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Electrical Properties and Temperature-Humidity Studies of Fluorocarbon Films Deposited from Pentafluoroethane/Argon Plasmas

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Fluorocarbon films were deposited from pentafluoroethane/argon plasmas in a parallel plate reactor at operating pressures of 0.75 and 1 Torr, substrate temperatures of 120, 180, and 240°C, and applied powers between 10 and 30 W. These films were subjected to an 85°C and 85% relative humidity environment for 100 h to assess reliability. Infrared spectroscopy showed no change in the bulk structure and composition of the deposited films after temperature-humidity exposure. Also, no OH related peaks were detected in the infrared spectrum, suggesting negligible moisture absorption. Indeed, moisture absorption studies showed less than 0.15 wt % increase for the investigated deposition conditions, as measured by a quartz crystal microbalance. Furthermore, humidity cycling studies indicated no chemisorption of water by the deposited films. Capacitance measurements of the fluorocarbon films yielded a dielectric constant ranging between 2.23 and 2.55 and a loss tangent on the order of 10^{-2}. The dielectric constant increased with an increase in deposition temperature and a decrease in operating pressure. The dielectric constant of the fluorocarbon films did not change after exposure to the 85°C/85% relative humidity environment, further confirming the IR and moisture absorption results. However, X-ray photoelectron spectroscopy (XPS) of the fluorocarbon films indicated a decrease in the F/C ratio and an increase in the O/C ratio after temperature-humidity exposure, which suggests that defluorination and oxidation occur primarily in the top few monolayers of the deposited films. C 1s spectral analysis indicated a decrease in the relative concentrations of CF_3, CF_2, CF, and C-CF_x moieties and a dramatic increase in the C-C/C-H concentrations. These changes were attributed to the formation of a thin layer of low molecular weight oxidized material, which could be dissolved by rinsing the film in an ethanol ultrasonic bath.
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During the past decade, there has been extensive research on plasma deposited fluorocarbons for use as interlevel dielectrics in future integrated circuits (IC).[1,2] Although fluorocarbons have desirable properties such as low dielectric constant and loss, low moisture absorption, and high chemical inertness, their reliability in harsh environments is still a matter of concern. Very few studies have been performed that investigate the effect of temperature and humidity on the structure and properties of these films. It is important that these materials retain their chemical structure and properties (electrical, mechanical, and thermal) when exposed to accelerated temperature humidity reliability tests. Previous studies[3] on fluorocarbon films deposited from C_3F_6 plasma have investigated the discharge power dependence of the oxidation rate under an accelerated testing condition of 65°C/85% relative humidity. X-ray photoelectron spectroscopy (XPS) of the deposited films indicated both defluorination and oxidation of the films on temperature-humidity exposure. However, these studies only pertain to chemical changes that occur in the top few monolayers of the deposited fluorocarbon films. Also, no experiments were performed to elucidate the effect of accelerated testing conditions on the bulk chemical structure, electrical properties, and moisture absorption of the deposited films.

In this paper, XPS and Fourier transform infrared spectroscopy (FTIR) were used to characterize changes in the surface and bulk chemical structure of the deposited films. Metal-insulator-metal capacitors were fabricated in order to investigate the effect of temperature and humidity on the dielectric constant of the deposited films. A quartz crystal microbalance was used to quantify the moisture absorbed by the fluorocarbon films with humidity. Furthermore, the sample was subjected to humidity cycling in order to determine water chemisorption.

Experimental

Fluorocarbon deposition studies were carried out in a radio frequency (rf) parallel plate reactor using pentafluoroethane/argon mixtures. Details of the reactor setup and operation are given elsewhere.[4] The powered and grounded electrodes were 4 cm stainless steel disks and were separated by 2.9 cm. Substrates for fluorocarbon deposition were placed on top of the grounded electrode, which was heated independently during deposition and its temperature controlled by a Syskon RKC temperature controller. Depositions were carried out at substrate temperatures of 120, 180, and 240°C and operating pressures of 0.75 and 1 Torr. The rf power for depositions ranged between 10 and 30 W.

Reliability studies were carried out in a temperature-humidity chamber at a temperature of 85°C and a relative humidity of 85% for 100 h. Temperature-humidity studies were chosen as the most appropriate form of failure of the fluorocarbon films because of concerns about defluorination and oxidation. Deposited films were initially characterized using IR, XPS, and dielectric constant measurements before being subjected to temperature-humidity studies.

