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ION BEAM SPUTTERING OF FLUOROPOLYMERS

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ABSTRACT

Etching and deposition of fluoropolymers are of considerable industrial interest for applications dealing with adhesion, chemical inertness, hydrophobicity, and dielectric properties. This paper describes ion beam sputter processing rates as well as pertinent characteristics of etched targets and films. An argon ion beam source was used to sputter etch and deposit the fluoropolymers PTFE, FEP, and CTFE. Ion beam energy, current density, and target temperature were varied to examine effects on etch and deposition rates. The ion etched fluoropolymers yield cone or spire-like surface structures which vary depending upon the type of polymer, ion beam power density, etch time, and target temperature. Also presented are sputter target and film characteristics which were documented by spectral transmittance measurements, X-ray diffraction, ESCA, and SEM photomicrographs.

INTRODUCTION

Over the last 10 years there has been significant interest in the sputtering of fluoropolymers. Most ion sputter etched fluoropolymer surfaces have cone or spire-like features which may find application in adhesive bonding as well as medical technologies¹⁻⁷. Deposition of fluoropolymer films proceeds at high rates which may satisfy industrial requirements for dielectrics, encapsulants for moisture sensitive components, and chemically inert-low friction surfaces^{8,9,10}.

Several authors have documented the crystallinity, surface chemistry, and surface morphology of sputtered PTFE targets using RF or ion beam systems^{1,3,9}. Previous investigations have also reported the optical, dielectric, crystalline, and mechanical properties of PTFE films^{2,9,10,11}. Very little information is available in the literature concerning sputter deposition and etch rates of fluoropolymers as well as the rates at which the ion etched surface texture develops.

This paper presents the influence of polymer temperature, ion current density, ion energy, and ion dose on etch and deposition rates of PTFE and FEP. Some of the morphological, crystalline, optical, chemical, and frictional properties of the sputtered materials are also reported.

APPARATUS AND PROCEDURE

An argon ion source, developed from electric propulsion technology programs, was used for the polymer etching and deposition experiments. Hollow cathodes were employed for the discharge chamber ionization and ion beam neutralization functions. Beam extraction was accomplished by a dish, two-grid ion optics system whose extraction diameter was 30 cm¹². In order to insure substrate cleanliness and also present a small view factor of the discharge chamber anode to the sputtered fluoropolymer flux, the extraction area was masked to either 10 or 15 cm diameter for ion etching and polymer

deposition. The vacuum chamber was 1.5 m diameter by 7.3 m long. Tests were conducted at a pressure between 7 and 12×10^{-3} Pa (5 to 9×10^{-5} torr).

Fluoropolymers evaluated were polytetrafluoroethylene (PTFE), fluorinated ethylene-propylene (FEP), polychlorotrifluoroethylene (CTFE), and perfluoroalkoxy (PFA). Ion incidence was normal to polymer target surfaces for etch rate determination. Polymers were placed behind a 0.03-cm thick tantalum shield with an opening of either 0.25 or 0.64 cm² to control the area of ion impingement. Etch rates were calculated from weight loss and etch time data. Micrometer measurements were periodically made to confirm the weight loss data. A biased planar probe was used to determine ion current density at the target location. The target reference temperature was measured by imbedding a thermocouple 0.07 cm under the polymer surface. The thermocouple was placed laterally 3 mm from the region of ion etching. Because significant temperature gradients existed across the fluoropolymer targets, the reference temperature measurement cannot be considered an average bulk temperature but rather an indication of thermal trends. Water cooled and actively heated polymer targets were used to determine the dependence of etch rate on target reference temperature. A thin layer of vacuum grease was used to thermally couple the polymer target to its water-cooled holder.

Fluoropolymer deposition was performed by 45 degree ion incidence upon a target whose dimensions were 12×15×0.6 cm. The target and substrate were parallel and generally separated by 14 cm. Films were deposited on glass plates which were partially masked by tape for film thickness determination using an interference microscope.

