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## Plasma Treatment of Polymer Dielectric Films to Improve Capacitive Energy Storage.

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### ABSTRACT

Demand for compact instrumentation, portable field equipment and new electromagnetic weapons is creating a need for new dielectric materials with higher energy storage capabilities. Recognizing the need for higher energy storage capacitors, the Army Research Lab at Fort Monmouth NJ, initiated a program years ago to investigate potential methods for increasing the dielectric strength of polyvinylidene difluoride (PVDF) film, which is the highest energy density material commercially available today. Treatment of small area PVDF films in a  $CF_4/O_2$  plasma showed that the dielectric strength of these films can be increased significantly. Sigma Labs continued this work using large area films that were plasma treated in production size equipment, and found that the dielectric strength of PVDF films can be increased by as much as 20% when treated in a 96%- $CF_4$ /4%- $O_2$  plasma. This 44% increase in energy storage of a PVDF capacitor, is significant considering that the treatment can be implemented in a conventional metallizing chamber, with minimum capital investment. The data shows that improved breakdown strength may be unique to PVDF film and the particular  $CF_4/O_2$  gas mixture, because PVDF film treated with 100% $CF_4$ , 100% $O_2$ , Ar gas plasma, and electron irradiation, shows no improvement in breakdown strength. Other data presented includes dissipation factor, dielectric constant and surface tension measurements.

### INTRODUCTION

Increasing requirement for device miniaturization, portable field equipment and new electromagnetic weapon systems, is creating a demand for new dielectric materials with improved electrostatic energy storage capabilities. There is a well defined need for new materials with higher dielectric constants and improved breakdown strength. New material development is driven by various commercial and military applications including flash lamps, copiers, implantable defibrillators, pulsed lasers, radar modulators, isotope separation lasers, directed energy weapons, electronic warfare and countermeasure pulse generators and a broad range of electronic equipment.

When designing high energy density capacitors polymer films are the materials of choice. Polymer films are used in most applications, because they can withstand higher electric stresses, are lightweight and relatively economical. Low loss materials such as polypropylene are used in high rep-rate, lower energy applications. For higher energy density and low rep-rate applications, polyvinylidene difluoride (PVDF) is used. Over the years refinements made in the overall quality of these films and the capacitor manufacturing process equipment has allowed small incremental improvements in capacitor energy

densities. Today the highest energy density commercial capacitors have densities of about 2.5J/cc and are made PVDF films. There is little evidence that new polymer chemistries may be available in the near future to surpass the energy density of PVDF film. Lately we have seen some new films with high temperature capabilities from 3M, Foster-Miller, Hoechst Celanese, Dow Chemical and Maxdem. Maldecorn et.al [1] have shown that all these new films have dielectric constants in the range of  $k=2.8$  to 3.6. When fully developed, these films may satisfy some surface-mount needs for low voltage metallized capacitor products and some high temperature applications, but they will have no impact in high energy density applications.

Addressing the need for increased demand for higher energy density capacitors in military and commercial applications, the Army Research Laboratory at Fort Monmouth NJ, initiated a development program to explore potential improvements in breakdown strength of capacitor films by treating these films in various gas plasmas [2-8]. This work among other findings showed that breakdown strength of small area PVDF films can be improved by exposure to a  $CF_4/O_2$  plasma. Sigma Labs was awarded an SBIR contract to investigate if this effect persists in larger area films, processed in a production size vacuum system under conditions that simulate a production environment.

This paper reports the results of plasma treatment of PVDF films in a full size metallizer, where the film is moved from one roll to another through a plasma zone. X-ray-Photoelectron-Spectroscopy (XPS) was used to study the surface chemistry of the films before and after the treatment. Small area capacitors were produced to measure breakdown strength and other electrical properties of the treated films. In order to explore the mechanism by which plasma treatment affects a bulk property such as the breakdown strength of the polymer, films are irradiated with electron radiation and the data compared to that of plasma treatment.