Infrared spectra of the deposited films were carried out in reflection mode at a grazing angle of 70° using a Nicolet Magna-IR Fourier transform infrared spectrometer. All spectra were recorded at a resolution of 4 cm^{-1} and averaged over 512 scans. Spectra of the fluorocarbon films were taken before and after temperature-humidity studies. Films were deposited onto metallized silicon substrates that had approximately 300 nm of Ti/Cu/Ti. The film thickness, as measured with a Dektak profilometer, ranged between 1 and 2 μm.

XPS was used to obtain the chemical composition and bonding configurations of the deposited films. Typically, thin films ranging from 10-20 nm deposited on titanium were used for analysis in order to reduce differential charging of the sample. All spectra were collected with a PHI model 1600 spectrometer using monochromatized Al Kα X-rays. An electron pass energy of 11.75 eV was used for high resolution analysis of the spectral regions of interest which included C 1s, F 1s, O 1s, N 1s, and Ti 2p. The binding energy shifts were corrected for charging by fixing the highest binding energy C 1s peak (corresponding to CF_3) at 293.2 eV. Each spectral region was deconvoluted into individual peaks assuming all peaks to be perfectly Gaussian and to have the same full width half maximum (fwhm). XPS spectra were taken for samples (*i*) as deposited, (*ii*) after temperature-humidity studies, and (*iii*) after temperature-

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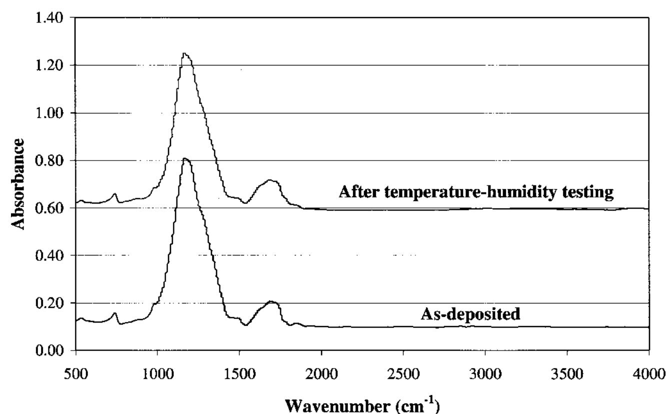

Figure 1. Infrared spectrum of a fluorocarbon film (a) as deposited and (b) after temperature-humidity exposure at 85°C/85% RH for 100 h. The deposition conditions were 10 W, 120°C, and 1 Torr.

humidity exposure followed by a 5 min rinse in an ethanol ultrasonic bath.

Moisture absorption measurements were recorded using a quartz crystal microbalance. Initially, the resonant frequency of the unloaded quartz crystal (no film) was noted. Fluorocarbon films with thicknesses in the range of 0.8 to 1.5 μm were deposited onto the quartz crystal. The difference in the resonant frequencies of the loaded (after deposition) and unloaded quartz crystal could be correlated to the mass of the deposited film. This quartz crystal was placed in a specially designed leak proof glass cell, which had provisions for dry nitrogen flow [0% relative humidity (RH)] and moist nitrogen. When the glass cell was purged with dry nitrogen, the measured relative humidity in the cell was 0%. This condition is referred to as dry environment in subsequent sections of the paper. The humidity of this cell could be controlled between 20 and 98% within an accuracy of 1%, by bubbling nitrogen through room temperature water and accurately controlling the dew point of the gas by use of a condenser. The change in the steady-state resonant frequency of the quartz crystal was recorded as a function of humidity. Also, humidity cycling was performed in order to determine if moisture was chemisorbed in the films. Typically, the highest humidity utilized for moisture absorption measurements of the deposited films ranged between 93 and 98%. All moisture absorption measurements were performed at room temperature.

Capacitance measurements were recorded on metal-insulator-metal capacitors at 10 kHz in order to obtain the dielectric constant and loss of the deposited films. Films were deposited on metallized silicon substrates while the top metal layer was sputtered through a shadow mask that had circular openings with diameters ranging between 3.5 and 13 mm. Dielectric constants of the deposited samples were measured both before and after temperature-humidity exposure.

