desirable.

Table 1. **Parameters Controlling Plasma Deposition**



3. Electrical Discharge Form and the Reaction Chamber

Plasma excitation, the growth of plasma excitation and a thin film, or the degree of separation (after glow discharge) are important points of difference. These are not just the common deposition of

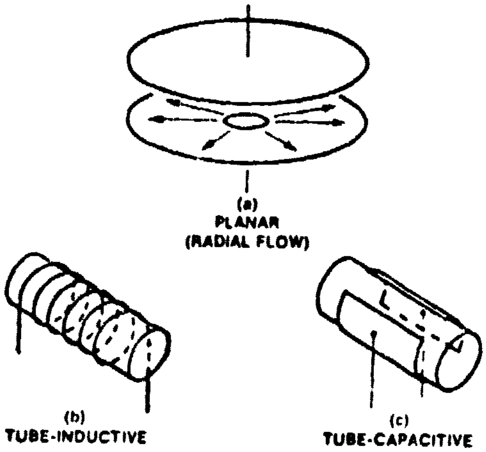


Overall mechanism of glow discharge polymerization.

Figure 1

of plasma chemistry reactions or growth. The reaction that accompanies ablation is also occurring at the same time. According to the estimates of both authors, the deposition rate is fixed. Yasuda [9] explains these mechanism as shown in Figure 1.

In a word, the ablation and deposition of plasma excitation are both relatively large. When the plasma excitation and substrates are separated, a degree of growth is dominant. However, the absolute minimum quantity of accumulation is not very large. The growth of the film not only improves the increase in the discharge glow, but because the optimum conditions are detected; there are several other necessary parameters.



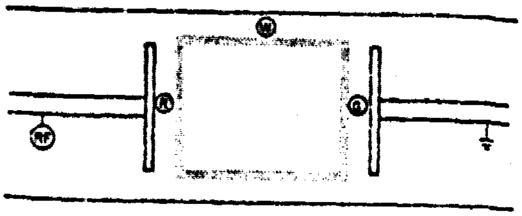
Various basic types of electrode configurations. In (a) the electrodes are normally inside the reactor directly interfacing with the plasma, while in (b) and (c) the electrodes are external to the plasma process (electrodeless excitation)

Figure 2

The origin of various plasma reaction chambers are considered from the viewpoint of engineering in Figure 2. There is an exterior electrical discharge and an interior electrical discharge.
(a) Capacitive coupling-parallel plate, (b) inductive coupling and (c) capacitive coupling forms are well known.

3.1 Monomer Supply and Gas Ventilation

In plasma polymerization by



Schematic representation of a capacitively coupled rf discharge in methane. The letters R, W, and G are labels for the dark space between the luminous plasma bulk and the rf electrode, container wall, and ground electrode, respectively.

Figure 3

high frequency glow discharge, the growth of the reaction products and the thin film is not necessarily found just in the discharge range between the electrodes. They are distributed in some parts of the reaction chamber. For example, Smolinsky [11] has measured the signs of polymer accumulation on the reaction chamber wall and on each part of the electrodes from the reaction chamber of the capacitively coupled interior discharge form, as shown in Figure 3. and Table 2. Beacuse an equal film forms in the ventilation opening, its connections are important for the method of supplying the monomer or the raw materials and ventilation in a vacuum. The bibliography should be referred to for various types of reaction chambers [12, 13].

Table 2

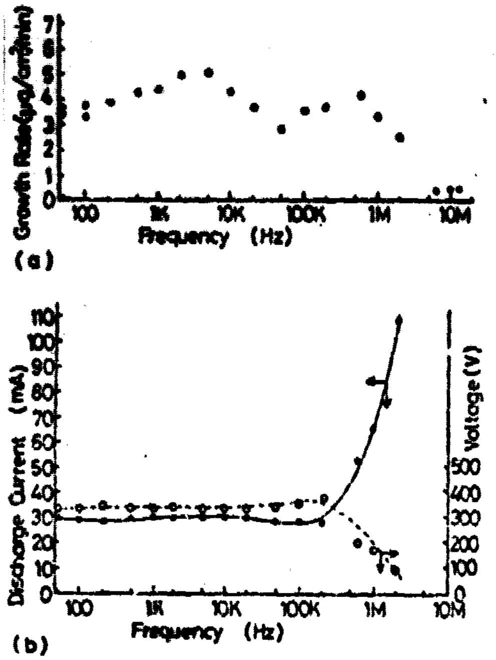
Comparison of the Rate of Methane Polymer Deposition on the Electrodes and Walls in a 150-V p-p rf Discharge [8] at Several Pressures