## EXPERIMENTAL TECHNIQUE

The experimental apparatus is shown in Figure 1. A full size metallizer with a 22" long drum was used. The film was treated by passing through a plasma zone that is formed between a plasma reactor and the rotating drum. The plasma reactor was a low power system in which RF power was coupled both inductively and capacitively to the plasma. The cylindrical reactor shell was water cooled and it can take a significant amount of power, although for this experiment we drove it with only 500W of real power (Forward power - Reflected power) using a manually variable tuning network. The reactor cylinder had a window facing the film that is 35.5cm long and 3.8cm wide. Therefore, based on the speed of the drum and real RF power transferred to the load, we can calculate a plasma power density in  $W/cm^2/sec$ . This value is an equipment specific number because it reflects the power input into the plasma reactor and does not account for ionization efficiency.

### DC Breakdown Measurement Technique

Breakdown measurements on the films, used a dry double-metallized non contact measurement technique, and were performed at high vacuum ( $<10^{-4}$  torr), to eliminate partial discharges and surface flashover. The breakdown system was built in a turbomolecularly pumped stainless steel vacuum chamber. Metallization masks allowed us to metallize small area stamp capacitors for breakdown measurements. Electrode contact was made to metallized pads that are outside the active area in order to prevent film damage. The voltage was ramped at about 500V/sec. For every breakdown measurement reported, at least 18 stamp capacitors were tested. We chose not to employ the more commonly used liquid impregnation technique for measuring breakdown strength of films. Since neither the film nor the electrodes are perfectly flat, there is always thin liquid layers involved in the breakdown. This results in

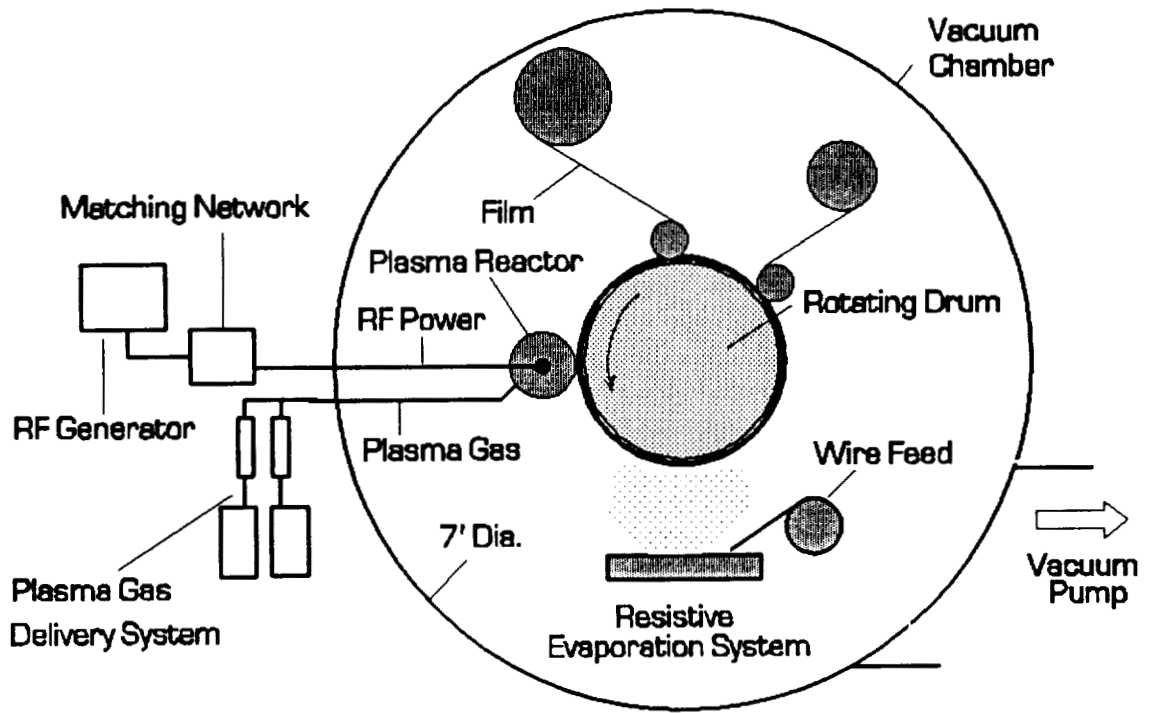


Figure 1. Schematic representation of the experimental set-up for plasma treating polymer films. The plasma reactor is placed against the rotating drum of a production size web coater, prior to the metallization station.