Results

Fluorocarbon films deposited from pentafluoroethane/argon plasmas were characterized for their chemical structure and electrical properties before and after temperature-humidity studies.

FTIR studies.—Figure 1 shows a comparison of infrared spectra of a deposited fluorocarbon film before and after temperature-humidity studies. The infrared spectra primarily consist of a broad absorption peak between 1100 and 1400 cm^{-1} corresponding to a random arrangement of saturated fluorocarbon species[5] such as CF_3, CF_2, and CF. The other major peak between 1600 and 1850 cm^{-1} is attributed to unsaturated fluorocarbon species[6] such as -C=CF, -C=CF_2, and -CF=CF_2 and to carbonyl species[7] such as acids (-COOH), esters (-COOR), acid fluorides (-COF), and ketones (-C=O). The oxygenated species arise from postatmospheric oxidation of trapped free radicals and dangling bonds in the deposited films.[8] These dangling bonds are typically unsatisfied chemical bonds, which arise as a result of exposure of the film to ion bombardment and ultraviolet light[9] emitted during plasma-assisted deposition. Thus, the concentration of oxygenated species could be taken as a qualitative measure of the dangling bond concentration in the deposited films. There may also be small concentrations of peroxide groups present in the films due to atmospheric oxidation. However, their IR absorbance is very weak. As shown in Fig. 1, there is no significant change in the intensities of the two major peaks, suggesting that little change occurs in the bulk chemical structure and oxygenated species concentration of the film with temperature-humidity testing. This suggests that the deposited films contain a low concentration of dangling bonds and that most of the dangling bonds reacted with water vapor or oxygen as soon as the film is exposed to atmosphere after deposition. The CH_x concentration in the deposited films is low as indicated by the negligible intensity of a C-H stretch between 2800 and 3100 cm^{-1}. Furthermore, little change is observed in the intensity of the hydrocarbon-related peaks after temperature-humidity exposure as indicated by IR. The intensity of hydrocarbon related peaks is at least two orders of magnitude lower than the major fluorocarbon peak. Also, no peak corresponding to -OH groups in the 3300-3600 cm^{-1} regime is detectable before or after temperature-humidity exposure, suggesting that the fluorocarbon films exhibit low moisture absorption. However, it must be

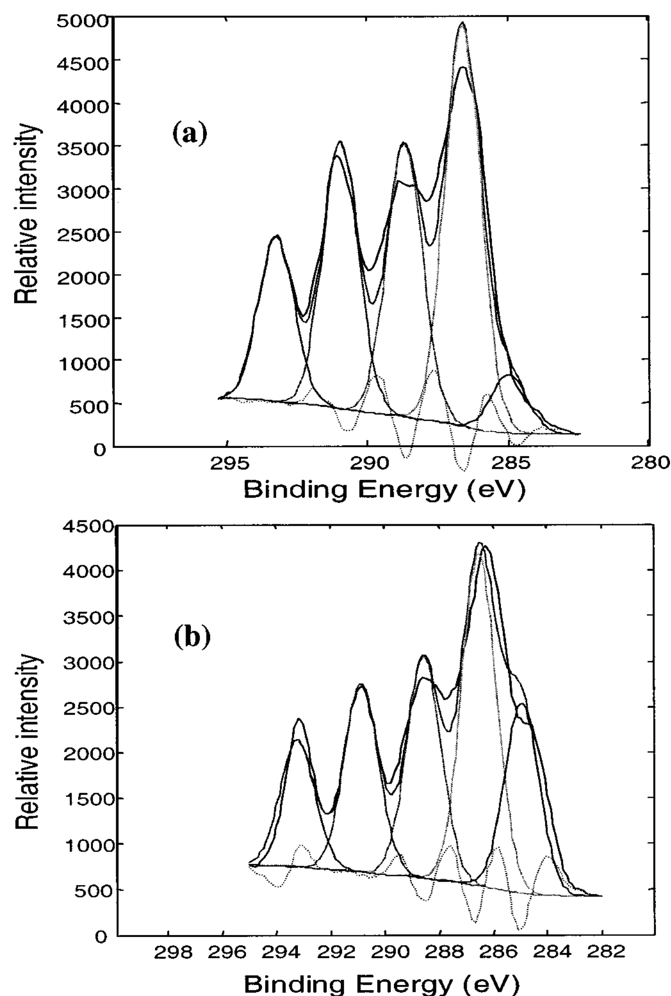

Figure 2. Comparison of XPS C 1s spectra of a fluorocarbon film (a) as deposited and (b) after temperature-humidity exposure at 85°C/85% RH for 100 h. The deposition conditions were 30 W, 180°C, and 1 Torr.

