

Construction of a Plasma Polymerization Reactor System for Laboratory Use

F. HUBER and J. SPRINGER*

Technische Universität Berlin, Institut für Technische Chemie, Fachgebiet Makromolekulare Chemie, Straße des 17. Juni 124, D-10623 Berlin, Germany

SYNOPSIS

A parallel-plate plasma polymerization reactor operating at radio frequency was constructed. The reactor is suitable for reproducible plasma deposition of ultrathin pinhole-free polymer layers onto various supports. Feed gas composition, plasma power, total gas flow, pressure, and substrate temperature can be selected independently of each other. The radio-frequency voltage applied to the excitation electrode can be measured. Optical plasma emissions registered by a spectroscope may be used to monitor the plasma process. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Thin-film technology provides the possibility of changing the properties at the surface of a substrate material (as, for instance, friction coefficient or hardness) without altering its bulk properties by application of an ultrathin layer of another material. On the other hand, in some applications, certain properties of the film prevail (as, e.g., the gas permeability of a thin dense layer on a porous material) and thus dominate the properties of the whole composite. Here, the substrate serves merely as a support to the film, only supplying the mechanical stability of the composite.

Plasma polymerization is often regarded as a fairly effective, but somewhat intricate and extraordinary tool for the production of ultrathin pinhole-free layers. This may be attributed to the complexity of chemical reaction steps in the glow discharge preceding the formation of the polymer, as well as to the variety of technical and physical parameters influencing the reaction.¹⁻⁴ Therefore, to guarantee the reproducibility of the process, constancy or exact measurements of the process parameters are crucial. Technical quantities such as feed gas composition, electric power, flow of feed gas, pressure of plasma

gas, and temperature at the substrate position may be selected freely by the operator of the reactor. Others, such as frequency or reactor geometry, are fixed once a reactor system has been installed or depend on other quantities like operating voltage. Besides, to provide a more detailed insight into reaction mechanisms, information about the concentrations or densities of reactive particles and sometimes even the knowledge of their respective energy distribution functions is necessary. This information may be partly obtained by utilizing the so-called nonintrusive techniques, which do not influence or disturb the plasma, and partly by making use of methods which do so.⁵⁻⁸ In this article, a description of a straightforward self-constructed radio-frequency (rf) plasma reactor system meeting most of the above requirements is given in detail.

EXPERIMENTAL

Apparatus

The reaction chamber (Fig. 1) is assembled similar to a plate capacitor, consisting of two parallel electrode plates of polished aluminum (thickness 20 mm) separated by a cylindrical glass tube (outside diameter 250 mm; inside diameter 232 mm; height 30 mm), in this way creating the reaction volume. The round upper plate (diameter 250 mm) serves as the excitation electrode and as the lid of the chamber

* To whom correspondence should be addressed.

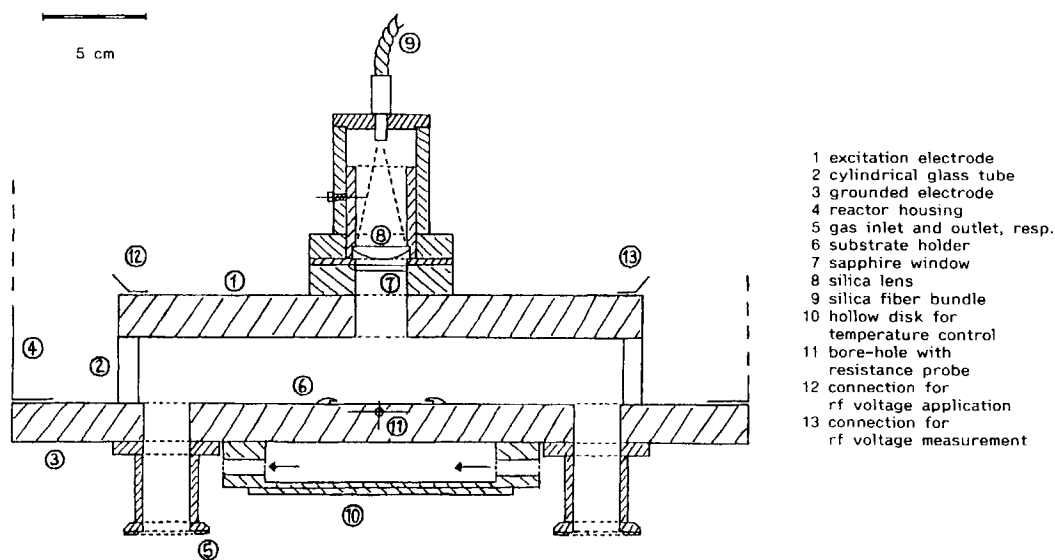


Figure 1 Schematic diagram of the reaction chamber.

simultaneously; the lower, grounded plate is the bottom of the chamber. Such a configuration gives a rather simple, laterally almost homogeneous electric field.