BREAKDOWN OF PLASMA TREATED PVDF FILM  
 $CF_4$  vs.  $CF_4/O_2$  vs. E-GUN

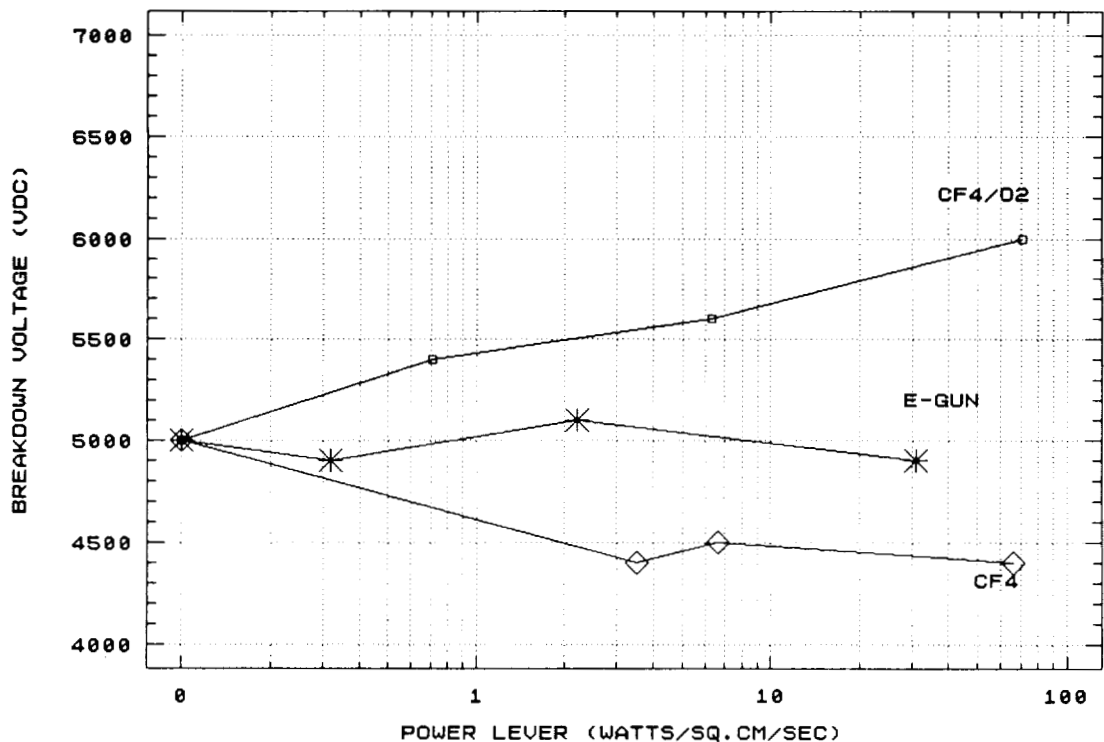


Figure 2. Breakdown voltage of 12µm PVDF film treated with a  $CF_4/O_2$  plasma, electron radiation and a  $CF_4$  plasma. Each breakdown point represents an average value derived from the breakdown of eighteen double metallized stamp capacitors. The maximum standard deviation of any of the above points is 500V. 346

slightly higher and more uniform breakdown values that often mask minor variations in film thickness that can result from film fibrils and microcrevices. The dry double metallized technique performed in a high vacuum environment produces results that depend strictly on the polymer film, and it eliminates any questions about the effects of the liquid impregnant.

## TREATMENT OF PVDF FILMS

### Plasma Treatment Using $\text{CF}_4$ Gas

Not knowing what effect a 100%  $\text{CF}_4$  gas plasma will have on the PVDF films we started the study using pure  $\text{CF}_4$ , to establish a baseline before proceeding to the  $\text{CF}_4/\text{O}_2$  mixture. We first exposed PVDF film to a plasma density of 0.3 W/cm<sup>2</sup>/sec. DC breakdown values of the  $\text{CF}_4$  plasma treated PVDF film were slightly lower than the control film (see Figure 2). When the plasma density was increased to 2.2 and 31.0 W/cm<sup>2</sup>/sec, and as shown in Figure 2, there was no significant effect on the breakdown strength of the film.