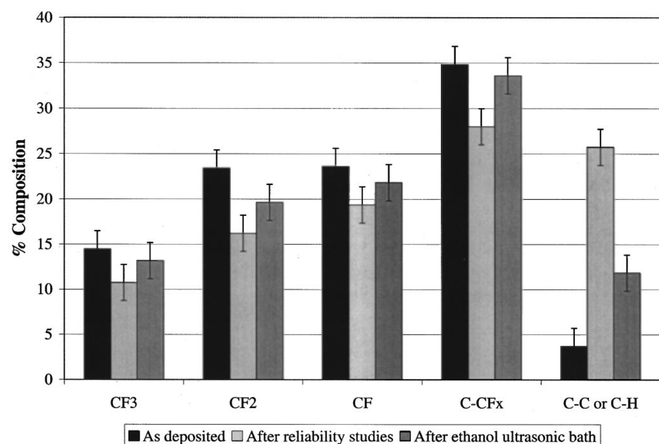

Figure 3. XPS concentrations of CF_3, CF_2, CF, C-CF_x, and C-C of deposited fluorocarbon films (a) as deposited, (b) after temperature-humidity exposure at 85°C/85% RH for 100 h, and (c) after ethanol ultrasonic bath. The deposition conditions were 30 W, 180°C, and 1 Torr.

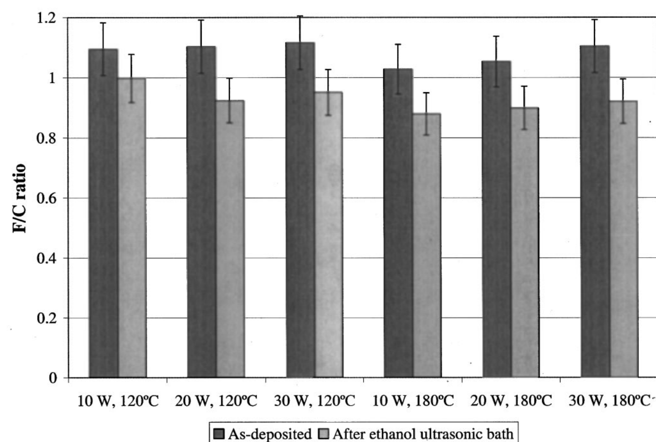

Figure 4. F/C ratio of deposited fluorocarbon films as a function of deposition conditions (a) as deposited and (b) after ethanol ultrasonication for 5 min. Operating pressure: 1 Torr.

noted that the sensitivity of IR to CH_x and OH species is very low and hence, no definite conclusions can be drawn based on IR alone.