Usually, plasma deposition occurs nearly everywhere on the inner surface of the reaction chamber. Because of the homogeneity of the field, the plasma polymer is generated in a chemically uniform way and with constant thickness in the central part of the chamber. Moreover, the chamber volume is the same as the glow-discharge volume. For that reason, all the feed gas will flow through the glow-discharge region, thus taking up the electric energy more or less proportionately.¹⁻³

Two rings made of Viton are used as sealings between the electrodes and the glass tube. This fluorine-containing rubber exhibits low gas permeability and high chemical resistance. Aluminum, glass, and Viton are not corroded under the circumstances of plasma polymerization.

The grounded electrode makes part of the reactor housing (height 255 mm; width 350 mm and 350 mm, respectively) consisting of zinc-coated sheet steel (thickness 1 mm) surrounding the chamber and shielding the rf. The gas inlet and outlet are located in the bottom side of the chamber. To achieve symmetric flow with regard to its central part, feed gas is poured in via a gas distributor inside.

The substrate is fixed in the middle of the bottom onto the ground by a flattened annular holder. Round, disk-shaped substrates (maximum diameter 46 mm) can be coated there homogeneously, covering an area of 40 mm in diameter.

Under the grounded electrode, a disk-shaped tube is installed, which is run through by water, allowing cooling of the bottom down to 0°C as well as heating of it up to about 80°C. A bore-hole ending directly under the middle of the bottom is driven horizontally into the bottom plate. It contains a PT-100 electric resistance probe measuring the temperature with an accuracy of 0.5°C.

Plasma emissions may leave the chamber through a round sapphire window (diameter, 25 mm) in the lid. They are focused onto a UV-grade silica fiber bundle by a UV-grade silica lens above the window and led to an EP 200 Mmd spectroscope (Verity Instruments, Dallas, TX). Provided that the width of the entrance slit is 100 μm , emissions in the range from 185 to 920 nm can be measured with a resolution of 0.4 nm. The sapphire window, showing a transmission of 80% at 250 nm, limits the performance of the system in the UV region.

The spectroscope supplies relative emission intensities of particles participating in the plasma reaction, in this way making it possible to monitor the process nonintrusively. In addition to that, by applying actinometric optical emission spectroscopy, even relative concentrations of several reactive species may be calculated.⁹⁻¹⁴

The reactor is operated at 27.12 MHz, which is one of the most frequently used rf's. Electric power can be chosen between 0 and 200 W infinitely variable by an HF 200 E generator (Dressler Hochfrequenztechnik GmbH, Stolberg, Germany). It has to be applied to the excitation electrode via a metal-braided shielded cable to prevent losses by radiation.

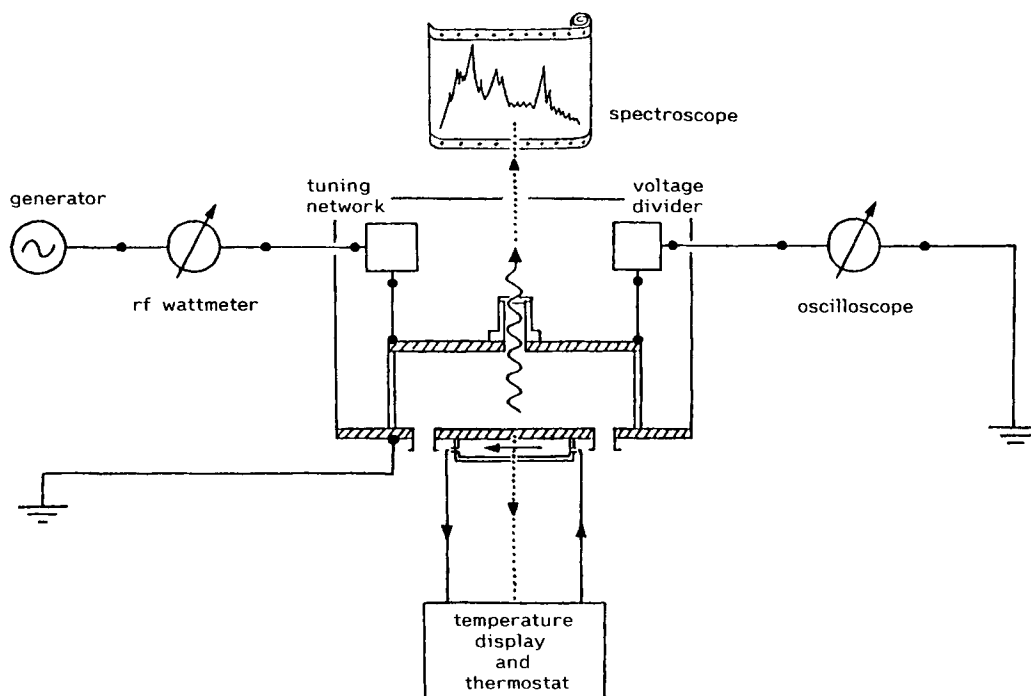


Figure 2 Arrangement of tools controlling and monitoring the plasma reactor system (vacuum system omitted).

