An Overview of Magnetron Plasma Polymerization for the Most Successful Industrial Scale Operation of Plasma Polymerization*

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Magnetron-AF (e.g., 15 kHz) plasma polymerization with a coaxial circular arrangement of magnetic field has a unique advantage that no deposition occurs onto a part of electrode surface corresponding to the toroidal glow, which enable us to operate the stable magnetron plasma polymerization continuously for a long period of time. Together with the confined glow that remarkably reduces the contamination of the reactor; the magnetron plasma polymerization has been shown to be one of the most effective modes of plasma polymerization in industrial scale operation. When the magnetron plasma polymerization is used in laboratory experiments, successful operations can be easily scaled up to industrial scale operations by maintaining parameters of the magnetron discharge and, if necessary, increasing the number of discharge units, instead of enlarging the discharge unit.

1. Historical background for magnetron plasma polymerization

In early 1970s, RCA undertook a very important, with respects to gaining fundamental knowledge in science and engineering of plasma polymerization, R&D project on video disc production, which utilized consecutive various vacuum processes.¹⁾ Magnetron plasma polymerization was used to lay down a dielectric layer in two repeating steps. It demonstrated that multi step vacuum process could be operated in a continuous manner in industrial production. The magnetron polymerization provided key elements in such a continuous operation, because the contamination of reactor could be kept unparallel low level compared to non-magnetron RF plasma polymerization. Although a large numbers of video discs were produced, the products had never been placed on market based strictly on the commercial judgment in the twilight of upcoming laser based technology and very little has been published on the magnetron plasma polymerization used in the project. Consequently, the magnetron plasma polymerization has been relatively unknown to most practitioners of plasma processes.

The author inherited the magnetron plasma polymerization from the project and has used the method wherever applicable. Due to some misconception, the method has not drawn attention of most researchers and engineers. In recent years, the magnetron plasma polymerization has been successfully utilized in the production of plasma polymer coated contact lens,²⁾ of which annual production could be conservatively estimated to be over 30 million lenses a year per reactor and the total production over 400 million a year, which is undoubtedly the most successful industrial applications of plasma

polymerization with consideration of the add-on value.

2. Magnetron plasma polymerization vs. magnetron sputtering

The electrodes used in the magnetron plasma polymerization are very similar to the magnetrons used in the magnetron sputtering of the cathode metal. **Table 1** summarizes the main difference of magnetron sputtering and magnetron plasma polymerization. The key differences are the gas used in the processes and the level of discharge powers. The first key factor could be best visualized by comparison of DC (direct-current) glow discharge of argon and that of an organic molecule such as trimethylsilane (TMS); Ar glow is the ionization glow which is separated from the cathode surface by the cathode fall dark space, but TMS glow is the dissociation glow that virtually attaches to the cathode surface. The ionization glow of TMS develops as the glow discharge continues, which is the ionization glow of H, one of the dissociation products of TMS.

The glow discharge of argon is a physical transformation of atom, i.e., ionization of argon, and the impact of

Table 1 Comparison of non-reactive magnetron sputtering and magnetron plasma polymerization

Operational Factors	Magnetron Sputtering	Magnetron plasma polymerization
Gas	Mainly, argon	Organic molecules
Power Input	High	Low
Metal	High sputtering rate	No to low sputtering rate
Ion	High energetic Ar ⁺	Low energetic H ⁺
Metal Sputtering	Yes	No
Material Formation from gas used	No	Yes

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ions on the cathode surface could cause the sputtering of metal from the surface depending on the power input level. The glow discharge of an organic molecule is a chemical transformation of molecules caused by the low-energy electron impact dissociation, and the main ions that strike the cathode surface is the low energetic hydrogen ions. Under the conditions of magnetron plasma polymerization, no sputtering of cathode surface occurs and plasma polymer deposition is not contaminated by the sputtered cathode material.³⁾

3. Magnetron plasma polymerization

Various forms of electrical discharge could be used for plasma polymerization. Although numerous discharge systems have been developed for plasma polymerization in last three decades, none of them could satisfy the general requirements of plasma polymerization, because plasma polymerization is system dependent, meaning that the material formation depends on what kind of reactor is used and also how plasma polymerization is carried out; i.e. a monomer (starting gas) does not yield a single plasma polymer, and the size and shape of substrates on which plasma polymers are deposited are crucially important factors.^{4,5)} Consequently, the proper selection of a plasma polymerization system for a specific objective is a very important factor that more or less determines whether or not the process developed in a laboratory could be successfully utilized in an industrial operation. In this particular aspect that the laboratory

experiment can be easily up scaled for industrial production, the magnetron plasma polymerization has the unique merit if the external surface coating is the main objective. **Table 2** highlights the difference of RF (radio frequency) plasma polymerization and AF (audio frequency) magnetron plasma polymerization for a specific purpose of coating the external or open surface of substrates.

Plasma polymerization is the chemical reactions triggered by the dissociation of molecule, of which reactive species are mainly free radicals. Ions play little role if any^{5,6)}, because the neutral species outnumber ions in order of 10^6 to 1 in the glow discharge of organic molecules⁷⁾.

The magnetron plasma polymerization could be carried out in an ordinary low-pressure RF plasma polymerization reactor with a pair of internal electrodes by simply adding the magnetic enhancement behind the electrode surface and driving them by a symmetrical AF (e.g., 10–50 kHz) power source. RF magnetron plasma polymerization loses most of advantages of the magnetron plasma polymerization because the magnetic field (as employed) has little effect on the oscillating electrons in the RF discharge.

Using high frequency power source, e.g., 10–50 kHz (AF), generally carries out magnetron plasma polymerization that maximizes the advantages of magnetron plasma polymerization. The unique advantages that are not obtainable by RF plasma polymerization are as follows. 1) The glow is confined in more or less the inter-electrode volume, which reduces the undesirable deposition elsewhere. 2) Very little deposition occurs to the electrode surface, which enables us to operate the process for prolonged period of time (e.g., for weeks to months). 3) The current control mode of high frequency discharge enables us to take advantage of the favorable feature of DC discharge that the plasma polymerization depends on only the discharge current, which is automatically controlled by the current control mode operation.

The AF polymerization is essentially alternating DC discharge⁸⁾, which is not suitable for plasma polymerization due to the predominant deposition on to the electrodes. The AF magnetron plasma polymerization changes the unfavorable AF plasma polymerization to the most favorable plasma polymerization system for coating open or external surfaces known today. The magnetron plasma polymerization cannot be applied to the inner surface of substrates, which can be done by RF plasma polymerization depending on the size of the internal surfaces. This comparison emphasizes the importance of the selection of plasma polymerization system for a specific need and that the plasma polymerization cannot be dealt in a generic sense based on hypothetical plasma models.

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Table 2 Comparison of RF plasma polymerization and AF magnetron plasma polymerization for external surface of substrates coatings

	RF Plasma Polymerization	AF Magnetron Plasma Polymerization
Energy Input Parameter	W/FM	I/FM
Creation of polymerizing species	Impact of oscillating electrons	Impact of low-energy electrons in linear motion
Location of dissociation	Dissociation glow distributed over the entire area of electrode in gas phase near the surface of electrodes	Localized toroidal dissociation glow in gas phase near the surface of electrodes
Confinement of glow	No	Yes
Yield of deposition on substrate	Low	High
Energy consumption per unit product	High	Low
Wall contamination by plasma polymer deposition	Moderate to heavy	Very little
Change of plasma polymerization behavior with reaction time	Considerable extent	Negligible
Continuous long time operation	Difficult	Easy
Scale up of process	Difficult to very difficult	Easy

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