XPS studies.—XPS analyses were performed on the deposited films in order to obtain the change in surface chemical composition and bonding configurations upon temperature/humidity exposure. The effect of deposition conditions on the structure and composition of deposited films has already been discussed in our previous publications.[4,8] The fluorine to carbon (F/C) ratio of the films was independent of the applied power within our range of operation and decreased with substrate temperature and operating pressure. The F/C ratio ranged between 0.95-1.15 for all deposition conditions investigated and was based upon the peak areas of the C 1s and F 1s spectra. Figure 2 shows a comparison of the C 1s spectra of deposited films before and after temperature/humidity exposure. Here C 1s peak deconvolution was performed assuming that all carbon was bonded to fluorine. Although some of the carbon is bonded to oxygen, it is very difficult to account for this in the C 1s spectrum deconvolution. Since the O/C ratio was less than 0.03, the above assumption of carbon being bonded only to fluorine is reasonable. As seen in Fig. 2, the C-CF_x concentration is the primary bonding configuration in the deposited films indicating that the films are highly cross-linked. After 85°C/85% humidity exposure, a decrease in the concentration of fluorinated species such as CF_3, CF_2, CF, C-CF_x and a dramatic increase in the C-C/C-H concentrations occur, as indicated in Fig. 3. The film F/C ratio decreases from 0.95-1.15 to 0.80-0.90 indicating surface defluorination while the O/C ratio increases from 0.03 to 0.04 upon temperature/humidity exposure. However, when the films are subjected to an ultrasonic ethanol bath for 5 min, the C-C/C-H concentration decreases drastically suggesting that there may be low molecular weight oxidized carbonaceous material on the film surface, which is soluble in ethanol. Indeed, there is a slight increase in the F/C ratio and a slight decrease in the O/C ratio, indicating the removal of low molecular weight oxidized material from the film surface. This effect has been observed by other researchers also.[3] Figure 4 shows the variation of F/C ratio for various deposition conditions for (a) as-deposited films and (b) after temperature-humidity testing and ethanol ultrasonication. Likewise, Fig. 5 shows the variation of O/C ratio for various deposition conditions for (a) as-deposited films, (b) after temperature-humidity testing, and (c) after ethanol ultrasonication. XPS O 1s spectra showed contributions from CF_n-O, COOR (ester), COOH (acid), COF (acid fluoride), and C=O ketone groups. Since the O 1s spectrum was just a broad peak, quantification of the individual concentrations of these groups was not feasible. There may also be contributions from peroxide groups (the result from postatmospheric oxidation of dangling bonds) in the O 1s spectrum. However, these peroxide groups are difficult to distinguish from C-OH groups since both these functionalities produce the same binding energy shift of 1.5 eV.[10]

Dielectric constant measurements.—Dielectric constants were measured for metal-insulator-metal capacitors at a frequency of 10 kHz. Figure 6 shows the variation in dielectric constant as a function of deposition conditions. Dielectric constants of the deposited films ranged from 2.23 to 2.55, and the loss tangents varied between 0.023-0.099 under all deposition conditions investigated. The loss tangents are higher than conventional polymers such as polyimides (loss tangent $\sim 10^{-3}$) and are typical of plasma-deposited films. These higher loss tangents can be attributed to trapped free radicals, unsaturated species, and interfacial charge. The dielectric constants increased with a decrease in operating pressure and an increase in deposition temperature. Both trends can be attributed to a decrease in the F/C ratio of the deposited films. The refractive index of films ranged between 1.41 and 1.42 for the deposition conditions investigated and is very close to that of Teflon, which has a refractive index of 1.38. Neither the refractive index nor the dielectric constant of the films changed after temperature-humidity exposure indicating

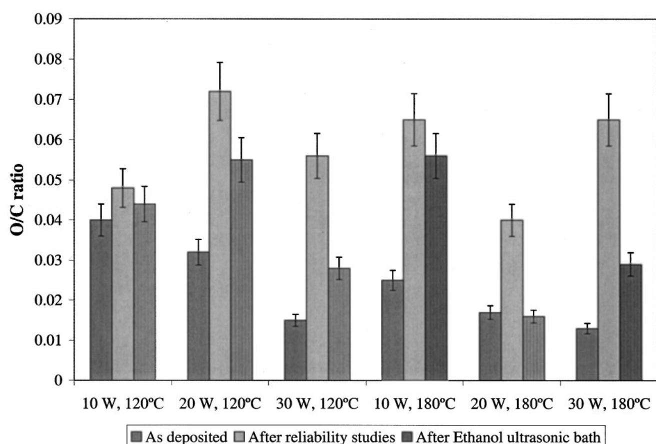

Figure 5. O/C ratio of the deposited fluorocarbon films as a function of deposition conditions (a) as deposited, (b) after temperature-humidity exposure at 85°C/85% RH for 100 h, and (c) after ethanol ultrasonic bath. Operating pressure: 1 Torr.

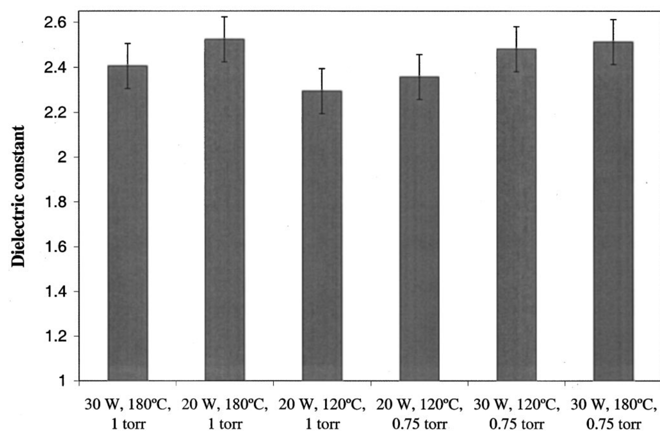

Figure 6. Dielectric constant (at 10 kHz) of the deposited fluorocarbon films as a function of deposition conditions.

