THE PROPERTIES OF FLUOROCARBON FILMS PREPARED BY PLASMA POLYMERIZATION OF 1,3-PERFLUORODIMETHYLCYCLOHEXANE

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ABSTRACT

Plasma polymerization of 1,3-dimethylperfluorocyclohexane in a dynamic magnetron supported plasma polymerization system was studied. Coatings with high content of fluorine could be deposited only at high deposition power, high flow of reactants, and low pressures.

1. INTRODUCTION

The plasma polymerization of organic vapors in a radio-frequency glow discharge has become an important technique for deposition of thin pin-hole-free conformal polymeric films.[1-3] The polymeric films formed in a plasma are highly cross-linked, insoluble, chemically inert, and have the ability to function as a thin dielectric or protective layer. Deposition of fluorocarbon films by plasma polymerization has been reported by several authors.[2,4,5,6] Recently, Yasuda and Hsu[7] reported the use of cyclic fluorocarbons as precursors for the deposition of plasma-polymerized fluorocarbon films.

This work is a study of the deposition parameters and properties of films deposited in a magnetron supported plasma polymerization system from 1,3-perfluorodimethylcyclohexane. The films were characterized using Auger electron spectroscopy, infrared spectroscopy, ellipsometry, and contact angle measurements. Auger electron spectroscopic depth profiles were used to correlate changes in the polymer composition with changes in the deposition conditions. The rates of deposition and their relationships to the changes in the chemical composition were determined at various flow rates and applied power levels.

2. EXPERIMENTAL

Film Deposition

The plasma-polymerized films described in this paper were deposited in a laboratory (46x76cm) vacuum system shown in Figure 1. This system is a small plasma discharge reactor utilizing a continuous flow of the reacting gases and parallel screen electrodes with 30 percent open structure.

The electrodes are capacitively coupled and are supported by magnetron structures to confine the primary glow to a "race track" on the screen surface.

The gases (precursors) to be reacted in the glow discharge were introduced at the top of the bell jar. This eliminated gas phase polymerization that occurred when a precursor was introduced in the vicinity of the electrodes. The precursors and carrier gases were premixed before introduction into the bell jar. The rate of the gas flow into the system, unless specified, was maintained constant for each experiment by adjusting the pumping speed to maintain a specified pressure for a given flow of nitrogen. The pressure in the system was measured using an MKS Baraton capacitive probe which is not sensitive to the composition of the gas mixtures. The relative positions of the gas sources and sinks with respect to the probe and to the discharge area were maintained constant throughout the deposition experiments, as their relative positions were critical for determination of the rates of deposition. To achieve uniform deposition, the substrate was rotated between the electrodes so that the area of interest was exposed only to the vertical bars of the race track.

A 10 kHz power supply giving a power density in the race track region of 0.3-2.5 W/cm^2 was used. Substrates to be coated were placed on a gounded plate and the potential between the electrodes was maintained at approximately 1000V. The power levels during the plasma depositions in this study were measured by the current supplied to the electrodes.

Film Characterization

Ellipsometry was used to determine the thickness and refractive index of plasma-deposited fluorocarbon films. Several authors[8-10] have discussed the theory and experimental technique used in ellipsometry. A commercial ellipsometer (O.C.Rudolph and Sons Incorporated) and a computer program developed by McCrackin[10] were used for calculating thickness and refractive index of the films. The refractive index of the plasma-deposited films was determined only for films thicker than 300A. This value for the refractive index was then used for computing the thickness of the thinner films.

Auger electron spectroscopy (AES) was used to determine the chemical composition of the plasma polymer films. Composition of the bulk of the sample was obtained by ion sputter etching, usually with 1-2 keV Ar ions, to expose a fresh surface. A continuous chemical depth profile was obtained by performing simultaneous ion etch and AES measurements. A multiplexer, which scans preselected peaks repetitively and plots the peak-to-peak magnitude, is used for automatically collecting data. A typical scan over six elements takes on the order of one minute, during which time only about 35Å of material has been removed. Hence, the depth resolution of this technique is quite good. The sputter etch rate is always given in terms of that for Ta_2O_5 under the given etching conditions. However, the actual rate will depend, in general, on the material composition at any given depth of interest.