Pressure (Torr)	Deposition rate (Å/min) for region[a]		
	R	G	W
0.8	11	11	3
0.5	16	16	5
0.3	31	26	11

3.2 Improvement of the Sample Holder

The growth of the film is not only carried out on the substrate surface. The quality of the sample holder and the surface temperature also have a large influence on the growth of the film. This fact was previously related to the idea that the plasma chemistry reaction was /63
a surface reaction or a gas phase reaction [14, 15]. However, its

positive introduction or applied purposes is an important factor in the design of the reaction chamber.



Effect of discharge frequency on the growth rate of plasma polymerized ethane and the discharge voltage and current of ethane at a pressure of 0.5 torr, a flow rate of 20 cm³ STP/min and a power level of 10 watts in room temperature. (a) Growth rate. (b) Discharge voltage and current

Figure 4

4. Frequency and Electrical Source for the Development of Plasma

4.1 Electrical Source Frequency

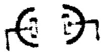
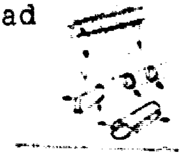
In the development of plasma, various frequencies are used, from a high frequency range of 2,450 MHz to a microfrequency of 50 or 60 Hz. The frequency zone used most often in manufacturing is 13.56 MHz for radio waves. The reason for using different frequency zones is that the flexibility of the electricity power source and the plasma load are considered. These characteristics are shown in Table 3. On the one hand the fact that the electric source of frequency is different brings out the characteristics of the plasma reaction. Namely, the amount of free radicals remaining in the plasma polymer after the reaction is related to the excited electricity source and it is known that it also influences that growth rate. Morita [16] has reported on the connection between the electric source of frequency and the growth rate, as shown in Figure 4.

The activated element that is excited by microfrequency has a long life span. Even though there is a lower class of plasma excitation, it is not easily made inactive. This can be related to the reaction and it is not always necessary to perform the treatment only in the vicinity of the electric discharge.

4.2 Electricity Source Output Wave Pattern

Generally, the wave pattern used in electrical discharges is a

Table 3. PLASMA EXCITATION CHARACTERISTICS

Plasma excitation method	Capacity of the electrical discharge	Engineering load	Reaction chamber
magnet micro-frequency  electric discharge tube 2,450 MHz cavitation microfrequency	relatively small scale	Cavitation is necessary [illegible] and load cannot be separated by a long distance	There are restrictions in the shape of the chamber.
between 50 and 60 Hz 	Can be relatively large and missing in plasma at equilibrium		Possible to apply to the load chamber of all shapes
inductive load  capacitive load high frequency 13.56 MHz	Uniform plasma at large capacity can be developed	High frequency and load separation is possible	Used in complex chambers

coupling wave pattern, like a sine wave. In the cases where the presence of ions is a problem during the electrical discharge (for instance when ions, which are formed in a previous electrical discharge cycle, influence the next cycle), we use the output of the electrical source in a pulse shape. The range of the pulse in this case is determined by the relation to the span of the ion.

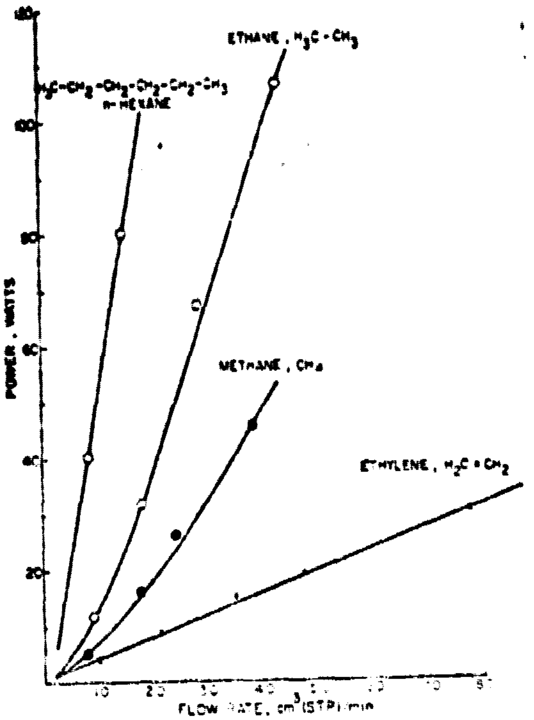
4.3 Electrical Discharge Power

Between the electrical discharge power and the monomer current rate and molecular weight, the following connection is reported by Yasuda [19]. Namely,

