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Ultrathin PTFE, PVDF, and FEP Coatings Deposited Using Plasma-Assisted Physical Vapor Deposition

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19.1. INTRODUCTION

The unique properties of fluorinated polymers have led to their wide use as surface protection coatings and as components within protective coating systems.¹⁻⁴ Applications are diverse, from cookware, through environmental protection coatings for architectural panel work, antigraffiti and soil-resistant coatings in the automotive industry, to low-friction coatings⁵ within the precision tool industry. This diversity reflects the chemical and thermal stability, hydrophobicity, and low surface energies associated with fluoropolymers.

Traditionally these coatings have been deposited by solvent-spraying, spin-coating, or powder-spraying technologies, resulting in coating thicknesses in excess of 10 μm . The increase in possible applications of ultrathin fluoropolymer coatings particularly for environmental protection and sensors^{6,7} has led to increased interest in plasma polymerization^{8,9} and sputtering¹⁰⁻¹⁹ techniques to produce such films.

This chapter examines the deposition of fluorinated polymers using plasma-assisted physical vapor deposition. Ultrathin coatings, between 20 and 5000 nm have been produced, using RF magnetron sputtering. The method of coating, fabrication, and deposition conditions are described.

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19.2. RF MAGNETRON SPUTTERING OF FLUOROPOLYMER FILMS

Over the last decade, selected papers¹¹⁻¹⁴ have examined the deposition of fluoropolymers, using RF magnetron sputtering. All of these papers have examined the deposition of PTFE, with some of them^{23,14} also studying the deposition of polyimide (PI) films. This chapter extends these studies and will report on the sputter deposition behavior of PTFE (polytetrafluoroethylene), PVDF (polyvinylidene fluoride), and FEP (fluorinated ethylene propylene copolymer) films.

19.2.1. The Process

The sputtering process shown in Figure 19.1, utilizes the phenomena associated with a low-pressure gas discharge. The system comprises an anode and cathode; generally the low-pressure chamber is earthed and forms an "infinite" area anode; the small cathode surface is the "target" material from which gas ion-etching occurs, resulting in condensation of the material onto workpieces within the vacuum chamber.

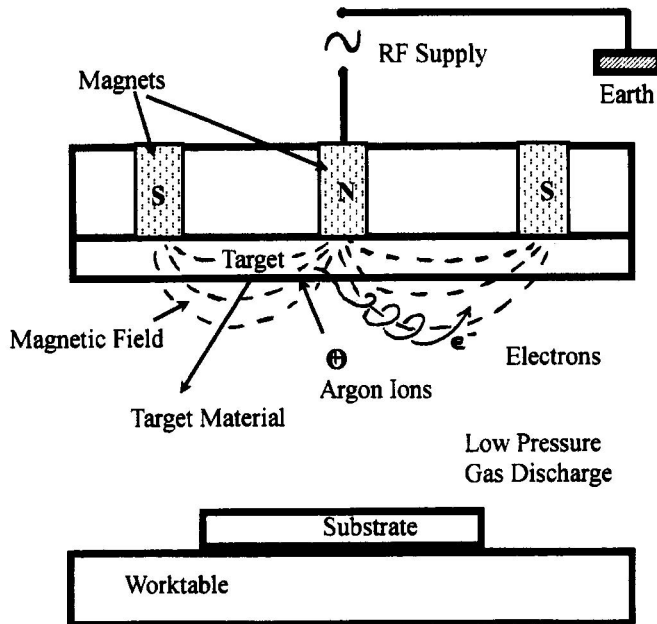


Figure 19.1. High-rate magnetron sputtering.

In order to be able to sputter dielectric materials, an RF glow discharge must be established. An RF voltage is coupled through the inductive/capacitive impedance presented by the electrode, dielectric target, and plasma. The ionization is maintained by electrons within the system. Normally the ion species is an inert gas (e.g., argon). The ion-etching of the cathode occurs owing to a net negative dc bias being established at the insulating surface of the target material. This is due to the high mobility of the electrons in the plasma in comparison with the ions. This net negative bias then accelerates ions to the target surface, resulting in ion-etching.

The magnetron arrangement incorporates magnets, behind the target electrode system, which trap further electrons within the discharge volume, resulting in enhanced ionization. This leads to an increase in etching rate but also traps electrons that might otherwise strike the workpieces to be coated, hence reducing heating that might be caused by these secondary electrons. This is a distinct advantage when depositing onto heat-sensitive materials or, indeed, sputtering heat-sensitive coatings.

As the source of material (sputtering target) is a solid, a variety of electrode configurations can be used; e.g., depositing material downward, upward or sideways. It is possible to electrically bias workpieces being coated. This can encourage a level of ion bombardment that can modify the surface and structure of a coating.