The reflectance infrared spectra of the polymer films, deposited on gold coated glass substrates, were measured with a Perkin-Elmer Model 457 Spectrophotometer.

The contact angle measurements were made by the sessile drop method at 23°C using an NRL goniometer, assembled by Rame-Hart Incorporated. Twelve test liquids, whose dispersive and polar components are known, were used. The polar and dispersive components of the surface free energy were calculated from the observed values of the contact angles, using the Girifalco-Fowkes-Young-Kaelble geometric mean approximation[11] and the procedure described previously.[12]

3. RESULTS AND DISCUSSION

The molecular composition of plasma-polymerized 1,3-perfluorodimethylcyclohexane (PFDMC) films was determined by using a reflectance infrared technique.[13] The IR spectra of the plasma polymerized PFDMC films were compared with the IR spectra of conventional polytetrafluoroethylene (PTFE)[14-16] and thin films of plasma-polymerized tetrafluoroethylene. Figure 2 shows reflectance IR spectra of bulk PTFE and films prepared by plasma polymerization of PFDMC and TFE in the absence of nitrogen [see below]. The intensity and position of CF_x vibrational modes in conventional PTFE depends on the crystallinity or long range order of the polymer. A vibrational mode at 1200 cm^{-1} is reported to be characteristic of the amorphous state and the 740 cm^{-1} mode is related to the crystallinity or long range order in PTFE.[16] A strong absorption band at 1200 cm^{-1} and a weak band at 740 cm^{-1} was observed in the plasma-polymerized PFDMC which indicated that this film was partially ordered but also contained significant amounts of amorphous fluoropolymer. The plasma-deposited TFE absorption bands at 1200 cm^{-1} and 740 cm^{-1} are weak which indicates a loss of fluorine and also that the film has less order than plasma-deposited PFDMC. Plasma-polymerized films of PFDMC and TFE both show a broad hydroxyl mode at 3200 cm^{-1} and a broad carbonyl mode at 1700 cm^{-1}.

As seen from Figure 3, addition of nitrogen to the glow discharge chamber reduced the intensity of CF_2 and CF modes at 1200 and 740 cm^{-1} and increased the intensity of hydroxyl or amine modes at 3200 cm^{-1} and carbonyl or amide modes at 1680 cm^{-1}. A nitrile mode at 2190 cm^{-1} was also observed for high N_2/PFDMC ratios in the glow discharge chamber. The intensities of polar groups such as hydroxyl, carbonyl, amide, and nitrile were greatly reduced when argon was used as carrier gas. In general, the polar groups increased with increasing N_2/PFDMC ratio in the reacting mixture.

The surface free energy of these films depends on their fluorine, nitrogen, and oxygen content. Figures 4 and 5 show the polar and dispersive components of the surface energy (γ_s^p and γ_s^d) as a function of the AES carbon/fluorine ratio and as a function of the sum of the AES atomic percent of nitrogen and oxygen at the surface. The dispersive contribution of the surface free energy was found to depend on the concentration of surface fluorine, whereas the polar contribution increased with the surface concentration of nitrogen and oxygen. The small amount of oxygen (<2%) observed could be due to the reaction, with atmospheric oxygen, of the free radicals in the coatings after their removal from the deposition chamber.