Friction measurements were made by sliding samples of polished stainless steel (0.010 gm, 8 mm² area) down an inclined fluoropolymer coated glass plate. Spectral transmittance measurements were made between wavelengths of 0.33 and 0.60 μm using an integrating sphere described in reference 13.

X-ray diffraction patterns of the various polymer forms were obtained using nickel filtered copper radiation excited by 40 KeV electrons. Polymer films were prepared for these measurements either by scraping the film from a glass plate or by chemically etching away a polycarbonate substrate.

ESCA (Electron Spectroscopy for Chemical Analysis) yields information on surface molecular composition by kinetic energy spectroscopy of electrons ejected from atoms irradiated with K_{α} X-rays^{14, 15}. The diagnostic technique reflected surface chemistry to depths of 0.002 to 0.005 μm ^{14, 15}.

RESULTS AND DISCUSSION

Ion Beam Etching of Fluoropolymers

PTFE and FEP exhibit extremely high sputter etch rates with resulting cone or spire-like surface textures. These characteristics are sensitive to ion beam parameters and target temperature.

Figure 1 shows the PTFE sputter etch rates as a function of argon ion energy for various ion current densities and target temperatures. Etch rates of PTFE, at constant ion current density, increased by about a factor of ten as the ion energy was varied from 250 to 1000 eV. The data of figure 1 exhibit etch rates from 3 to 1700 $\mu\text{m/hr}$ and sputter yields ranging from 5 to over 100 CF_2 groups per incident ion. Mathias and Miller¹⁶ have reported that the main gaseous product of PTFE, thermally decomposed in a RF plasma, is C_2F_4 which was probably the result of combination of CF_2 radicals.

From figure 1, it is also apparent that the sputter etch rates of FEP, CTFE, and PTFE are approximately the same at 750 eV ion energy and 0.5 ma/cm^2 .

The etch rate of PTFE at 1 KeV is not linearly related to the ion current density. The nonlinearity of etch rate with current density was primarily due to substantial increases in the temperature of the radiation cooled targets as the beam power increased. The polymers were difficult to water cool due to

their extremely low thermal conductivities. At a beam power density of 1.25 w/cm^2 the spire-like surface texture no longer existed and there was evidence of local melting. The mechanism for the high etch rates at power densities greater than 1 w/cm^2 was probably local thermal decomposition and subsequent scission fragment evaporation.

The PTFE etch rate for radiation cooled targets ($\approx 3 \text{ mm}$ thick) may be roughly correlated with beam power density⁵ such that

$$R \approx 1000 P^{1.4}$$

where

R is the PTFE etch rate, $\mu\text{m/hr}$

P is the ion beam power density in w/cm^2

The etch rate is apparently not strongly affected by the development of surface texture. For example, at a beam power density of 0.2 w/cm^2 the etch rate was $35 \mu\text{m/hr}$ after 10 minutes of sputtering and rose to $50 \mu\text{m/hr}$ average etch rate after 200 minutes. The difference in etch rates was probably due to an increase in target temperature.

When the beam power density was less than 1 w/cm^2 and target temperatures less than 200°C , the "cone" peak heights were approximately 10 to 20 percent of the PTFE (or FEP) mean etch depth. At low ion beam power densities (fig. 2(b)) the surface texture was composed of high density spire-like features while at higher beam power densities between 0.3 and 1 w/cm^2 , truncated cone features were apparent (fig. 2(c) and (d)).

Also examined was the influence of target temperature on the PTFE etch rate at fixed ion beam parameters (750 eV , 0.5 ma/cm^2). The etch rate increased from $180 \mu\text{m/hr}$ to $640 \mu\text{m/hr}$ as the target reference temperature increased from 200° to 280°C . At the 280°C condition, photomicrographs indicated evidence of local melting. The ion etch rates tended to asymptote to

approximately 100 $\mu\text{m/hr}$ at target temperatures below 150 $^{\circ}\text{C}$. This implies that physical sputtering probably dominates over thermal processes at target reference temperatures less than 150 $^{\circ}\text{C}$.