19.2.2. Sputter Deposition of PTFE, PVDF, and FEP

The sputtering equipment was used with sputter-up and sputter-down configurations. 150-mm-diameter disks of the materials were used, with the PTFE and PVDF being 5 mm thick and the FEP 2.3 mm thick. The targets were loosely clamped to the sputtering electrodes to allow for thermal expansion. High-purity argon gas was introduced into the chamber as the glow discharge gas.

The vacuum chambers were pumped down by means of an oil diffusion pump backed by a rotary vane vacuum pump. The base pressure achieved was 1×10^{-5} Torr (1.33×10^{-3} Pa). High-purity argon gas was bled into the chamber, the high-vacuum valve throttled, and the chamber pressure maintained as close as possible to 2×10^{-2} Torr (2.66 Pa). For some of the experiments, the dc self-bias on the magnetron electrode was also measured.

The parameters that were varied were: (a) change from electrically earthed to electrically isolated work table; (b) argon gas mass flow over the range 12–27 sccm; and (c) RF power density over the range 0.18–1.13 W/cm². The detailed process parameters for each deposition are summarized in Table 19.1. A range of substrate materials have been used, primarily soda lime glass slides, but also nickel, aluminum, silicon, and gold- and silver-coated glass slides.

Table 19.1. Deposition Parameters for Fluoropolymer Films

Material	RF power density W/cm ²	Work table	Substrate	Rate of deposition (nm/h)
PTFE	0.3	Electrically isolated	Glass	126
PTFE	0.57	Electrically isolated	Glass	4140
PTFE	1.13	Electrically isolated	Glass	9000
PVDF	0.18	Electrically isolated	Glass	126
PVDF	0.3	Electrically isolated	Glass	300
FEP	0.18	Electrically isolated	Glass	552

19.3. RESULTS AND DISCUSSION

19.3.1. Deposition of PTFE

This work has shown that PTFE films can be deposited using RF magnetron sputtering over a range of deposition conditions, with power densities varying from 0.3 to 1.13 W/cm². In all cases adherent films were produced showing no delamination even after extended exposure times (out to 16,000 h). The rate of deposition was found to increase in a near linear manner with deposition power, as can be seen in Figure 19.2.

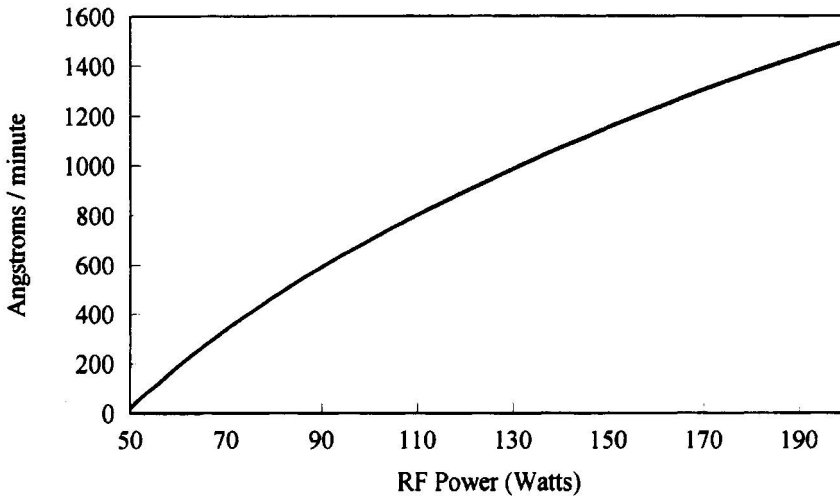


Figure 19.2. Sputter deposition rate of PTFE vs. RF power.

Measurements of the IR absorption spectrum of the as-deposited film was similar to that for the target material, implying similar bonding to that in target material. Figure 19.3 shows the IR reflectance spectrum obtained from a 10- μm PTFE coating sputtered onto a polished silicon slice. The RF power density to the target was 0.57 W/cm^2 . The periodicity at the higher wave number values is due to optical interference. The spectra of films deposited at higher power densities were similar, with absorption peaks through 1110 to 1360 cm^{-1} and 610 to 735 cm^{-1} . Previous studies¹²⁻¹⁴ had similarly found that RF-sputtered PTFE films possessed attributes similar to the bulk material and that they also closely resembled those deposited by plasma polymerization.¹⁴

In this current work, films between 20 nm and $15 \mu\text{m}$ have been produced, the latter at relatively high rates of deposition ($3 \mu\text{m h}$). The previously reported problems⁹ associated with depositing thicker films were not observed in this study.

Equally in this study, changes in the RF power level did not appear to result in significant optical degradation of the coating. In previous studies^{13,14} the inability to deposit at high rates, and hence thickness, was thought to reflect damage to the films owing to argon-ion bombardment. Such damage was not observed in these studies, as this would have been evident in the color of the films.