Between the generator and the excitation electrode, a Π -type tuning network is inserted to match the complex input impedance of the entire reactor to the wave resistance (50 ohm) of the shielded cable (Figs. 2 and 3). If input impedance and wave resistance differ, power is lost to the plasma and reflected back into the generator, which may destroy it. Correct adjustment will result in a reflected power equal to zero.¹⁵ The power source is capacitively coupled to the excitation electrode through a blocking capacitor joined to the tuning network as is the standard procedure in most rf plasma systems.¹⁶ The forward power emitted by the generator and the reflected power can be metered with an accuracy of at least 5% by a ThruLine 4410-A Wattmeter (Bird,

Cleveland, OH) mounted between the generator and the tuning network.

An HM 1005 oscilloscope (Hameg, Frankfurt-Niederrad, Germany) serves for the registration of the rf voltage. The excitation electrode is connected to the oscilloscope via a capacitive voltage divider (to avoid load of the oscilloscope with high rf voltages) and a metal-braided shielded cable (length 3650 mm for full signal transmission, equal to one-half of wavelength in the conducting material) in series. The series connection was calibrated with a high-tension voltmeter.

The arrangement of the vacuum system is shown in Figure 4. In the range from 0.01 to 13.3 mbar, operating pressure is determined independently of

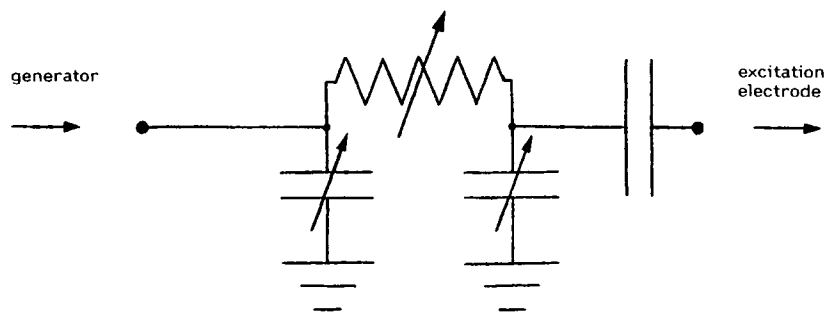


Figure 3 Π -type tuning network for adjustment of reactor input impedance, with blocking capacitor.

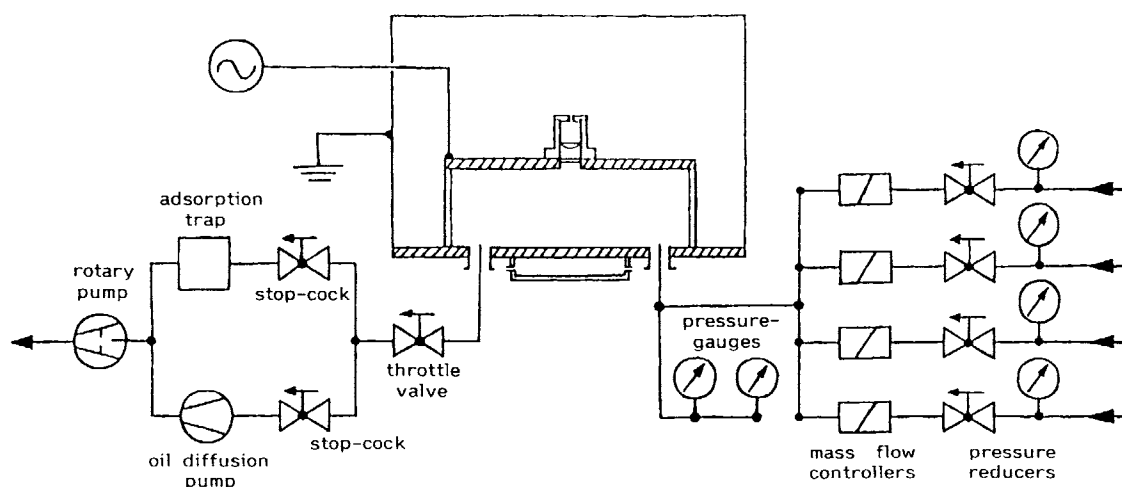


Figure 4 Schematic diagram of the vacuum system.

the type of gas using a CM 100 capacitive pressure transducer (Leybold, Cologne), whereas between 10^{-6} to 10^{-2} mbar, a Leybold Penningvac PR 32 pressure gauge working dependently on the type of gas is utilized.