ESCA spectra of ion etched PTFE were obtained to determine if significant changes in surface chemistry occurred with variations in ion beam parameters. Shown in figure 2 are the $\text{C}_{1\text{S}}$ ESCA spectra and corresponding photomicrographs of PTFE before and after exposure to the various ion doses shown in figure. The fluorocarbon peak is located at a binding energy of 296 eV (uncorrected for charging) and a hydrocarbon peak is centered at 289 eV. The control or unetched PTFE sample may have been contaminated by absorbed hydrocarbons as indicated by the peak at 289 eV. Qualitative inspection of the $\text{C}_{1\text{S}}$ spectra of the ion etched specimens indicate exposed fluoropolymer in all cases and a low intensity or nonexistent hydrocarbon peak of 289 eV. The $\text{C}_{1\text{S}}$ fluorocarbon peak, however, becomes broader after ion beam etching indicating the possible existence of unresolved peaks in the neighborhood of 296 eV³.

These measurements of the ion etched surfaces still reflect a rich composition of fluorocarbons extending 0.002 to 0.005 μm into the polymer. The ion etched PTFE surface composition was unlike surfaces treated with Na/NH_3 chemical etches where the fluorocarbon ESCA peak nearly disappears and hydrocarbon, carbonyl, and carboxyl species dominate¹⁴. Higher resolution instrumentation and curve fitting techniques, however, are required to better quantify the contribution of hydrocarbons and other molecular species to the surface chemistry of ion beam etched PTFE.

From an applications standpoint, thin polymer sheets may be ion beam textured and subsequently epoxy bonded to surfaces for moisture protection. Textured polymer sheets may be bonded to metals for load bearing surfaces. Because local melting and mechanical distortion of the ion etched polymer are dependent upon beam power density and target thickness, tests were conducted

to determine the maximum beam power density for a given PTFE target thickness. No distortion or local melting of the ion etched, radiation cooled PTFE targets occurred if

$$P < t^{0.37}$$

where

t is the PTFE thickness, cm

$$0.6 > t > 0.002 \text{ cm}$$

P is the ion beam power density, w/cm^2

FEP, CTFE, and PFA may be safely textured at ion beam power densities approximately 50 percent lower than that of the PTFE limits.

The surface textures of ion beam etched fluoropolymers FEP, CTFE, and PFA have also been shown to be suitable for high strength adhesive bonding¹⁷.

Ion Beam Sputter Deposited Fluoropolymer Films

FEP and PTFE films were ion beam sputter deposited to obtain deposition rate information as well as preliminary data relative to optical, crystalline, and friction properties of the films. Figure 3 indicates there is very little difference between the sputter deposition rates of FEP and PTFE. Rates vary from 0.3 to 16 $\mu\text{m/hr}$ as the beam power density increased by a factor of eight. The shape function of the deposition rate curve (fig. 3) is nearly identical to the etch rate curve (fig. 1) for an ion current density of 0.5 ma/cm^2 . Thus there exists a linear relationship between etch and deposition rates of PTFE for ion current densities of approximately 0.5 ma/cm^2 and ion energies ranging up to 1 KeV. Thus, for these conditions there was no substantial loss of sputter products in the form of noncondensables as beam parameters and target temperature were increased.

Optical and frictional properties of the sputter deposited FEP films are not severely affected over a wide range of deposition conditions. Conditions tested

included ion energies from 500 to 2000 eV (at 0.6 ma/cm^2), film thickness from 1.3 to $40 \text{ }\mu\text{m}$, and deposition rates from 1.5 to $20 \text{ }\mu\text{m/hr}$. Over this range of parameters, the spectral transmission (at $0.60 \text{ }\mu\text{m}$) of the films deposited on microscope slides varied only from 0.93 to 0.95. The static and kinetic coefficients of friction ranged from 0.3 to 0.4 and 0.2 to 0.3, respectively.