Although physical, chemical, and mechanical properties have not been evaluated so far for these films, the implication from the works of Yamada *et al.*,¹² Ochiai *et al.*,¹³ and Hishmeh *et al.*¹⁴ is that these ultrathin films are excellent insulating materials, with good hydrophobicity and superior chemical resistance. Ochiai also observed that the contact angle was 100° at room temperature, similar

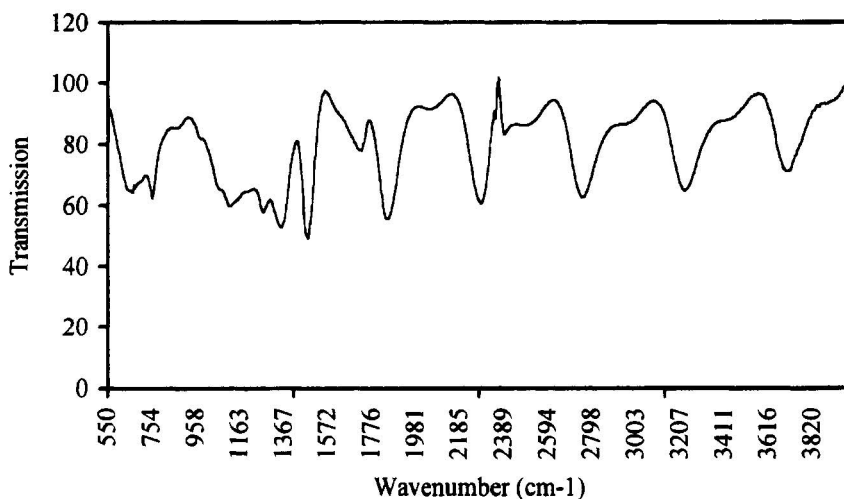


Figure 19.3. IR reflectance spectrum of $10 \mu\text{m}$ of PTFE on silicon.

to conventional PTFE, which further confirms that the morphology of this coating would be similar to conventional PTFE.

19.3.2. Deposition of PVDF and FEP Films

The sputter deposition of PVDF and FEP films has not been widely reported in the open literature. In this work, both materials have been studied with films deposited in the thickness range 30 nm to 4 μm . The processing conditions that have been used are summarized in Table 19.1. Generally the films that were formed were adherent, although more prone to degradation during deposition than the PTFE films.

For PVDF it was observed that small changes in power density can lead to a rapid increase in deposition rate. From Table 19.1 it can be seen that increasing the power from 0.18 to 0.3 W/cm^2 increased the rate of deposition by a factor of 2.4 (0.125 to 0.3 $\mu\text{m}/\text{h}$). By comparison, the deposition rate for PTFE varied in a near linear manner with sputtering power density, as can be seen in Figure 19.2, and rates typically eight times higher than for PVDF could be achieved.

The sputter deposition of FEP showed that high rates of deposition are possible at low power (0.55 $\mu\text{m}/\text{h}$ at 0.18 W/cm^2). Thus FEP can be deposited at approximately four times the rate of PVDF at the same power density. High rates of deposition for PVDF onto glass resulted in films with poor adhesion, although similar films deposited onto a metal substrate gave good adhesion. Conversely, for the FEP films low rates of deposition resulted in optical degradation of the films. Clearly, the morphology and structure of the deposited films are a result of a careful balance between the rate of film deposition and growth, the degree of argon-ion bombardment, and the extent of backsputtering that can occur. For PVDF, high rates of deposition can result in insufficient ion bombardment during deposition to ensure good adhesion, while for FEP films at low deposition rates, the increase in argon-ion bombardment, relative to the deposition rate gives rise to color centers and therefore optical degradation of the films.

Hishmeh *et al.*¹⁴ in their study of RF magnetron sputtering of PTFE films reported that the films they produced could be readily damaged by argon-ion bombardment, being reduced to CF- containing groups. Although not observed for PTFE films in this study, such damage could account for the color centers observed in the FEP-deposited films obtained at low deposition rates.

19.4. CONCLUSIONS

The deposition rate of PTFE varied nearly linearly with RF power density. High rates of deposition could be achieved owing to its temperature tolerance allowing higher power densities. The coatings retained PTFE-like properties with

good adhesion. PVDF sputtered at rates that were nonlinear with RF power density, resulting in coatings with variable adhesion. However, at equivalent power densities, PVDF sputtered at about twice the rate of PTFE. FEP sputtered at high rates for low power densities, about four times that of PVDF for the same power density. However, low rates resulted in film degradation as evidenced by film discoloration.

This work has shown that it is possible to deposit a number of fluoropolymer films by RF magnetron sputtering by carefully controlling the rate of deposition to degree of ion bombardment during film formation. Films from 20nm to 15 μ m have been produced that are of high integrity and adherent. The fluoropolymers deposited in this study included PTFE, PVDF, and FEP; of these only PTFE had been extensively studied by RF magnetron sputtering prior to this work.

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