W: electrical Power

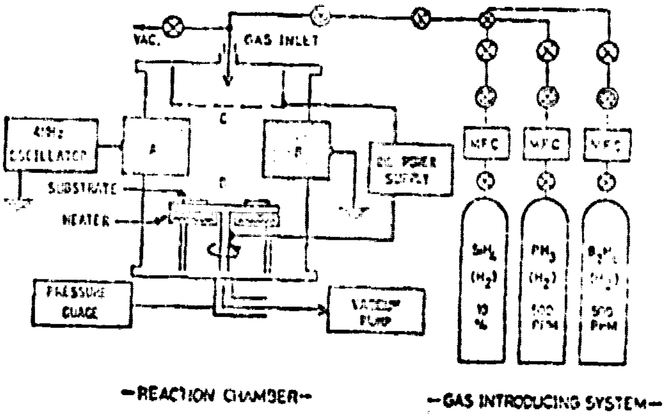
F: monomer current rate (STP)

M: molecular weight of monomer



The dependence of discharge power to obtain a comparable level of glow discharge polymerization on the flow rates of starting materials. The discharge power is greatly dependent on the molecular weights of the starting materials.

Figure 5



Schematic diagram of the plasma deposition system.

Figure 6

The connection between the electrical power and the molecular weight is formed as shown in Figure 5. This explains the formation of an influential parameter.

4.4 Efficiency of a Third Electrode

A third electrode is placed inside one pair of exterior electrical discharge reaction chambers. A substrate is set on the third electrode and a direct current electrical discharge is produced between the main electrical discharge electrodes. High frequency voltage is added between the anode and the third electrode and an electrical discharge is produced. By doing this we control the formation of the film on top of the substrate [20]. As shown in Figure 6, the direct current electrical potential of the substrate changes and screening of the ion in the narrow range is aimed for. However, the extent of this efficiency is not explained in detail.

5. Reaction Chamber and the Degree of Vacuum

5.1 The Influence of the Vacuum Inside the Reaction Chamber

The pressure change inside the plasma reaction chamber increases and decreases the electrical discharge energy. A change in the electrical field strength changes the energy of the electrically charged particles. The parameter of the plasma strength can be expressed as the connection between the pressure (P) and the strength of the electrical field (E), or E/P. Consequently, in order to maintain the conditions for developing plasma, which is the same as giving a uniform electrical field to the plasma, the pressure conversion must be controlled. Automatic pressure maintenance equipment, which was produced for this purpose, also is marketed.

5.2 Factors and Countermeasures in Pressure Conversion

In normal plasma polymerization and CVD tests, the reaction chamber pressure at the time of the test is about 0.1 to 1 torr (13-133 Pa), which is a relatively low vacuum. An oil rotating pump is used in the vacuum maintenance. When the remainder of the gas in the reaction chamber is not wanted, we use a diffusion vacuum pump or turbo mole- /66
cular pump.

The possible occurrences, other than the change in the conversion of the exhaust capacity of the pump, are factors of pressure change. These are caused by

(1) the introduction of the monomer and gas,

(2) the development of reaction products or secondary products, and

(3) the use of a pump with a cooling trap.

Since there is a peculiar reaction that is produced while the plasma polymerization repeats the dehydration reaction (for example, the reaction in formulas (1) and (2) are accompaned by the development of hydrogen), the pressure within the reaction chamber is changed.

In the case of ethylene, we have

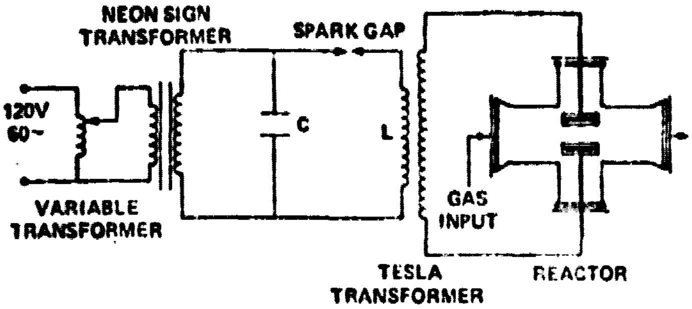
$$C_2H_4+e^- \longrightarrow C_2H_2+2H\cdot+e^- \cdots\cdot \qquad (1)$$