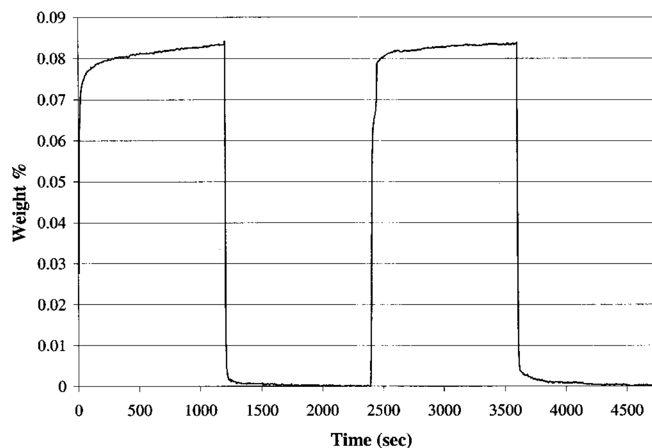

Figure 8. Weight percent increase of the deposited fluorocarbon film as a function of time for two absorption-desorption cycles. The deposition conditions were 10 W, 120°C, and 1 Torr.

that there was little incorporation of polar groups such as -OH and -C=O groups during temperature-humidity exposure. This result corroborates the absence of -OH groups observed by infrared spectroscopy.

Moisture absorption studies.—Moisture absorption studies were carried out using a quartz crystal microbalance in order to quantify the percent weight change due to moisture absorbed by the deposited films at various relative humidity atmospheres. Figure 7 shows that the weight change of the polymer was less than 0.15% for all the deposition conditions investigated, and is nearly ten times lower than that observed for conventionally used microelectronic polymers such as polyimides (PI 2611).[11] Also, the weight of the films rises with an increase in the relative humidity due to an increase in the driving force for mass transfer from the ambient into the film.

Humidity cycling experiments indicated that moisture did not chemisorb in the sample. Figure 8 shows the percent weight change of the deposited films for two absorption-desorption cycles. The weight increase during absorption (dry to wet environment) was equal to the weight decrease during the desorption cycle (wet to dry environment). This result accounts for the absence of OH groups in infrared spectra and also for the invariance of the film dielectric constant after temperature-humidity exposure.

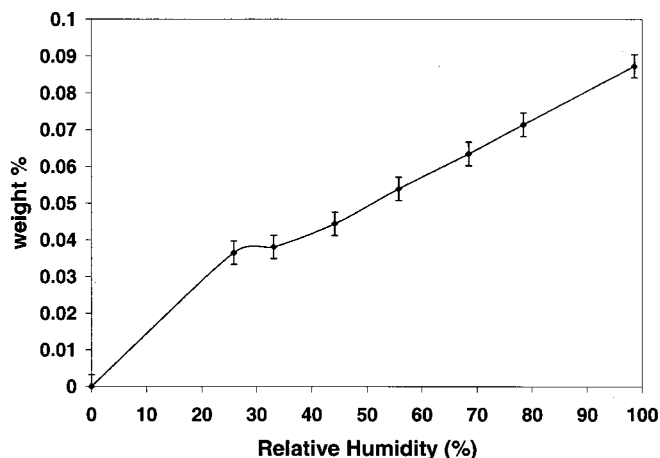

Figure 7. Steady-state weight percent increase of the deposited fluorocarbon film as a function of relative humidity (%). The deposition conditions were 10 W, 120°C, and 1 Torr.