It was also found that the spectral transmittance of films from PTFE and FEP targets did not differ by more than 1 percent over a wavelength range from 0.33 to $0.60 \text{ }\mu\text{m}$. In this case polymer films were $1.2 \text{ }\mu\text{m}$ thick deposited at rates between 0.25 and $1 \text{ }\mu\text{m/hr}$.

At $1.2 \text{ }\mu\text{m}$ FEP film was ion beam sputter deposited on 0.8 mm fused silica to compare optical performance with RF sputtered PTFE films¹¹. The spectral transmittance of the FEP-silica was 0.81, 0.91, and 0.95 at wavelengths of 0.33, 0.40, and $0.60 \text{ }\mu\text{m}$, respectively. Film transmittance of the ion beam sputtered FEP was considerably higher than RF sputtered PTFE films previously reported¹¹. Films deposited from FEP and PTFE targets develop a light yellow color if the film thickness exceeds about $5 \text{ }\mu\text{m}$. Thus, thicker films will probably yield lower optical transmission the the UV and blue wavelengths.

X-ray diffraction analysis, using nickel filtered copper radiation, was performed on FEP and PTFE in bulk, ion etched, and deposited film forms to qualitatively determine if there was a regularly ordered arrangement of atoms in the ion etched and film forms. Deposited films were clear with a thickness of 1.5 to $3 \text{ }\mu\text{m}$. Ion etch rates were approximately $300 \text{ }\mu\text{m/hr}$; deposition rates were $2.5 \text{ }\mu\text{m/hr}$.

Similar diffraction patterns were obtained for bulk, ion etch and film forms of PTFE and FEP. Along with amorphous structure, dominant diffraction peaks were observed for $2\theta = 18, 32, 37$, and 42 degrees where θ

is the Bragg diffraction angle. This result indicates the quasi-crystallinity of both ion beam etched targets and deposited polymer films.

CONCLUDING REMARKS

Unique characteristics of ion etched fluoropolymers are the extremely high etch rates and the resulting surface texture due to selective ion etching. The etch rates of PTFE ranged from 3 to 1700 $\mu\text{m/hr}$ depending on ion beam power density and target temperature. The polymers FEP and CTFE had ion etch rates comparable to PTFE. Local vaporization of thermal decomposition fragments was probably the dominant mass loss mechanism for polymer targets whose bulk temperatures exceeded 200⁰ C. ESCA examination of ion etched targets indicated a surface still rich in fluorocarbon composition.

At low ion beam power densities the surface texture was composed of high density spire-like features while at higher beam power densities between 0.3 and 1 w/cm^2 , truncated cone structures were observed. The texture or "cone" peak height was approximately 10 to 20 percent of the PTFE (or FEP) mean etch depth. Polymers PTFE, FEP, CTFE, and PFA exhibit rough surface textures suitable for adhesive bonding applications.

Deposition rates of PTFE and FEP on the order of 10 $\mu\text{m/hr}$ are readily attainable. One micrometer thick sputter deposited FEP films on quartz exhibited spectral transmittance values of 0.81 and 0.95 at wavelengths of 0.33 and 0.60 μm , respectively. One micrometer films deposited from FEP or PTFE targets had nearly identical optical transmittance values over the visible region. Ion etched and sputter deposited film forms of FEP and PTFE are quasi-crystalline and yield X-ray diffraction patterns similar to the unetched polymers.