The deposition rates were determined as a function of the initial equilibrium pressure (IEP) in the system before the initiation of the glow. When this pressure was changed, it was done by changing the flow of the reactants into the system. The initial pressure of the chamber decreased

as the glow started and usually reached an equilibrium of 50-70 percent of the initial value within 30 seconds. When films were made from nitrogen/PFDMC mixtures, the partial pressure of nitrogen was equal to that of PFDMC. The rate of deposition of the film (A/min) was determined at currents of 300 and 500 ma, and is shown in Figure 6. The solid and dashed lines represent the deposition rates of pure PFDMC and PFDMC/nitrogen mixtures, respectively. The deposition rate is linear at low pressures of PFDMC, while a limiting value is reached at high pressures. The value of the IEP of PFDMC at which the rate of deposition reached its limiting value depends upon the deposition power and presence of nitrogen in the system. For a given power level, the deposition rate was higher when nitrogen was present. The increase in the deposition rate caused by nitrogen was more pronounced at the higher power level (500 ma). The deposition rate for various IEP of gaseous reactants was also determined as a function of power level and is shown in Figure 7. The rate of deposition varied linearly with applied power.

The kinetics of the deposition, in a dynamic glow discharge system, is a complicated function of the molecular structure of the reactants, distribution of electric field, and residence time of the reactants in the glow zone. The kinetics of deposition can be explained using the simplified gas kinetics of highly reactive gaseous reactants.[17,18]

The effect of power in the glow is to generate reactive species, and their concentration, at constant IEP and flow is proportional to the applied power and is limited by the availability of the precursor. The film deposition rates seem to be governed by competition of the unimolecular reaction between radical and substrate with reactions involving bimolecular removal of radicals from the deposition zone.

Two separate regimes can be identified. In the first regime, the deposition rate is limited by the decomposition rate of the precursor and diffusion rate of the reactants into the glow region. In this regime, which we call starved, the IEP is low enough and the corresponding mean free path and velocity of the radicals are high enough for them to reach the substrate before colliding with molecules of precursor or each other. The unimolecular reaction between radicals and substrate prevails and the deposition rate is proportional to IEP of the precursor.

The second regime, which we call saturated, starts where the initial pressure of the precursor increases to the point where more precursor diffuses into the glow region than can be fragmented and polymerized in a given time by the available power, or the mean free path of the radicals is low enough so that they collide and react with each other. In this regime, bimolecular reaction between radicals is favored and the rate of deposition becomes independent of the precursor pressure and reaches a limiting value dependent upon applied power.

The presence of nitrogen increases the deposition rate and moves the entire system toward the starved condition. Figure 8 shows that some of the nitrogen gets incorporated into the coating; however, this cannot account for the increase in the deposition rate. While the mechanism of deposition in the presence of nitrogen is not clear, it is most probable that the presence of nitrogen inhibits the bimolecular recombination of radicals in the glow region. The above analysis is supported by a comparison of the amount of fluorine incorporated into the coating for

various deposition conditions.

The AES atomic ratio of carbon to fluorine, as a function of IEP at two power levels, is shown in Figure 9. The degree of incorporation of fluorine into the coatings depends linearly upon the IEP of PFDMC and nitrogen, and power level. The incorporation of fluorine in the film increased with the addition of nitrogen into the glow discharge chamber. The highest fluorine concentration was obtained at or below 10 µm of initial equilibrium pressure of PFDMC. At this pressure, C/F ratios become independent of power and the presence of nitrogen. As the IEP is raised above 10 µm, the fluorine concentration decreases and reaches a constant (lower) value at IEP of PFDMC greater than 40 µm.

The chemical composition of the plasma-deposited PFDMC films was correlated with the measured refractive index. Figure 10 shows that the refractive indices of the deposit depend on the amount of fluorine in the film, irrespective of deposition parameters. As more fluorine is incorporated into the film, the refractive index increases and approaches a value close to that of Teflon® (1.8).

The incorporation of a high concentration of fluorine in the plasma-polymerized films at a reasonable deposition rate is desirable for a useful fluorocarbon film. In order to determine the optimum deposition rate for a desirable plasma-deposited fluorocarbon film, we plotted the AES C/F ratio as a function of the deposition rate for all the plasma-deposited PFDMC films. This is shown in Figure 11.