$$C_2H_4+e^- \longrightarrow C_2H_2+H_2+e^- \cdots\cdot \qquad (2)$$

Consequently, the capacity of the reaction chamber is large when the influence from the formation of hydrogen is small. The countermeasure of adopting a good pump with exhaust characteristic related to hydrogen is necessary. Yasuda [22] has carried out various investigations concerning the use of a liquid nitrogen trap and suggested caution in its use.

5.3 1 atm Glow Discharge

The use of special vacuums has become common when the glow discharge can be maintained. The most recent research has been done by a NASA group [23]. In their recent report, ethylene plasma polymerization was carried out at 1 atm and they obtained results that were almost identical to plasma polymerization under low pressure. Figure 7 shows the experimental systems.



Schematic of the discharge circuit and reactor

Figure 7

6. Monitoring of the Reaction Process

6.1 Discharge Monitor

When plasma conditions can be detected and controlled by an outside method, very influential control techniques are produced. Shinkai [24] has adopted a needle probe method in plasma polymerization of inverse permeation films. The needle probe method is a classical method for measuring plasma conditions. He has reported on a test for plasma electron temperature and optimum conditions of film formation. Figure 8 shows this. On the one hand, control is also carried out by the radiation spector of plasma measurement control and its development by light is anticipated. A quadrupole mass analyzer is good for measuring each ion and reaction products and is a conventient monitor. /67
As for the fact that we should observe measurement and control

techniques, strong anticontact techniques are desired because reaction products result from the direct probe method.

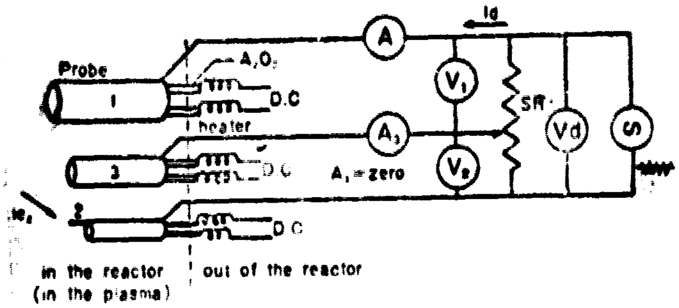
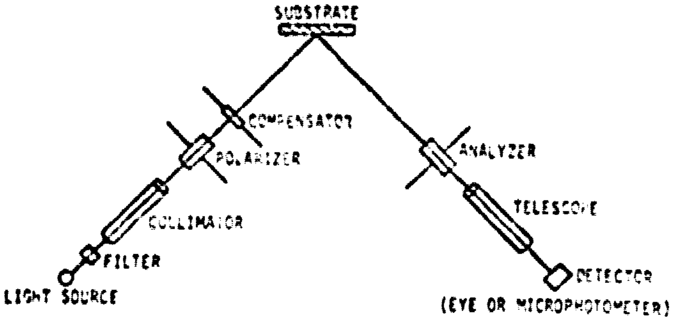


Figure 8
Thermal Needle Probe (ATPM)

6.2 Film Origin Monitor

The most influential control of film origin is a He-Ne laser (6328 Angstroms) monitor. The laser passes through the quartz walls of the reaction chamber and the laser beams are irradiated on the film surface. This takes light from the windows of the opposite side. This technique is used as a polymerized film formation monitor. Along with CVD or PSG, Si_4N_4, the film coats metal surfaces.



Schematic representation of the optical arrangement of the ellipsometer

Figure 9

6.3 Computer Control

Many test parameters have been explained in plasma chemistry. These parameters are considered as control methods when we use an all-purpose microcomputer. Because the molecule beam epitaxy gives the smae results from the same techniques, much research will be on the MBE in the future.

7 Conclusion

In the use of unequal plasma, the example which gives the most success is probably dry etching in the semiconductor production process by freon processing. Recently, the parameters mentioned above have been gathered and various monitoring techniques have been introduced. These techniques have been put into use. On the other hand, when plasma polymerization and CVD are complex, it is not a handicap since there are many test approaches and techniques. From now on various types of research will progress and universal data can be obtained from the many test parameters. We should put more effort into equipment production.

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