### Plasma Treatment Using a $\text{CF}_4/\text{O}_2$ Plasma Gas

Implementing the process developed by Mammone et-al [4], a gas mixture of 96% $\text{CF}_4$ /4% $\text{O}_2$  was used for plasma treatment. As shown in Figure 2, this particular gas mixture at plasma densities as low as 0.71 W/cm<sup>2</sup>/sec has a significant effect in the DC breakdown values of the treated PVDF films. Following the  $\text{CF}_4$  plasma treatment results, we did not expect the addition of a small amount of  $\text{O}_2$  to have such a significant effect in the breakdown values under the same plasma conditions. This data supports the small area data derived by the Army ETDL group and illustrates that breakdown strength of large area PVDF film can be improved using a plasma treatment arrangement that simulates a production process. It should also be noted that the small area samples were immersed in the plasma whereas in our work only one side of the moving film was exposed to the "hot plasma", while the other side of the film was maintained at 25°C (water cooled drum).

### Electron Beam Treatment of PVDF Films

Breakdown strength of a polymer film is considered to be a bulk property and one would not expect that a surface treatment would effect it. Given the high plasma power level and breakdown results, it is possible that the thermochemical treatment extends beyond the film surface. One postulation is that layers of the film close to the surface (up to 1-2 $\mu\text{m}$  deep) are cross linked by the plasma radiation. Such modification of the polymer film results in a segment of the film that has superior breakdown strength. In order to separate the cross linking effect from the chemical effects of the plasma gas, an electron beam was used to irradiate PVDF film. Based on our experience with electron beam curable dielectrics [9,10], we used a 15kV accelerating voltage to penetrate 1.5 $\mu\text{m}$  to 2.5 $\mu\text{m}$  into the film and varied the beam current to obtain power densities similar to those used in the plasma treatment. The results of this experiment shown in Figure 2, show that the breakdown strength of PVDF film is virtually unchanged. This observation suggests that if PVDF film can be radiation cross linked, this effect alone may not be responsible for the increased breakdown strength. In fact the data suggests that the film may be damaged by electron irradiation. The results of the pure  $\text{CF}_4$  and  $\text{O}_2$  plasma treatments also support this view, because cross linking radiation derived from different plasmas (mostly electrons and energetic photons) is not expected to differ much from that of  $\text{CF}_4/\text{O}_2$  plasma.

## Dissipation Factor and Dielectric Constant Measurements

The data in Table 1 show that there are fluctuations in the DF and  $k$  values of treated films. Films treated with  $CF_4/O_2$  have measurably lower values of DF at lower temperatures and at 100Hz and 1kHz, while at higher temperatures and 10kHz, the DF values are somewhat higher. At this point we do not have an explanation for this behavior. It is interesting to note that we do not see a reduction in the value of  $k$  at higher plasma densities as observed by Mammone et-al [4]. There are some key differences between the present experimental set-up and the one used by Mammone et-al [4]. PVDF used in this work had a higher dielectric constant ( $k=13$  versus  $k=10$ ), and in this investigation films were treated only on one side. It should also be noted that in the previous work, the  $k$  was lowered only during long exposure to the plasma. Under those conditions films could heat-up enough to recrystallize and affect the value of the dielectric constant.

## XPS Analysis of the Treated Films

XPS analysis conducted on control and  $CF_4/O_2$  plasma treated PVDF films shows that the F/C ratio increased as a function of the level of plasma treatment. We also found that aluminum is sputtered onto the PVDF film surface from the plasma reactor, which is fabricated from aluminum metal. High resolution spectra in the C1s region are shown in Figure 3. Analysis of these peaks indicates that as the level of plasma treatment increases, the ratio of C-N, C-O and C-C to C=O increases. One could also suggest that the effect of the peroxy and carboxylate peaks may also be visible. Using high resolution spectra of the C1s, F1s, O1s and Al2p peaks, elemental ratios can be calculated for each of the spectra. The F/C, O/C and Al/C ratios are shown in Figure 4, as a function of  $CF_4/O_2$  plasma treatment level. The most significant observation that can be made from this data, is that additional fluorine is incorporated in the polymer as a function of plasma treatment.

