
PROCEEDINGS

THE SECOND ANNUAL
INTERNATIONAL CONFERENCE
OF
PLASMA
CHEMISTRY
AND
TECHNOLOGY

EDITED BY: HERMAN V. BOENIG, PH.D.

PROCEEDINGS

**THE SECOND ANNUAL
INTERNATIONAL CONFERENCE
OF
PLASMA
CHEMISTRY
AND
TECHNOLOGY**

San Diego, California, USA
November 12-13, 1984

Edited by Herman V. Boenig, Ph.D.,
Professor, Golden State University, California

Published in the Western Hemisphere by
Technomic Publishing Company, Inc.
851 New Holland Avenue
Box 3535
Lancaster, Pennsylvania 17604 U.S.A.

Distributed in the Rest of the World by
Technomic Publishing AG

©1986 by Technomic Publishing Company, Inc.
All rights reserved

No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior written permission of the publisher.

Printed in the United States of America
10 9 8 7 6 5 4 3 2 1

Main entry under title:
Proceedings: The Second Annual International Conference of
Plasma Chemistry and Technology

A Technomic Publishing Company book
Bibliography: p.

Library of Congress Card No. 85-51980
ISBN No. 87762-445-3

The Second Annual
International Conference of
Plasma Chemistry and Technology

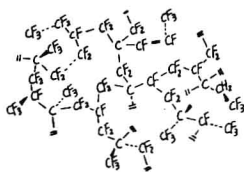
INTRODUCTION

The second International Conference of Low-Temperature Plasma Chemistry and Technology in San Diego, California, was highlighted by the enlightening lecture of Professor Herman F. Mark, who discoursed on the intriguing subject: "Research Projects for the Next Decade." The speaker, widely known and revered as the "Father of Polymer Chemistry" and honored on this occasion of his ninetieth birthday, was hailed by the chairman as one of the most decorated scientists of this century, recognized worldwide for his brilliant discoveries during the last six decades and honored by presidents and heads of state for his innovative genius and for the indelible marks he left as a renowned educator. Although Herman Mark's concept does not primarily apply to reactions in a plasma environment, the reactive species found in such glow discharges may well be ideally suited for many of Herman Mark's scientific approaches.

As always, the presentation by this nonagenarian eminence was electrifying, delivered without using his prepared text and with an *éclat* unchanged from the time I first observed and knew him thirty years ago. It was then that he became the quiet ambassador, travelling among the scientific communities of the world, spreading knowledge and wisdom.

The papers presented during this conference disclosed, perhaps for the first time, the deep penetration that low-temperature plasma technology has made worldwide and on a broad spectrum of applications. They also evidenced the considerable commitment to this technology, not only by countries known for their long record of scientific and engineering advancement but also by countries which have more recently evolved high technology, such as Poland, Czechoslovakia, Bulgaria, Hungary, Yugoslavia, Turkey, Korea, and China.

Professor Chen Jie from the Changchun Institute of Applied Chemistry in Jilin, People's Republic of China, disclosed in his work on ESCA characterization of plasma-deposited tetrafluoroethylene the structural model of the film formed in the glow region showing the presence of CH_2 , $-\text{C}-$, CF (CHF), CF_2 , and CF_3 groups:



Professor Tolmachev from the Leningrad State University in the USSR dealt with the ionization processes occurring from the collisions of metastable and resonant helium atoms with metal and heavy noble gas species, as well as with the formation of excited ions in Penning reactions. Using simple optical methods, the researchers showed that it is the helium atoms, not the electrons, that are the direct donors of excitation energy for the species.

Professor Lawless from the Carnegie-Mellon University in Pittsburgh described a most interesting computer program designed to determine plasma-reaction rates by estimating them using artificial intelligence concepts. In contrast to computer programs that merely recall reaction rates from tables, the estimates were derived from basic parameters such as atomic masses, electronegativities, bond energies, etc.

Professor J. Amouroux, the distinguished scientist from the Pierre et Marie Curie Université in Paris, outlined an original method of plasma polymerization at atmospheric pressures, providing the economic advantages of operating a plasma system without the need for vacuum equipment.

Another interesting and potentially significant development was reported by Professor W. James from the University of Missouri in Rolla. Professor James effected the synthesis of contiguous mirror-like thin zinc films from deposition of diethylzinc in a glow discharge. The films proved to be virtually free from carbon and oxygen.

Also, a most intriguing theoretical approach was offered by Professor Yu. L. Khait from the Ben Gurion University of the Negev in Israel. Dr. Khait presented a summary of recent developments of a new kinetic "Many-Body" theory of sputtering by low-energy plasma species involving particles in the energy range $\varepsilon = 1$ to 10^3 eV. In this context, the following observations have been made:

The most outstanding obstacle against a quantitative analysis of sputtering phenomena was the virtually complete lack of sound knowledge about the motion of low-energy (1–1000 eV) atomic particles in solids. Present improved understanding of sputtering is not so much due to an (still not very substantial) improvement in the knowledge of low-energy atomic motion, but rather due to the use of high-energy particle beams in sputtering.*

Professor Brosse from the Université de Maine in LeMans, France, reviewed work on surface modifications of natural and synthetic polymers in cold plasmas, such as commercial polymers, elastomers, elastomer additives in sulfur dioxide, tetrafluoromethane and oxygen plasmas.

