

# Effects of $\text{CF}_4/\text{O}_2$ Gas Plasma Power/Exposure Time on Dielectric Properties and Breakdown Voltages of PVDF Films

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## SYNOPSIS

Dielectric properties and electrical breakdown strengths were measured on 12- $\mu\text{m}$ -thick poly(vinylidene fluoride) films before and after exposure to various power levels and exposure times in a 96%  $\text{CF}_4/4\%$   $\text{O}_2$  gas plasma. Significant changes in dielectric constant, dielectric losses, and breakdown voltages were observed. Breakdown voltages for PVDF films as a function of exposure time and plasma power appear to go through a maximum.

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## INTRODUCTION

High quality, high reliability wound film capacitors for high energy density applications require high quality dielectric films with good insulation properties and high electric field breakdown strengths. Performance of organic polymers, which are extensively used as capacitor dielectrics, is limited by poor insulation resistance and/or low dielectric breakdown strengths. Dielectric breakdown strengths  $V_b$  expressed in  $\text{V}/\mu\text{m}$  thin films, play a key role in determining maximum attainable energy densities in film capacitors because attainable energy densities increase with the square of applied voltage across the capacitor. If  $V_b$  of polymer films can be increased, spirally wound capacitors using these films as dielectrics can either be operated at higher voltages (which translates into higher energy densities) or can be made considerably smaller since the thickness of the films can be reduced.

Poly(vinylidene fluoride) (PVDF) with a backbone of  $-\text{CH}_2-\text{CF}_2-$  repeat units, or its copolymer with trifluoroethylene,  $-\text{CF}_2-\text{CFH}-$ , has been widely investigated and exploited as potential

dielectric films for high energy density capacitor applications. These polymers have drawn attention on account of their unusually high dielectric constant which is desirable for reducing capacitor size. The large dielectric constant of PVDF is also important in piezoelectric and pyroelectric applications such as hydrophones. It has long been recognized that electrical properties of PVDF are closely related to its crystalline structure which can be altered by drawing (stretching) or poling techniques. The large dielectric constant of PVDF is due to the large dipole moment of the  $\text{C}-\text{F}$  bond, its mobility, and number per unit volume.

We have previously shown that briefly exposing PVDF to various low pressure, low temperature, and gas plasmas is an inexpensive procedure for systematically altering surface properties.<sup>1</sup> Gas plasmas are created when low pressure gases at room temperature are subjected to electric discharge, e.g., radio or microwave frequencies. As a whole, the plasma is neutral. However, a small fraction of the gas is excited by the discharge and creates free electrons, ions, radicals, excited molecules, and photons. These activated species interact with exposed surfaces in different ways. The final result depends on the gas used, length of treatment, and parameters associated with the equipment such as gas flow, energy input, and geometry. Surface and bulk properties such as

wettability, adhesion of vapor deposited aluminum, and even  $V_b$  can be changed. Exposing 12- $\mu\text{m}$ -thick PVDF film to 96%  $\text{CF}_4$ /4%  $\text{O}_2$  gas plasma, for example, has been shown to increase subsequent adhesion of vapor deposited aluminum<sup>1</sup> and produce an 11% increase in dc  $V_b$ .<sup>2,3</sup> However, since in those studies only one power level and a brief exposure time was used, little change in dielectric constants were detected.

In this note we report results of using  $\text{CF}_4/\text{O}_2$  plasma to change bulk properties, such as dielectric constants and  $V_b$ , of PVDF films and attempt to determine optimum power levels and exposure times in 96%  $\text{CF}_4$ /4%  $\text{O}_2$  gas plasma that is required in order to optimize  $V_b$ . Effects of other gas plasmas (such as ammonia, sulfur dioxide, or carbon dioxide) on dielectric and breakdown properties of PVDF as well as chemical depth profiling will be reported separately.<sup>4</sup>