## Wetting Angle Measurements

Contact angle measurements made with a system that has a 35:1 magnification with an adjustable focus allowed us to make wetting angle measurements with an accuracy of better than 5 degrees. A pipet was used to dispense a controlled size droplet of deionized water. Contact angle measurements were made for both control films and films treated with  $CF_4$ ,  $CF_4/O_2$  as well as electron radiation. Control films have a contact angle of about 65-70°. This angle remains very much unchanged for all treatments and power levels except for the higher power  $CF_4/O_2$  plasma treatment, where it drops to about 35-40°. Since PVDF is highly polar, we did not expect to measure significant changes in the contact angle, unless there are major changes in the polarity and/or morphology of the film surface. Lowering of the contact angle at higher plasma levels suggests that there are significant changes on the surface of the film. If we also consider the DF data in Table 1, we may conclude that chemical changes extend into the bulk. Our experience in corona and plasma treating films is that even in less polar films such as polypropylene, a conventional surface treatment that is used to promote metal adhesion does not affect the DF of the film. This data supports the conclusion drawn from breakdown voltage measurements, that plasma treatment can alter chemical and physical properties of films beyond the surface layers.

## SUMMARY

$CF_4/O_2$  plasma treatment results in a significant increase in the breakdown voltage of the PVDF film. When considering a common PVDF capacitor design that utilizes double metallized paper electrodes and

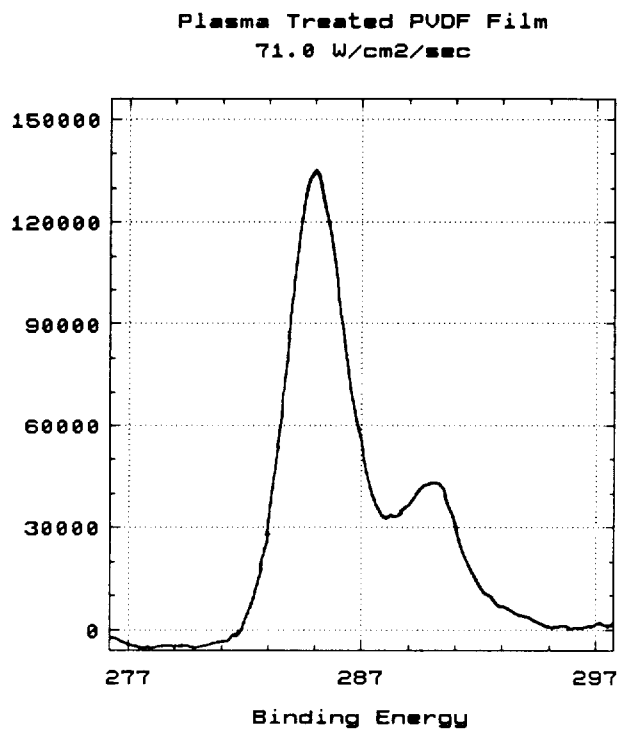
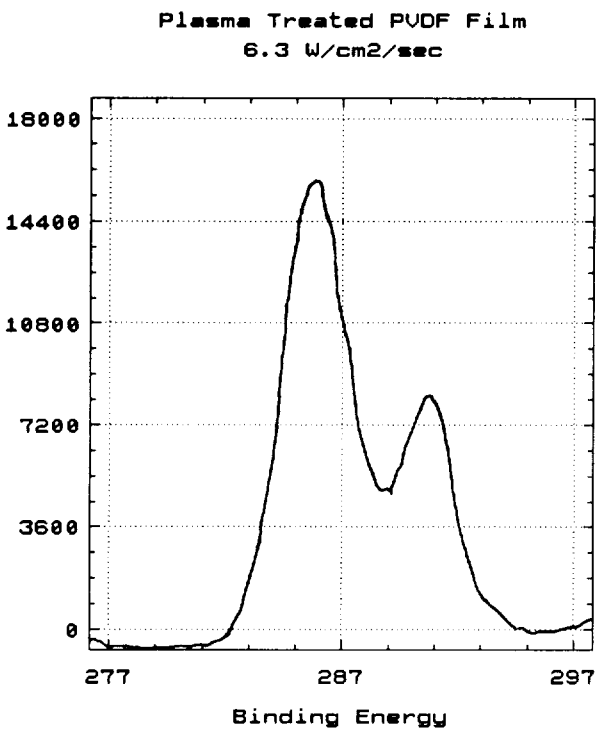
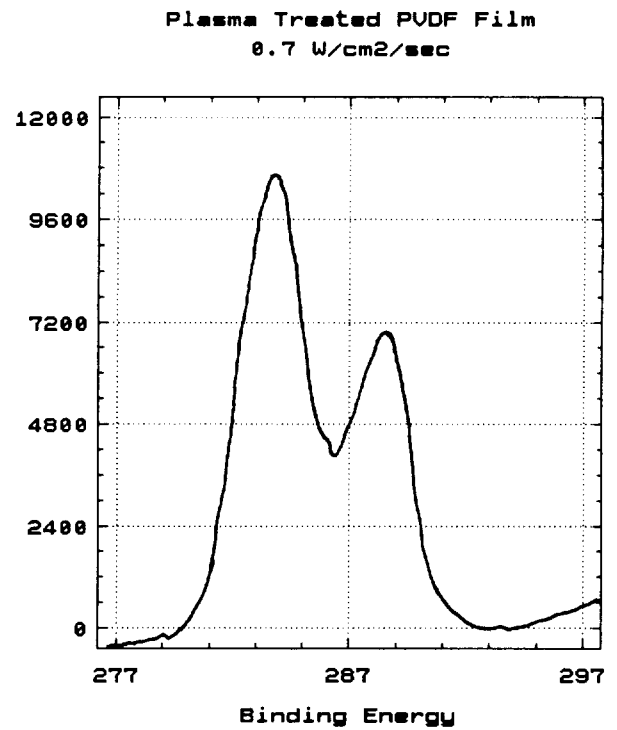
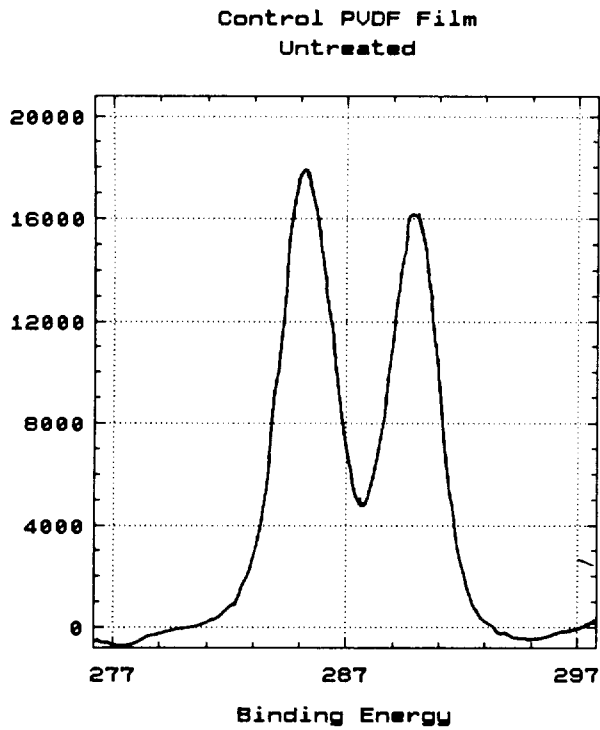