Another interesting paper was submitted by Professor Inagaki from the Shizuoka University in Japan. He discussed his work on glow-discharge polymerization of fluorocarbons, such as tetrafluoromethane, perfluoromethylcyclohexane and perfluorotoluene. Another outstanding work was reported by Professor Hamann from the Technische Hochschule Karl-Marx Stadt in East Germany. His contribution deals with semiconducting glow-discharge polymerization films showing that polyconjugated polymers, doped with iodine, display a rapid decrease in mass due to loss of iodine when the temperature is raised. This is associated with a reduction in electrical conductivity. However, when phthalic acid dinitrile was used, the iodine-doped films remained essentially stable upon being heated to 525 °C.

Professor Spangenberg from the Bulgarian Academy of Sciences submitted a paper on important aspects of reactive ion etching of thin chromium photomasks. He and his colleagues used a two-layer resist system consisting of a submicron thin silver halide film deposited on a polyimide substrate, thus combining high resolution and sensitivity to light and electron beams with the outstanding masking ability of the polyimide layer during reactive ion etching. This scientist demonstrated that both the thermal stability and masking efficiency against intensive RIE processes are three times

*Ascribed by Khait to Sigmund.

greater when using this two-layer system, compared to what is observed in conventional photoresists. He pointed out that the two-layer resist system comprising an evaporated silver halide film and a masking polyimide sublayer represents a new alternative in RIE microstructures with micron and submicron dimensions.

Dr. Buerge, researcher from Switzerland, submitted a review on plasma polymer coatings used in transmission optics. He pointed out that both chemical selectivity and very low process temperatures are prerequisites of coating processes for the attainment of high optical quality levels in transmission optics.

The distinguished scientist from Vienna, Professor Czeija, discussed the status of development in the field of membranes for reverse-osmosis prepared in low-temperature plasma, a subject which the audience greeted with considerable response.

Perspective was provided with the help of Professor Eckert's magisterial account of the one hundred year history of low-pressure induction plasmas. The distinguished researcher from California moved from J.J. Thompson's pioneering inquiries to recent advances including his own models for determining electron densities and his experiments with a current-preserving plasma transformer that used ferromagnetic cores.

Finally, the chairman reviewed in greater detail the effects of a plasma environment on adhesive properties, showing that all phenomena related to adhesive properties, such as the total decontamination of surfaces, drying, activation of the surface particles of materials via processes like the formation of radicals and ions, wettability, introduction of polar moieties via ion implantation, grafting, surface molecular substitution, enhancement of the zeta potential of material surfaces, strengthening of weak boundary layers via crosslinking (CASING) and applications of primers, are induced and/or produced in a low-temperature plasma environment.

Herman V. Boenig

TABLE OF CONTENTS

INTRODUCTION.....	VII
SURFACE MODIFICATION OF POLYMERIC SUBSTRATES AND SILICON BY A NON-EQUILIBRIUM PLASMA IN AN ATMOSPHERE OF ORGANIC COMPOUNDS (APPLICATION TO TEXTILE AND PAPER INDUSTRY).....	1
F. Arefi and J. Amouroux, <i>Laboratoire de Génie Chimique, E.N.S.C.P., 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05</i>	
F. Rouzbehi, <i>Institut Textile de France, 35 rue des Abondances, 92100 Boulogne</i>	
M. Goldman, <i>Laboratoire de physique des Décharges, C.N.R.S., Ecole Supérieure d'Electricité, Plateau du Moulon, 91190 Gif/Yvette</i>	
RECENT ADVANCES IN THE EFFECT OF LOW-TEMPERATURE PLASMA ON THE ADHESION OF MATERIALS: PART 2.....	17
Herman V. Boenig, <i>The Research Institute of Plasma Chemistry and Technology, Box 1653, Carlsbad, CA 92008</i>	
SURFACE MODIFICATION OF NATURAL OR SYNTHETIC POLYMERS BY COLD PLASMAS.....	29
G. Legeay, <i>I.R.A.P. (Institut de Recherche Appliquée sur les Polymères), Route de Laval 72000 Le Mans, France</i>	
F. Epailard and J. C. Brosse, <i>Laboratoire de Chimie Organique Macromoléculaire, Université du Maine, Route de Laval 72017 Le Mans, France</i>	
MEMBRANES FOR REVERSE OSMOSIS.....	41
Karl Czeija, <i>Gusshausstrasse 12, A-1040 Vienna, Austria</i>	
PLASMA-POLYMERIZED THIN FILMS FROM FLUOROCARBONS.....	51
N. Inagaki, <i>Laboratory of Polymer Chemistry, Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatsu, 432 Japan</i>	
FORMATION OF CRYSTALLINE ZINC FILMS IN A GLOW DISCHARGE....	61
W. J. James and Pei-Li Tseng, <i>Departments of Chemistry and Chemical Engineering and The Graduate Center for Materials Research, University of Missouri-Rolla, Rolla, MO 65401, U.S.A.</i>	
ABLATION AND POLYMERIZATION MECHANISM OF OCTAFLUOROCYCLOBUTANE PLASMA POLYMERIZATION.....	71
Chen Jie, Yie Mu, and Lu Lizhen, <i>Changchun Institute of Applied Chemistry, Academia Sinica</i>	