The initial part of the curve corresponds to the starved condition where the unimolecular reaction between radicals and substrate predominates. The steeper part of the curve corresponds to the saturated condition when the reactive species have longer residence time in the glow, leading to bimolecular recombination and further fragmentation. The deposition rates and compositions of the coatings are determined by complex bimolecular reactions. This may explain the spread of the data in this part of the curve. Films with higher fluorine content are deposited in the starved regime which can be extended to higher deposition rates as shown by the dashed line in Figure 11. This was achieved by increasing the throughput of the reactants through the glow region. The throughput was increased by simultaneously increasing the pumping rate and flow rates. As a result, the IEP of reactants remains the same but their residence time in the glow is shorter.

4. CONCLUSIONS

The following conclusions can be drawn from these results:

a) 1,3-Perfluorodimethylcyclohexane plasma-polymerized in a dynamic magnetron glow discharge system, under certain conditions, deposited a highly cross-linked fluorocarbon film with low surface energy.

b) The rate of deposition was limited by the initial equilibrium pressure of the PFDMC in the chamber and the throughput rate of the gas reactants, and depended linearly on applied power.

c) Two deposition regimes can be identified -- one "starved" in which the deposition rate is limited by the availability of the precursor and its diffusion rate into the glow region, and the second "saturated" in which the deposition rate is limited by the decomposition

rate of the precursor.

d) When nitrogen is present during the deposition, it is incorporated into the coating and moves the system toward a starved condition.

e) The coatings deposited in the starved region are highly cross-linked and have low surface energy.

f) The dispersive component of the surface free energy is related to fluorine content and the polar component relates to the amount of nitrogen and oxygen on the surface.

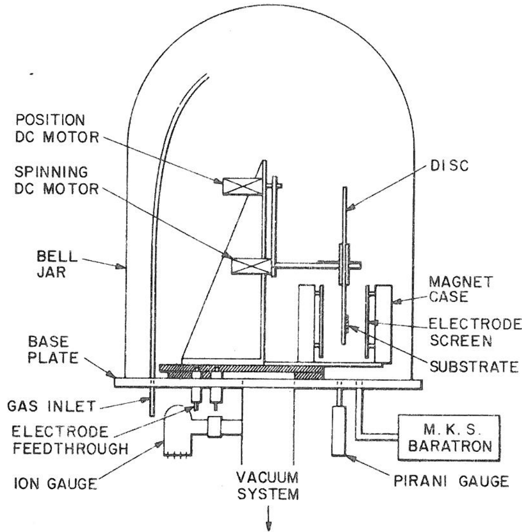

Fig. 1. Deposition system.

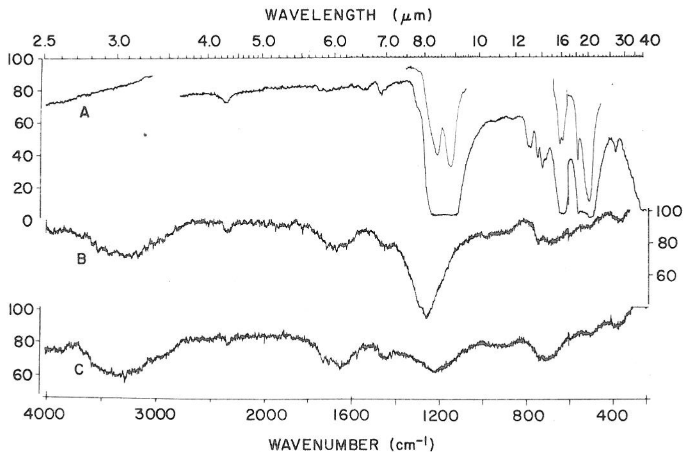

Fig. 2. Reflectance IR spectra of (A) conventional polytetrafluoroethylene, (B) film plasma-polymerized from PFDMC, (C) film plasma-polymerized from tetrafluoroethylene.