## EXPERIMENTAL

PVDF films ( $4 \times 12$  in.) cut from a roll of KF film (Kureha, P-20) were exposed to 96%  $\text{CF}_4$ /4%  $\text{O}_2$  gas plasma at 150 torr pressure and gas flow rates of 0.3 mL/min in a Branson/IPC Model 4150 gas plasma barrel etcher. Elapsed time between exposure

to the gas plasma and the time that the various dielectric measurements were made was about 1 month. This implies that observed changes in dielectric properties taking place in PVDF after exposure to  $\text{CF}_4/\text{O}_2$  gas plasma last at least 1 month.  $V_b$  was measured under silicone oil at room temperature by placing PVDF film samples between  $\frac{1}{4}$  in. brass electrodes and linearly ramping the voltage (at 500 V/s) from 0 V until breakdown occurred. Applied voltage was monitored with a Nicolet digital oscilloscope.

## RESULTS AND DISCUSSIONS

### Dielectric Constant and Dielectric Losses

Dielectric constants, dielectric losses, and  $V_b$  of PVDF films that had been exposed to 96%  $\text{CF}_4$ /4%  $\text{O}_2$  plasma depended strongly on RF power levels and lengths of time in the plasma. This is because exposure to high RF power levels and/or for long time periods in a gas plasma allow reactive species to diffuse beneath film surfaces and react deep in the bulk. These reactions can result in altered bulk properties. For example, if fluorination of PVDF is occurring, an undesirable decrease in dielectric con-

**Table I Dielectric Loss, Dielectric Constant, and Breakdown Voltage of 12- $\mu\text{m}$ -Thick PVDF Film as a Function of Applied Power and Exposure Times in 96%  $\text{CF}_4$ /4%  $\text{O}_2$  Gas Plasma**

Power (W)	Time (min)	Dielectric Loss			Dielectric Constant			Breakdown Voltage (kV/mil)	V/ $\mu\text{m}$
		100 Hz	1 kHz	10 kHz	100 Hz	1 kHz	10 kHz		
0	0	0.0091	0.0101	0.0204	10.61	10.48	10.31	14.8	583
125	1	0.0104	0.0106	0.0205	10.31	10.1	9.99	18.4	724
	2	0.0101	0.0105	0.0205	10.27	10.14	9.98		
	4	0.0094	0.0103	0.0202	10.45	10.32	10.15		
	8	0.0098	0.0104	0.0206	10.49	10.36	10.19		
	16	0.0099	0.0101	0.0187	8.58	8.50	8.38	18.2	717
250	0.5	0.0102	0.0102	0.0196	10.55	10.42	10.25	17.3	681
	1	0.0103	0.0102	0.0196	10.51	10.37	10.21		
	2	0.0103	0.0103	0.0197	10.51	10.37	10.21		
	4	0.0131	0.0113	0.0197	10.41	10.26	10.09		
	8	0.0099	0.0092	0.0158	8.35	8.28	8.18	16.4	646
500	0.25	0.0098	0.0101	0.0195	10.41	10.27	10.11	16.7	657
	0.5	0.0100	0.0101	0.0194	10.60	10.46	10.30		
	1	0.0099	0.0101	0.0194	10.46	10.32	10.16		
	2	0.0106	0.0107	0.0197	10.70	10.55	10.38		
	4	0.0104	0.0104	0.0187	10.00	9.88	9.74	16.6	654

stant may result because PVDF becomes more PTFE-like. On the other hand, for short reaction times and/or low power levels, little reaction into the bulk occurs, and fluorinated layers may comprise too small a fraction of total film thickness to yield improvements in  $V_b$ .