Chen Chuanzheng and Yue Jin, Research Institute of Jilin Chemical Industry Corporation	
SEMICONDUCTING GLOW DISCHARGE POLYMERIZATION FILMS	81
G. Kampfrath, D. Duschl, and C. Hamann, <i>Sektion Physik/Elektronische Bauelemente, Technische Hochschule Karl-Marx-Stadt, GDR</i>	
J. Finster, <i>Sektion Chemie, Karl-Marx-Universität, Leipzig, GDR</i>	
RECENT PROGRESS AND APPLICATIONS OF THE KINETIC MANY-BODY THEORY OF SPUTTERING BY LOW ENERGY PLASMA PARTICLES	91
Yu. L. Khait, <i>Department of Physics, Ben Gurion University of the Negev, Beer Sheva, Israel</i>	
LEILA: AN EXPERT SYSTEM FOR ESTIMATING CHEMICAL REACTION RATES	115
B. E. Sauk, <i>Department of Electrical and Computer Engineering, Carnegie-Mellon University</i>	
J. L. Lawless, <i>Department of Mechanical Engineering, Carnegie-Mellon University</i>	
POLYMER SCIENCE AND ENGINEERING FACTS AND TRENDS	131
Herman F. Mark, <i>Polytechnic Institute of New York</i>	
REACTIVE ION ETCHING OF THIN CHROMIUM FILMS USING TWO-LAYER RESIST SYSTEM OF POLYIMIDE AND EVAPORATED SILVER HALIDE	137
B. Spangenberg and V. Orlinov, <i>Institute of Electronics, Bulgarian Academy of Sciences, Sofia 1184 Bulgaria</i>	
G. Danev, E. Spasova, and J. Malinovski, <i>Central Laboratory of Photoprocesses, Bulgarian Academy of Sciences, Sofia 1040 Bulgaria</i>	
PENNING IONIZATION AND EXCITED IONS FORMATION IN A LOW-TEMPERATURE PLASMA	145
Yu. A. Tolmachev, Ph.D., <i>Leningrad State University, USSR</i>	
THE HUNDRED YEAR HISTORY OF INDUCTION DISCHARGES	171
Hans U. Eckert, <i>3901 Via Pavion, Palos Verdes Estates, California 90274</i>	

SURFACE MODIFICATION OF POLYMERIC SUBSTRATES AND SILICON BY A NON-EQUILIBRIUM PLASMA IN AN ATMOSPHERE OF ORGANIC COMPOUNDS

(APPLICATION TO TEXTILE AND PAPER INDUSTRY)

F. AREFI AND J. AMOUROUX, *Laboratoire de Génie Chimique, E.N.S.C.P., 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05*

F. ROUZBEHI, *Institut Textile de France, 35 rue des Abondances, 92100 Boulogne*

M. GOLDMAN, *Laboratoire de physique des Décharges, C.N.R.S., Ecole Supérieure d'Electricité, Plateau du Moulon, 91190 Gif/Yvette*

ABSTRACT

The authors compare polymerization mechanisms with different substrates and reagents. Characteristics of polymeric films obtained from certain organic monomers at low pressure are presented. By the use of ESCA and IR analysis, they determine the nature of chemical bonds produced during these reactions with stress on the grafting of organic molecules to the substrate. Surface energy and dielectric properties, esp. dielectric losses, permitted the measurement of porosity of the deposited films. The nature of substrate (e.g., Si, NaCl) interferes directly in polymerization or etching processes. Polymerization of $C_2H_2F_2$ at atmospheric pressure by a corona discharge was carried out. By increasing the volume of the reactor and discharge power, the rate of polymerization and fluorine content, increase, reach saturation level and decrease. Pretreatment in hydrofluorocarbon 1,1 difluoroethylene gas at atmospheric pressure allows one to modify the hydrophobicity and dielectric properties of materials like paper.

INTRODUCTION

THE FORMATION OF THIN POLYMER FILMS IN A LOW PRESSURE HIGH-FREQUENCY glow discharge has been demonstrated for a wide variety of monomers and has been discussed in several recent reviews.⁽⁶⁻⁹⁾ This report describes first the characteristics of the polymeric films obtained from different organic monomers at a low pressure and secondly presents an original method of plasma polymerization⁽¹⁾ realised at an atmospheric pressure, which provides the economic advantages of operating a plasma system without the need for vacuum equipment or batch processing. Mono-crystalline silicon plates and the NaCl discs have been chosen as substrates in order to study the mechanisms of low pressure polymerization in an atmosphere of $CH_4 + CF_4$ and $C_2H_2F_2$. As for the polymerization of the organic gas $C_2H_2F_2$ at an atmospheric pressure, the polymeric substrates such as PET films and paper have been employed.