Discussion

Electrical and optical properties.—Dielectric constants of the plasma deposited fluorocarbon films ranged between 2.23 and 2.55, which is slightly higher than that of Teflon ($k = 2.10$). These higher dielectric constants can be attributed to a lower F/C ratio and the presence of polar carbonyl-based groups, which arise from postdeposition atmospheric oxidation. The refractive index of these films was also slightly higher than Teflon, which is consistent with the higher electronic polarization that arises from the lower fluorine content. In all films, electronic polarization is the dominant mechanism and accounts for more than 70% of the measured permittivity (based on $k = n^2$). The presence of polar groups increases the ionic and orientation polarization components, thereby increasing the dielectric constant of the deposited films. Film dielectric constants increase with an increase in substrate temperature. This increase can be attributed to both a lower F/C ratio as indicated by XPS analyses and a lower free volume (higher density) in films deposited at higher temperatures.[12] At higher substrate temperatures, the film deposition rate is low, and the impinging reactive species have higher surface mobility, permitting more dense packing. Furthermore, desorption of fluorine-rich species from the growing film is favored at higher temperatures, which results in a lower F/C ratio and consequently, a higher dielectric constant. The increase in dielectric constant with lower operating pressure can be explained in a similar manner. Here, the lower F/C ratio can be attributed to the lower deposition rates and higher energy ion bombardment that ablates loosely bound fragments and end groups such as CF_3 and CHF_2.

Temperature-humidity effects.—Based on the infrared spectra in Fig. 1, no significant change in the bulk chemical structure and composition of the deposited films occurs upon temperature/humidity exposure. Also, no OH groups are detected after temperature-humidity exposure indicating negligible moisture absorption. Indeed, the weight percent change of the deposited films measured using a quartz crystal microbalance was less than 0.15% even at relative humidities >95%. This low moisture absorption can be attributed to the high hydrophobicity of the deposited fluorocarbon films and to very low concentrations of polar groups such as C=O, COOH, COOR (ester), and -OH to which water can attach via hydrogen bonding. Also, higher free volume could increase the moisture absorption. Oxygen-containing polar groups arise primarily from the postdeposition atmospheric oxidation of trapped species and dangling bonds present in plasma-deposited films. Hence, a low concentration of oxygen-containing polar groups signifies a low dangling bond concentration. In fact, XPS analyses of the deposited films indicated an O/C ratio less than 0.03 for all deposited films,

which is consistent with the lack of oxygen containing polar groups as indicated by IR and moisture absorption measurements. Furthermore, humidity cycling experiments showed that there was essentially no moisture retained in the deposited film. This result indicates that nearly all the dangling bonds present in the films are oxidized immediately upon exposure to air and only a few of them remain to chemically react with moisture during absorption experiments. Similarly, the dielectric constant does not change after temperature-humidity exposure since nearly all moisture desorbs upon termination of moisture exposure; thus, no significant change in bulk composition or incorporation of polar groups into the deposited films occurs. This result indicates that negligible degradation or moisture absorption occurs even when the films are subjected to both elevated temperature and humidity environments.

Another important aspect of the absorption-desorption experiments (Fig. 8) is the high diffusivity of water (based on the steep slope of absorption and desorption curves in Fig. 8) in these films. The estimated diffusivity (assuming a step change in relative humidity) was at least $\geqslant 10^{-10}$ cm^2/s for all the deposited films. The high water diffusivity in these films can be attributed to the lack of polar molecules or trapping sites that would interact with water and thereby hinder diffusion.[13] Thus, the diffusion mechanism is dominated by transport of free water molecules (no interaction with polar groups), which is typically much faster than the rate associated with interaction of water molecules with polar moieties. The time required for steady-state moisture absorption in the deposited films was less than 10 min, while it was less than 2 min for desorption experiments. A significant part of the time to reach steady state is attributed to the lag time for the chamber humidity to reach its final value. This lag time for moisture absorption experiments was around 4-5 min, while 20 s was needed for moisture desorption. Indeed, Fig. 8 demonstrates that moisture desorption from the fluorocarbon film is much faster than moisture absorption. A detailed study of moisture absorption is beyond the scope of this paper.

XPS analyses showed a decrease in the F/C ratio and a slight increase in the O/C ratio of the deposited films after temperature-humidity exposure, which indicates that most of the chemical changes occur only in the top few layers of the film. These two effects can be attributed to the formation of low molecular weight oxidized material on the film surface. When the sample is subjected to ethanol ultrasonification (after temperature-humidity testing), most of this low molecular weight layer is dissolved away; hence, there is an increase in the F/C ratio and a decrease in the O/C ratio. This trend further confirms our hypothesis that most of the defluorination and oxidation occurs only in the top few layers of the deposited film. It is expected that there are a larger number of defects, dangling bonds, and loosely bound fragments on the surface of the film, which are more likely to be attacked by moisture and oxidized upon exposure to ambient.