Figure 3. High resolution XPS spectra in the region of the C1s peak for control and CF<sub>4</sub>/O<sub>2</sub> plasma treated 12 μm PVDF film, at different plasma power densities. The binding energy scale is approximate and measurements are made after a calibration is performed on the individual spectra.

TABLE 1. Dielectric measurements of 12um PVDF film, treated in a CF<sub>4</sub>/O<sub>2</sub> plasma.

Plasma Density (W/cm <sup>2</sup> /sec)	Test Temp. C	Dissipation Factor (%)			Dielectric Constant (k)			DC Break Voltage (KV)
		100Hz	1kHz	10kHz	100Hz	1kHz	10kHz	
0.0	30	1.48	1.73	3.28	12.9	12.7	12.3	5.0
	50	1.59	1.66	2.68	13.2	13.0	12.6	
	70	1.95	1.81	2.30	13.8	13.5	13.2	
	90	2.37	2.07	2.21	14.5	14.0	13.6	
	90	2.37	2.07	2.21	14.5	14.0	13.6	
0.7	30	1.20	1.57	3.48	12.4	12.2	11.8	5.4
	50	1.20	1.42	2.91	12.6	12.4	12.1	
	70	1.37	1.41	2.33	13.0	12.8	12.5	
	90	2.24	2.00	2.54	14.3	13.9	13.5	
6.3	30	1.20	1.52	3.30	12.4	12.2	11.9	5.6
	50	1.23	1.39	2.69	12.7	12.5	12.2	
	70	1.48	1.46	2.25	13.2	13.0	12.7	
	90	2.56	2.21	2.45	14.7	14.2	13.8	
71.0	30	1.27	1.48	2.95	12.5	12.2	12.0	6.0
	50	1.30	1.43	2.67	12.6	12.4	12.1	
	70	1.54	1.52	2.47	12.1	12.8	12.5	
	90	2.46	2.16	2.70	14.3	13.9	13.5	