1. EXPERIMENTAL APPARATUS

Low Pressure Installation

The schematic of the radio-frequency low pressure glow discharge apparatus is shown in Figure 1. The reactor used was an electrodeless one. Power for the discharge was supplied by a Tocco-stel generator operating at 40 MHz. The film was deposited on substrates inserted in a hook-like sample holder (the location of the middle of the induction coil was taken as the zero point of the distance and the samples were placed 10 cm away). The reactor was designed with four different gas inlets. The pressure of the system was determined by a Divac-N gauge. Using this equipment, it was possible to operate over the range of 0 to 120 cm³/min at STP in flow rate and 10⁻¹ to 1 mbar. The experiments were carried out either by injecting the fluorocarbons through the coil and the methane laterally or vice versa.

High Pressure (Corona Discharge) Installation

For corona treatment a wire-cylinder corona discharge cell was used. It is placed in a controlled atmosphere (shown in Figure 2). The cell volume is almost 1 lit³. The cylinder is a stainless steel rotating roller (driven at 4 rev/min), 65 mm in diameter. It is covered with a dielectric (insulating) material (PET film $d = 50 \mu\text{m}$) and connected to the ground. The second electrode is a stainless steel wire (250 μm in diameter and 10 cm in length) generating an AC corona discharge in a 1 atm gas flow of appropriate composition for polymerization. The gap between the electrodes is adjustable from 1 to 10 mm. It should be emphasized that the time mentioned in the experiments is the duration of the rotation of the cylinder and not the exposure time.

In order to characterize the physico-chemical properties of the thin organic film obtained by the two installations, presented above, the following methods of analysis were used: IR and ATR spectroscopy, ESR, ESCA, contact angle measurements and SEM.

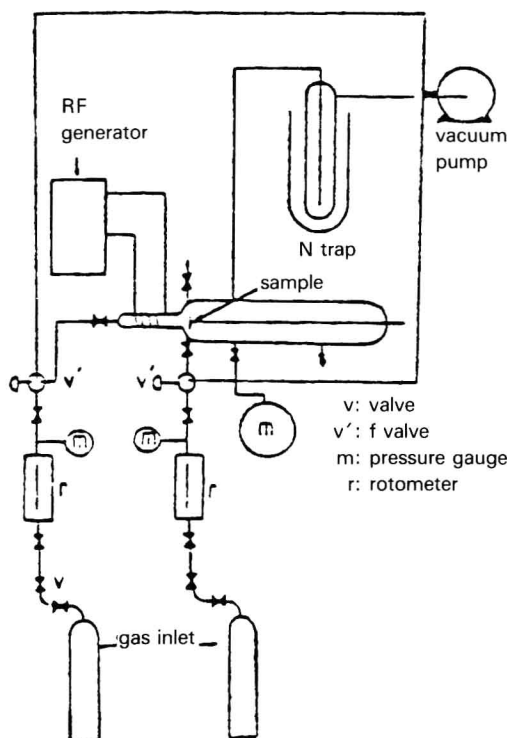


Figure 1. Schematic of the low pressure apparatus (glow discharge).

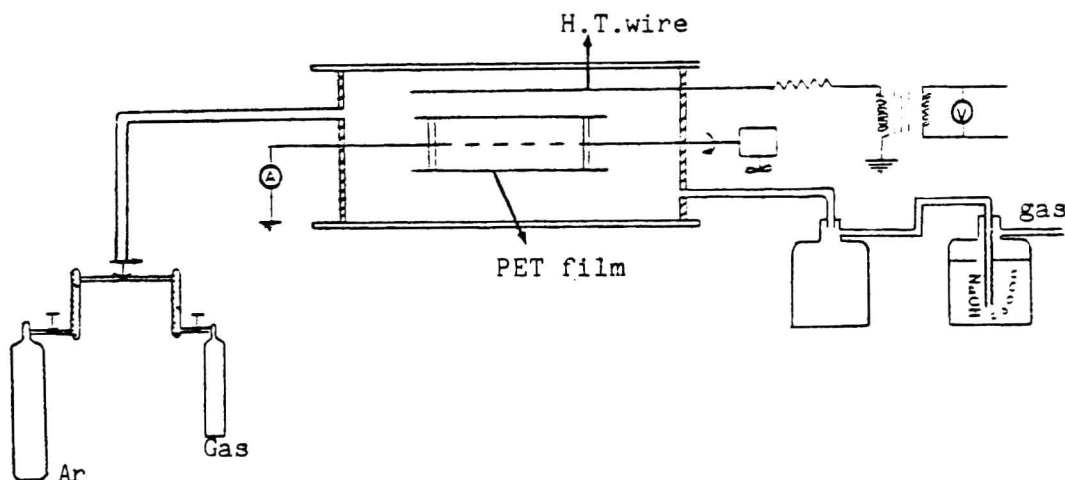


Figure 2. Schematic of high pressure apparatus (corona discharge).

2. LOW PRESSURE PLASMA POLYMERIZATION

By using the classical technique of molecular activation by plasma radiofrequency electrolysis, we have to point out the role of the excited molecule in the polymerization process.

a. CH_4/CF_4 Mixtures

The plasma reactor permits us to realize the same gaseous composition with the selective excitation of CH_4 or CF_4 .