As shown in Fig. 3, there is a decrease in the XPS detected concentrations of CF_3, CF_2, CF, C-CF_x and an increase in the C-C/C-H concentrations upon temperature-humidity testing, which is consistent with defluorination. The loss of fluorine may be attributed to the reaction of moisture with loosely bound fluorine to form C-OH moieties in the film and HF. Second, there may be peroxide groups, which can lead to chain scission and consequently the formation of low molecular weight species. Although the detection of peroxide by IR and XPS is difficult, it is likely to form by the reaction of molecular oxygen with dangling bonds in the film upon postdeposition exposure to atmosphere. Also, acid fluoride (COF) groups present in the film can be hydrolyzed to form acid groups (COOH) and HF. Both of these mechanisms could account for the slight increase in the oxygen content of the film. Although oxidation of any remnant dangling bonds may occur, this effect appears minimal based on moisture absorption measurements. Most of the dangling bonds are immediately consumed when the sample is exposed to atmosphere after deposition.

Previous studies[3] reported that there was a critical deposition power beyond which film surface oxidation is rapidly enhanced upon exposure to a temperature-humidity (65°C, 85% RH) environment. This enhancement of oxidation was attributed to the difference in deposition mechanisms with an increase in applied power. In our studies, no indication of enhanced oxidation rates within our narrow range of applied powers was observed. Previously, we have shown that the deposition mechanism with the PFE monomer was the same within our range of operating powers,[4] consistent with the XPS data. Also, the low film deposition rates with this monomer permits more time for reaction at the film surface, thereby reducing the concentration of trapped free radicals and unsatisfied bonds in the film. Furthermore, argon bombardment during film growth may release loosely bound species, promote cross-linking reactions and hence lead to the formation of a dense film. It is likely that all our depositions were performed below the critical power level discussed in Ref. 3.

Conclusions

Fluorocarbon films deposited from pentafluoroethane/argon mixtures were subjected to temperature-humidity exposure at 85°C and 85% RH for 100 h. Infrared spectra of the deposited films did not show significant changes in the bulk chemical structure and composition of the films after temperature-humidity testing. Specifically, OH-related moieties were not detected either before or after temperature-humidity testing suggesting negligible moisture absorption. Also, there was no significant change in the concentration of oxygen-related species after temperature-humidity testing. Moisture absorption measurements indicated less than 0.15% weight change at steady state when the films were subjected to relative humidities greater than 90%. This low moisture absorption is attributed to the hydrophobicity of fluorocarbon films and to the lack of significant concentrations of polar groups to which water can bond. Humidity cycling experiments showed no permanent change in the weight of the films, indicating negligible chemisorption or reaction of moisture with the deposited films. Essentially all dangling bonds in the films are oxidized immediately upon postdeposition exposure to atmosphere. Dielectric constants of the deposited films ranged between 2.23 and 2.55, depending upon deposition conditions. The dielectric constant increased with an increase in deposition temperature and a decrease in operating pressure. Both trends are attributed to a decrease in the F/C ratio and an increase in the density (lower free volume) of deposited films. Furthermore, the film dielectric constant did not change after temperature-humidity studies, which is consistent with their extremely low moisture uptake. In addition, all water desorbs upon cycling the sample from a wet environment to a dry environment. XPS analyses detected oxidation and defluorination in the top few monolayers of the deposited films after temperature-humidity studies, which is primarily attributed to the formation of a low molecular weight oxidized layer. Likewise, XPS C 1s spectra showed a decrease in the concentrations of CF_3, CF_2, CF, and C-CF_x moieties and an increase in the C-C/C-H moieties. The low molecular weight oxidized layer was soluble in ethanol as indicated by a decrease in the O/C and an increase in the F/C ratio upon subjecting the fluorocarbon films to ethanol ultrasonification. Finally, within our range of operation, there was no significant effect of applied power on the extent of oxidation of the deposited films due to temperature-humidity exposure.

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