XPS ANALYSIS OF PLASMA TREATED PVDF FILM  
CF<sub>4</sub>/O<sub>2</sub> PLASMA - 3 LEVELS

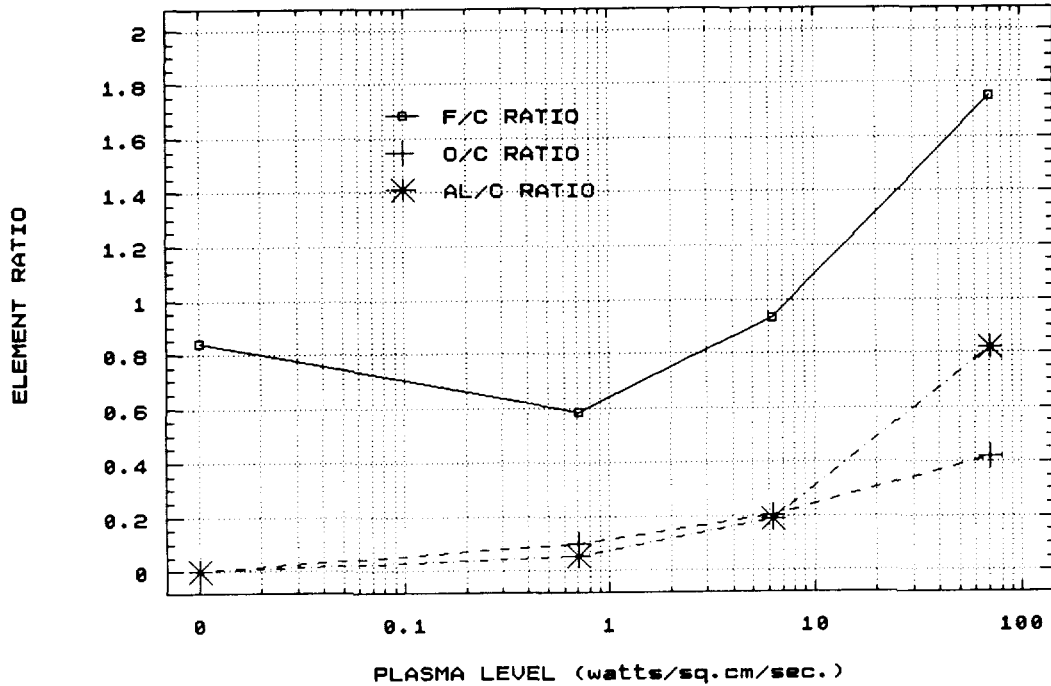


Figure 4. Fluorine, oxygen and aluminum / carbon ratios as a function of plasma power density, derived from high resolution XPS analysis of control and CF<sub>4</sub>/O<sub>2</sub> plasma treated 12µm PVDF films.

has a delivered energy density of 2.44J/cc (current design by a major capacitor manufacturer), plasma treated PVDF film can raise this value to 3.51J/cc. What is even more significant is that the additional cost for this benefit may be minimal because process and equipment are relatively simple, and if the film is to be metallized, the treatment can be performed inline with the metallization process in the same chamber. Furthermore, the lower wetting angle of the surface of the treated film will improve the capacitor impregnation process and thus reduce air voids that can lead to partial discharges during the operation of the capacitor. Minimization of the partial discharge activity can lead to improved performance and reliability under a broad range of operating conditions.

Although such an increase in energy density and reliability may not satisfy the longer term objectives of several government programs that require capacitor energy densities as high as 10J/cc, plasma treated PVDF represents a significant step in this direction that is relatively easy to attain. In the short term this improvement can benefit several electromagnetic weapon programs, and it can have an impact on commercial capacitor products for applications such as portable defibrillators, flash lamps, and pulse generators.

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