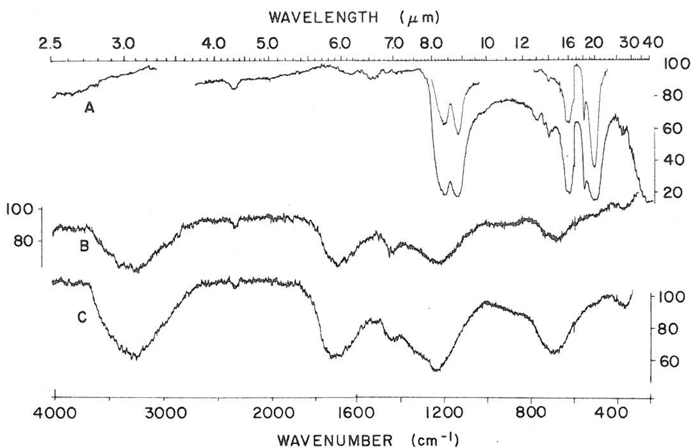

Fig. 3. Reflectance IR spectra of (A) conventional polytetrafluoroethylene, (B) film plasma-polymerized from nitrogen and PFDMC (10μ each, 300 mA), (C) film plasma-polymerized from nitrogen and tetrafluoroethylene (10μ each, 300 mA).

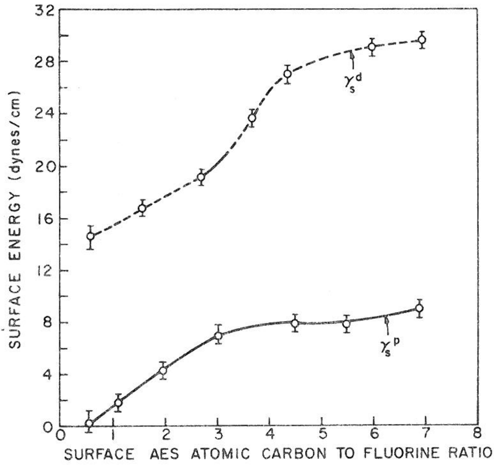

Fig. 4. Variation of γ_s^p and γ_s^d as a function of AES carbon/fluorine ratio.

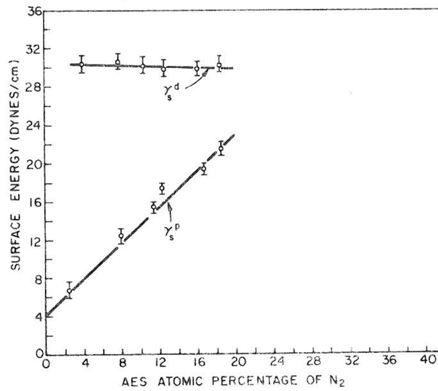

Fig. 5. Variation of γ_s^p and γ_s^d as a function of the sum of AES nitrogen and oxygen concentration on the coating surface.

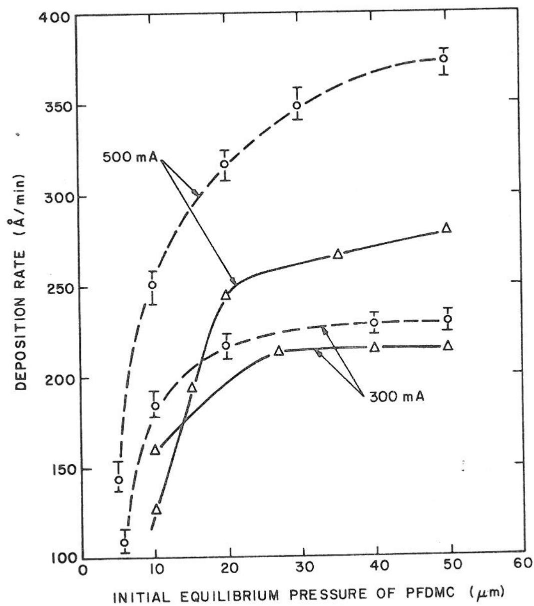

Fig. 6. Deposition rate of coatings made from PFDMC at a function of IEP for various power levels.