Dielectric constants, dielectric losses and  $V_b$  of PVDF films that had been exposed to  $\text{CF}_4/\text{O}_2$  plasma for different power levels/exposure times are listed in Table I. There are several things we can learn from Table I: First, for total power times of approximately 2000 W min, bulk dielectric constants for PVDF sharply decrease. Second, for identical total W min exposure times, i.e., 125 W for 16 min (2000 W min) or 500 W for 4 min (also 2000 W min), bulk dielectric constants differ substantially. Apparently, long exposure times, even at lower power levels, have a greater effect in reducing bulk dielectric constants than shorter exposures at higher power levels. This is consistent with the assumption that changes in bulk dielectric properties following exposure to gas plasmas are indeed diffusion-related. That means that exposure time plays a more important role than power levels in affecting bulk dielectric properties. Third, although dielectric constants show about a 20% decrease after extensive exposure to  $\text{CF}_4/\text{O}_2$  gas plasma, dielectric losses are relatively constant (or decrease very slightly). The 20% decrease in dielectric constant may be due to the fact that PTFE-like material (perhaps formed on PVDF surfaces after exposure to gas plasma) has a lower dielectric constant than untreated PVDF. Further work in this area is needed before definitive mechanisms for these results can be advanced beyond speculation. It is interesting to note that exposing PVDF to 500 W of  $\text{CF}_4/\text{O}_2$  plasma for 2 min yields slightly higher dielectric constants and slightly lower losses at 1 and 10 kHz than does unexposed PVDF. Thus, plasma treatment of PVDF under these conditions can actually improve performance of PVDF as a dielectric material for capacitors.

### Dielectric Breakdown Strength

Table I also puts into perspective the relationship between  $V_b$ , RF power, and exposure time in 96%  $\text{CF}_4/4\%$   $\text{O}_2$  gas plasma. We confirm that  $V_b$  of PVDF films definitely increased even after brief exposure to  $\text{CF}_4/\text{O}_2$  gas plasma.  $V_b$  of PVDF as a function of gas plasma power and/or exposure times appear to go through a maximum. In addition, PVDF films exposed to very high RF power levels for long times

yield lower  $V_b$  than unexposed PVDF films. This may be due to extensive fluorination within the PVDF bulk. Apparently, a trade-off exists between the (desirable) increased  $V_b$ , on the one hand, and the corresponding (undesirable) decrease in dielectric constant, on the other.

### UV-Vis and IR Spectra

UV-Vis spectra of PVDF films before and after exposure to  $\text{CF}_4/\text{O}_2$  plasma (4 min at 500 W) showed essentially no differences other than a slight offset of absorption over the complete 200–400 nm frequency range. This could be attributed to simple surface roughening by the gas plasma.

IR spectra of PVDF films after exposure to  $\text{CF}_4/\text{O}_2$  plasma (4 min at 500 W) were essentially superimposable on IR spectra of unexposed PVDF and did not show any major changes in absorption bands. The only exceptions were changes in four bands, all of which are commonly assigned to the alpha form of PVDF. Three of these bands showed an increase in transmission, i.e., a decrease in absorption. These bands, at  $766\text{ cm}^{-1}$  (assigned to in and out of phase bending of  $\text{CF}_2$ <sup>5</sup>),  $855\text{ cm}^{-1}$ , and  $978\text{ cm}^{-1}$  (assigned to a skeletal vibration<sup>5</sup>) all showed approximately 75% decrease in absorption after exposure to  $\text{CF}_4/\text{O}_2$  gas plasma. This implies that the percent alpha character of PVDF film had *decreased* after exposure to gas plasma. Although such structural changes are normally associated with high field electrical poling of PVDF, our results were obtained at temperatures only slightly above room temperature and with no electric field applied to the samples. Our data imply that beneficial effects of poling can be achieved in PVDF without resorting to lengthy and/or difficult poling procedures.

One band, at  $615\text{ cm}^{-1}$  (assigned to in phase  $\text{CF}_2$  wagging<sup>5</sup>) showed an approximately 50% *increase* in absorption after exposure to  $\text{CF}_4/\text{O}_2$  plasma. We do not have an adequate explanation for this observation.

### CONCLUSIONS

The results presented here clearly illustrate the feasibility of easily changing bulk dielectric properties and breakdown voltages of PVDF films by briefly exposing them to 96%  $\text{CF}_4/4\%$   $\text{O}_2$  gas plasma. Increased  $V_b$  of PVDF after exposure to a  $\text{CF}_4/\text{O}_2$  gas

plasma implies that PVDF can be safely poled at higher fields without fear of breakdown occurring.

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