The target substrate (NaCl or Si) is located at 10 cm from the coil region.

The excitation of CH_4 molecules by the plasma, and the injection of CF_4 at the outside of the plasma zone gives us a hydrocarbon polymer which contains a low concentration of fluorine (CF , CF_2 , etc.) radicals.⁽³⁾

The excitation of CF_4 molecules by the plasma, and the injection of CH_4 at the outside gives us a fluorocarbon polymer with a low concentration of CH_2 bonds (Figure 3).

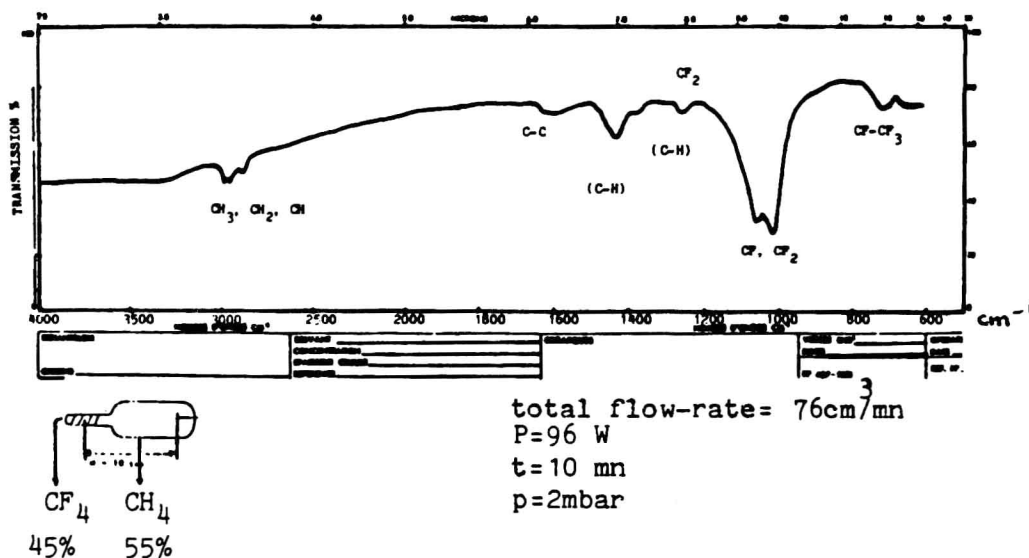


Figure 3. Infra red spectroscopy of the film deposited at low pressure.

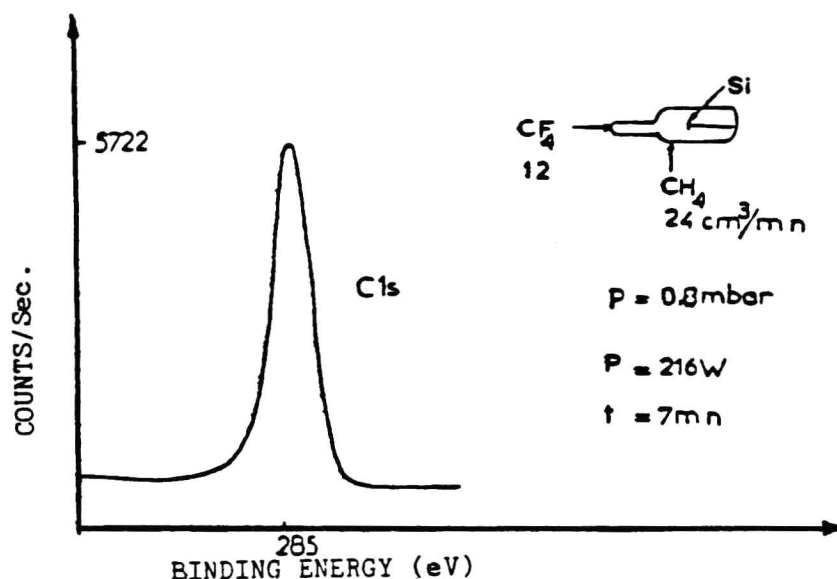


Figure 4. Typical C_{1s} ESCA spectrum for a film deposited on mono-crystalline silicon plates from a CH_4/CF_4 mixture.

This experimental data demonstrates clearly the role of the excited species in producing the polymers.

The radicals and the excited species produced by the plasma react easily and polymerize on the surface of the substrate.

However, in the case of silicone wafers, the formation of fluorocarbon polymer after a few minutes of treatment disappears to produce volatile molecules by reacting with the substrate and the fluorocarbon film. Thus the form of the C_{1s} portion of the ESCA analysis obtained were symmetrical showing a structure which contained mainly the $-CH_2-$ groups (Figure 4).^(7,8,9)

The plasma produces volatile compounds such as SiF_2 , SiF_4 , etc., and in this way the silicon is etched. The extent of the plasma polymerization or etching which takes place on the silicon plates varies with the different experimental parameters.^(3,11) The nature of the substrate and the nature of the excited molecule play an important role in the physicochemical processes in the plasma and on the polymeric structure obtained.