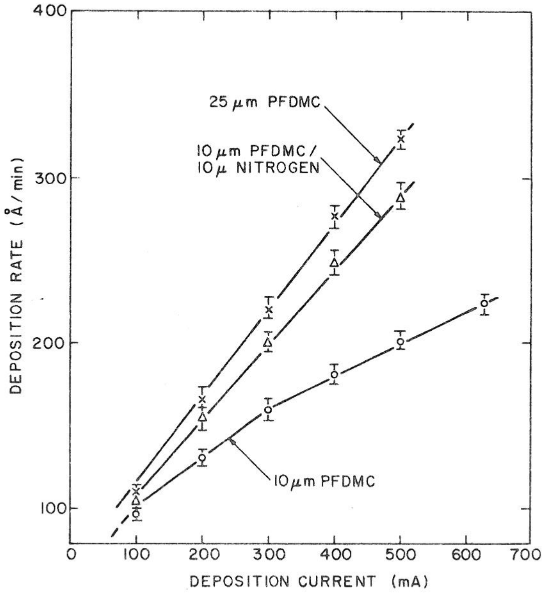

Fig. 7. Deposition rate of coatings made from PFDMC as a function of deposition current.

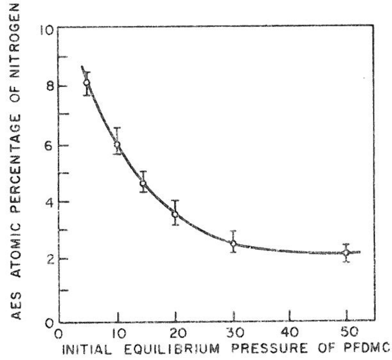

Fig. 8. Nitrogen concentration in the coating as a function of IEP of PFDMC and nitrogen.

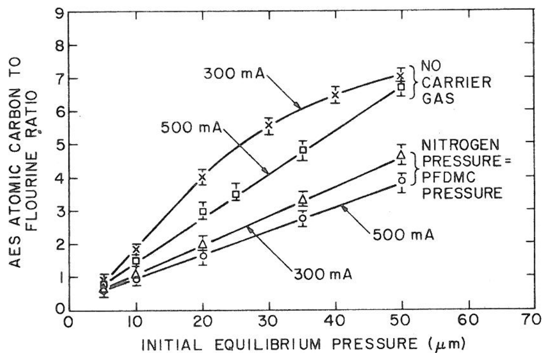

Fig. 9. Carbon to fluorine ratio in the coating as a function of IEP of PFDMC and nitrogen.

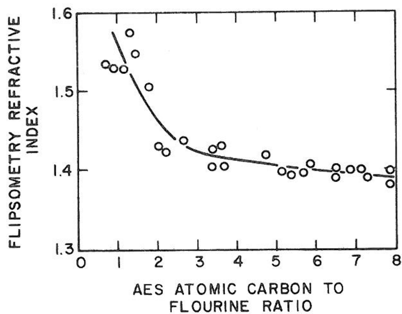

Fig. 10. The refractive index of the coating as a function of fluorine content in the film.

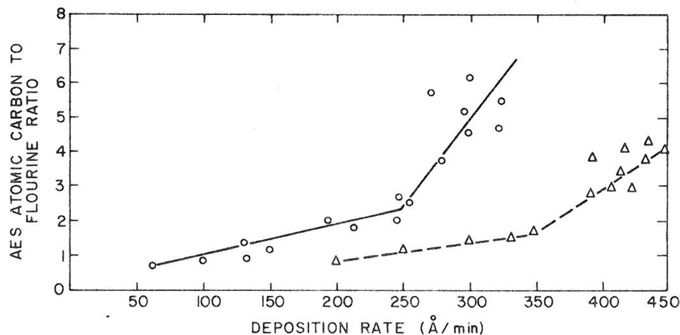

Fig. 11. Carbon to fluorine ratio in the film as a function of the deposition rate for two throughputs of the reactants through the glow region.

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