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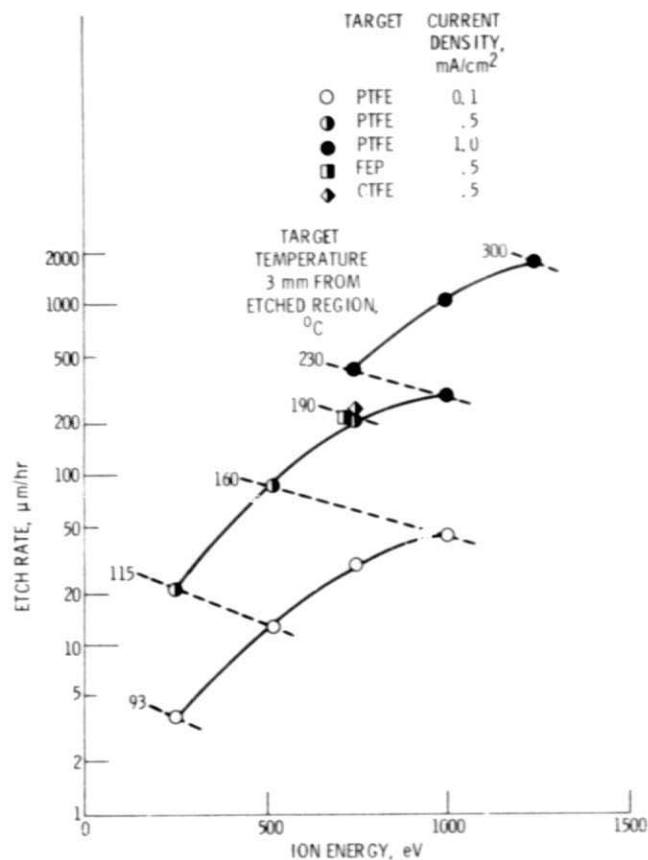


Figure 1. - Ion beam sputter etch rate of fluoropolymers as a function of argon ion energy. Targets were radiation cooled.

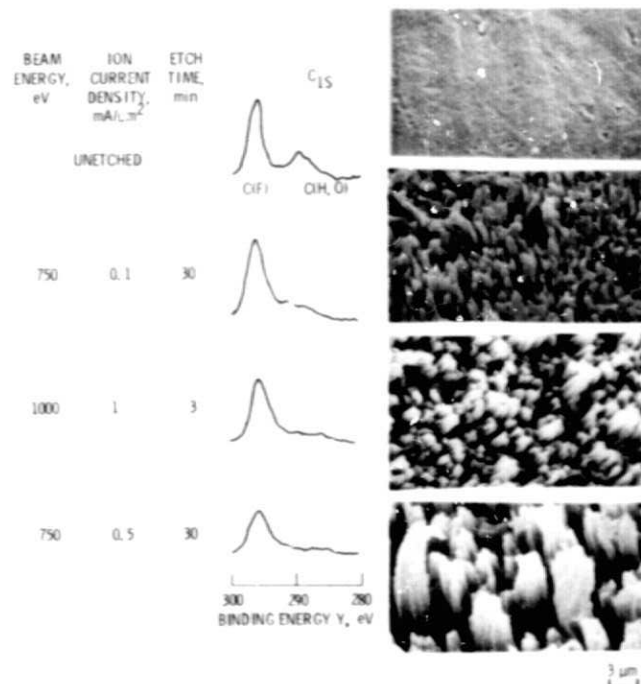


Figure 2. - ESCA C_{1s} spectra and corresponding photomicrographs of PTFE before and after ion beam etching. Vertical scales are arbitrary.

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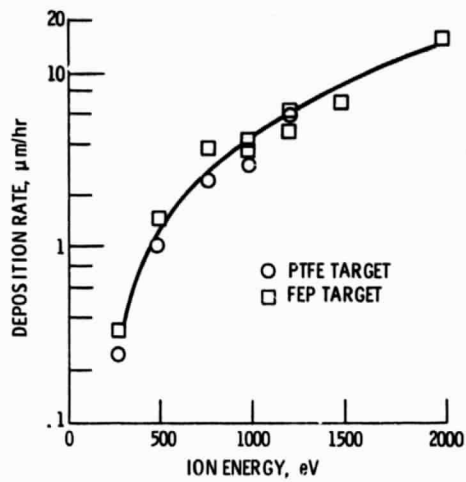


Figure 3. - Fluoropolymer deposition rate as a function of ion energy. Ion current density at target $\approx 0.6 \text{ mA/cm}^2$. Target to substrate separation, 14 cm.