Monomer: $C_2H_2F_2$

The 1,1 difluoroethylene polymerizes easily with a rate of deposition in the order of $0.6 \text{ mg/cm}^2\text{min}$ on mono-crystalline plates. Contrary to the first mixture, where the C_{1s} peak of the ESCA analysis consisted of a single peak, by the decomposition of the C_{1s} peak of the polymeric film obtained it has been possible to identify four Gaussian peaks located at 292.0, 289.3, 287.4 and 285.0 eV (Figure 5). These peaks can be assigned to CF_2 , CF , $C-C$ and CH_x groups respectively.⁽⁹⁾ It can be pointed out also that at higher

F

powers the fluorine content of the polymer decreases due to the destruction of the intermediate oligomers and the elimination of the fluorine atoms in the form of volatile CF_2 and CF and HF components.

The polymer deposition rate in glow discharge polymerization of $C_2H_2F_2$ is presented in Figure 6 as a function of the applied power. This distribution curve represents a maximum probably due to a competition between the deposition of the polymer and its ablation at higher power ($P > 50 \text{ W}$).

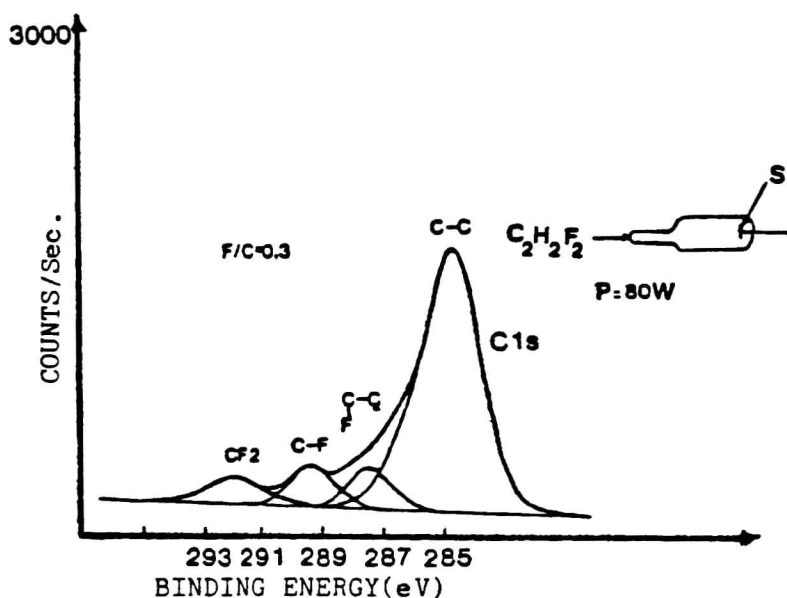


Figure 5. Decomposed $C1s$ ESCA spectrum for a film deposited on silicon plates from the monomer $C_2H_2F_2$.

The film prepared by the plasma polymerization of $C_2H_2F_2$ on the monocrystalline silicon was found by ESR to contain a considerable concentration of free radicals and consisted of a single symmetrical line approximately 15 G wide (Figure 7).

The peak obtained is similar to that observed by Yasuda for the same monomer ($C_2H_2F_2$)⁽⁷⁾ and can be assigned to the polyene-type radicals with long conjugational length, very stable, trapped in the polymeric structure bearing the form:

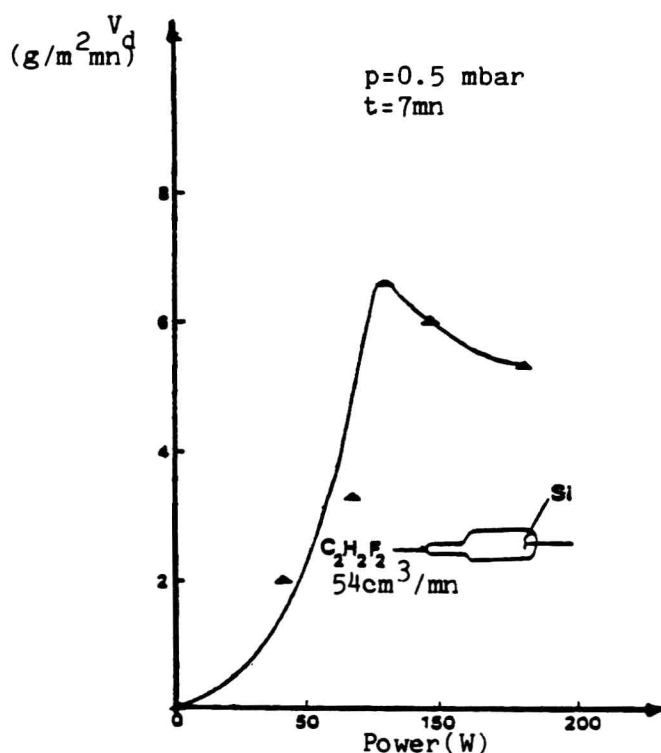


Figure 6. Polymer growth as a function of the power.

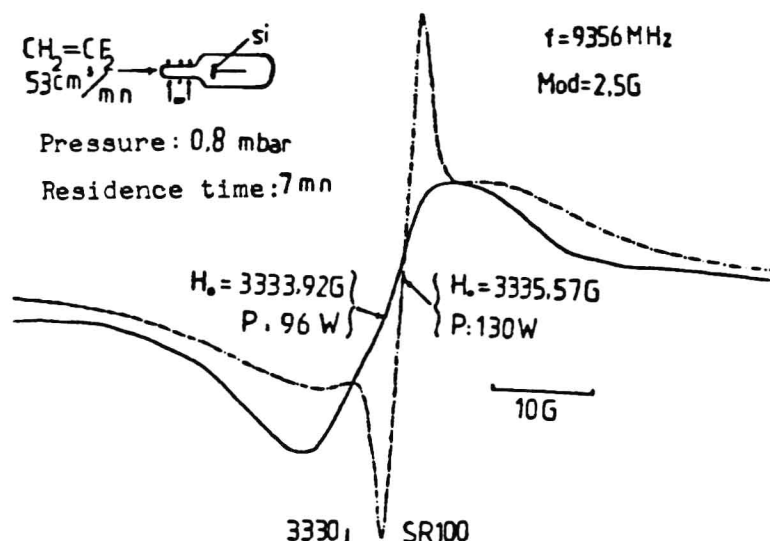
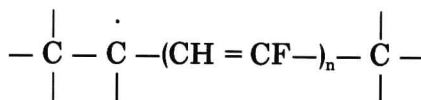


Figure 7. ESR spectra of a film deposited on silicon plates from $C_2H_2F_2$ monomer.



It has been found that at higher powers, the ESR peak of the polymeric film obtained presents a peak similar to that observed above (at $P = 96$ W) but also another single narrow ($\Delta H \cong 4$ G) line. For the appearance of the narrow peak the following hypothesis can be proposed.

1) At higher powers another type of polymer is formed with a smaller fluorine content (the larger the fluorine atom content of the radical, the larger the line width observed by ESR due to the large coupling constant of fluorine atoms). This is in agreement with the results obtained with the other methods of analysis (ESCA, polymer growth).

2) However, there is another hypothesis which is that due to a nonhomogeneous distribution of the radicals in the form of clusters at higher powers we can point out a narrowing of the peaks (Heisenberg exchange). This hypothesis however is less probable, because in all of the cases the radical concentration is not very important (a high gain has been utilized) and that in this case we should have seen only one narrow peak).

The rate of polymer growth shows a maximum and then decreases at high powers ($P > 50$ W), showing in this way the competition between the polymer deposition and the polymer or monomer ablation.

3. HIGH PRESSURE CORONA DISCHARGE POLYMERIZATION

Material: The PET films and the rolls of paper were treated in a corona discharge of a controlled atmosphere of the 1,1 difluoroethylene ($C_2H_2F_2$) gas. Our PET is a Terphane type (deposited trade mark: Rhone Poulenc Industries) $50 \mu m$ thick. Our paper roll consists of a non-impregnated paper (supplied by the Centre Technique de Papier) $100 \mu m$ thick (Figure 2).

The purpose of this work is to form a thin polymeric layer on the substrates in order to decrease the wettability and to improve their dielectric properties.

Between the different parameters of action, which play an important role in the polymerization of $C_2H_2F_2$ gas at an atmospheric pressure, electrical discharge parameters such as the current intensity and the interelectrode distance have been studied.

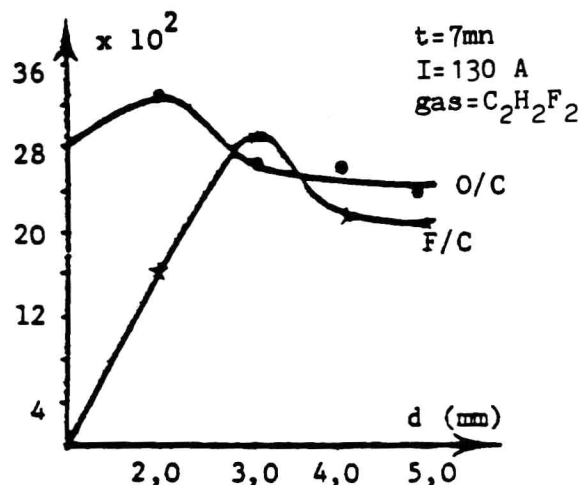


Figure 8. F/C and O/C ratio obtained by ESCA analysis in function of the interelectrode gap.

a. Interelectrode Distance

Figures 8 and 9 show the F/C and O/C ratios obtained by ESCA analysis for the PET films and the paper sheets respectively at different interelectrode distances. We can point out a maximum of the F/C ratio at an interelectrode gap $d = 3$ mm for both of the substrates. The O/C ratio also decreases slightly because of the hydrofluorocarbon polymer layer deposited on the substrate.

The superposition of the C_{1s} portion of a typical ESCA spectrum of the pretreated substrate on that of the non-pretreated one is illustrated in Figures 10 and 11 for PET and paper respectively. By examining these Figures we can identify new chemical bonds at 228 ± 0.3 , 289.6 ± 0.2 and 291.6 eV that can be assigned to C-C, CF and CF_2 groups respectively.

The surface free energy (calculated by means of the measure of the contact angle of a drop of liquid laid on the surface of the pretreated substrates) decreases extremely with respect to that of the non pretreated substrate and illustrates a minimum for the two substrates (PET and paper) at the same inter electrode distance $d = 3$ mm where the ratio F/C had been maximum (Figures 12 and 13).

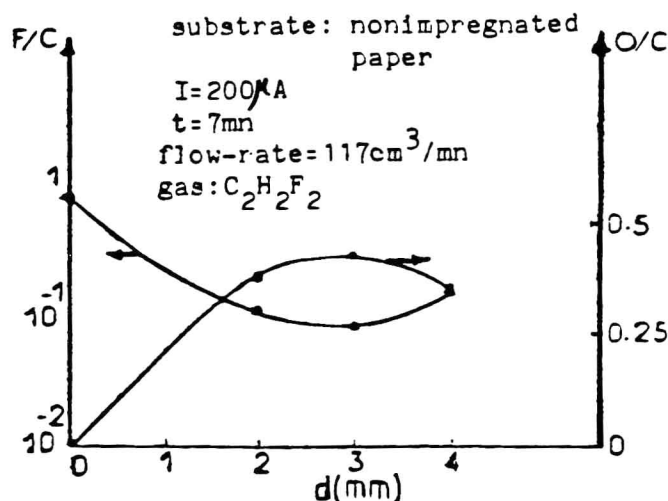


Figure 9. F/C and O/C ratios obtained by ESCA analysis as a function of the interelectrode gap.

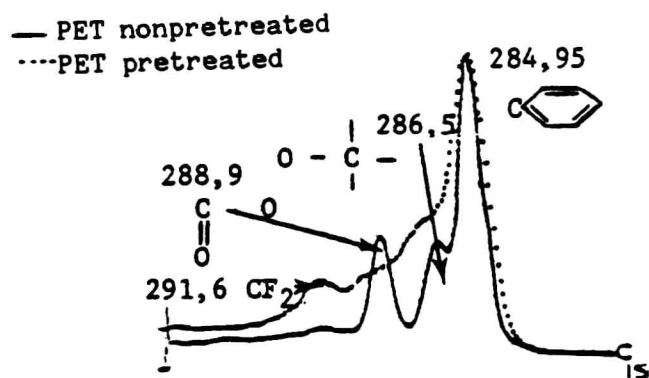


Figure 10. Superposition of the C_{1s} spectra of a pretreated PET film on a nonpretreated one. (ESCA analysis.)

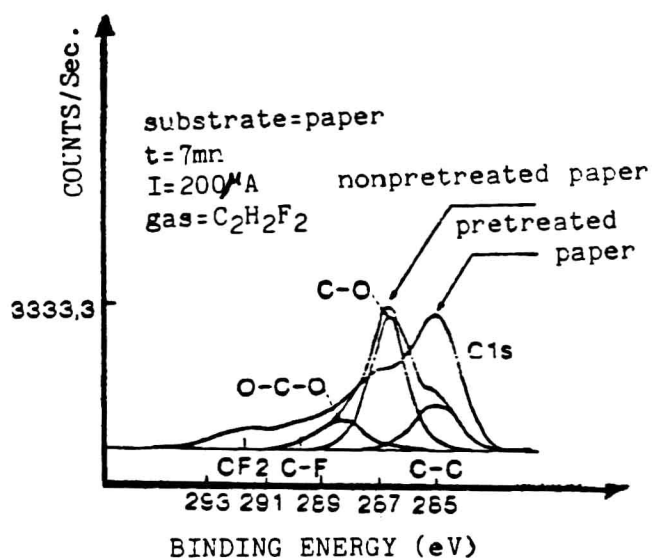


Figure 11. ESCA analysis of the carbon peaks for a pretreated sheet of paper and a nonpretreated one.

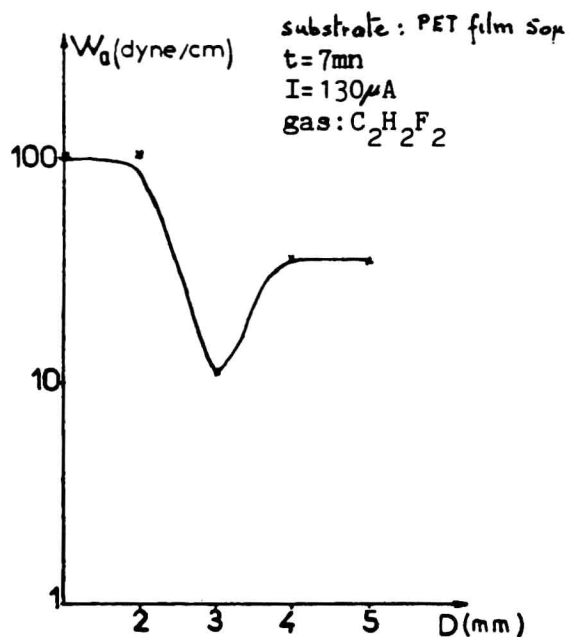


Figure 12. Surface free energy of PET film as a function of the interelectrode gap.