Feed gas is admitted passing through WFC 020 mass-flow controllers (Manger und Wittmann, Garching-Hochbrück, Germany). The pertinent Wigha 2000 electronic control unit enables choice of gas flow from about 2 to 100 mL (STP)/min for up to four gases at once.

During operation of the reactor, the product gas is led through a zeolith-filled adsorption trap and pumped with a D 6 Leybold rotary pump. The rotary pump is filled with mineral oil which will get dirty as a result of the plasma process and, hence, has to be changed frequently. To permit adjustment of operating pressure independently of gas flow and performance of the pump (which depends on the type of gas), a throttle valve is installed between the reactor and the pump. To evacuate the reaction chamber, a Leybodiff 170 oil-diffusion pump of Leybold may be connected in series with the rotary pump. The oil-diffusion pump can only be used when the plasma is not ignited. Minimum pressure in the reactor chamber is about 1.5×10^{-4} mbar.

Plasma Polymerization

To investigate their gas permeability and gas selectivity, plasma polymers were deposited from C_2F_6/H_2 mixtures onto microporous Anodisc 47 aluminum oxide membranes (Anotec Separations Ltd., Banbury, UK) as a support. Feed gas composition was varied using mixtures of hexafluoroethane and hydrogen at 30 different volume ratios between 1 : 2

to approximately 6 : 1, whereas all other process parameters were held constant (plasma power 16.5 W; operating pressure 1.1 mbar; substrate temperature $20^\circ C$; total gas flow 20 mL [STP]/min). In each case, the polymerization time was 2 h. To carry out actinometric optical emission spectroscopy (AOES), small quantities of 0.75–1.5% argon were added (see below). To remove hydrocarbons and dust, the aluminum oxide membranes were rinsed with tetrachloromethane before use. Results of gas permeability and gas selectivity measurements will be published soon.

AOES

Optical emission spectroscopy (OES) yields relative emission intensities which are proportional to excitation rates of the emitting particle or, in other words, to relative concentrations of its excited state. However, since the majority of particles are not excited, from the chemical viewpoint, in most cases, relative concentrations of ground-state species will be of much greater importance. Provided that certain preconditions are satisfied, actinometric OES (AOES) will produce relative ground-state concentrations of the species of interest. To transform excited-state into ground-state concentrations, the relative emission intensity from the observed particle is divided by the relative emission intensity from an inert gas (the actinometer) which is admixed to the plasma in small amounts. This will take into account a change in emission intensity not caused by an actual change in species concentration, but by a change of excitation efficiency of electrons resulting from a change in electron density or electron energy distribution function.^{9,10,12,14}

Argon (750.4 nm) and hydrogen (656.3 nm) atomic lines¹⁰ were used to perform AOES. Both emission cross sections show a similar dependency of excitation cross section on electron energy (threshold values of electronic excitation: Ar 13.47 eV; H 12.09 eV).^{17,18} Division of relative hydrogen emission intensity by relative argon emission intensity will yield relative concentrations of atomic hydrogen in its electronic ground state.

X-ray Analysis

The content of carbon and fluorine in the plasma polymers was determined with a Kevex Delta 5 X-ray analyzer. Electron energy was 10 keV, corresponding to an information depth of about 2 μm . The analyzed area of the sample amounted to around 100 μm^2 . For better electric conductivity, the samples were coated with a thin carbon layer (thickness of around 10 nm). Since the sum of element percentages has never been exactly 100%, ratios of fluorine to carbon molar content were calculated, which are more reliable.

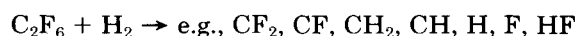
SEM

SEM was employed to determine the layer thickness of the deposited plasma polymers. The aluminum oxide membranes coated with plasma polymer were broken and their surface of fracture being perpendicular to the layer surface was micrographed. To achieve good electric conductivity, the samples were sputtered with gold before examination. The measurements were done on a Hitachi S-2700 scanning electron microscope. Layer thickness was divided by deposition time (2 h) to yield the deposition rate.

RESULTS AND DISCUSSION

Reproducibility

The first reaction step of plasma polymerization of hexafluoroethane/hydrogen mixtures¹⁰⁻¹³ produces numerous radicals and molecules by gas-phase decomposition of the feed and subsequent reaction of these decomposition products with each other:



Pure hexafluoroethane does not polymerize (or at best slowly) because atomic fluorine generated in the plasma will etch the plasma deposition.

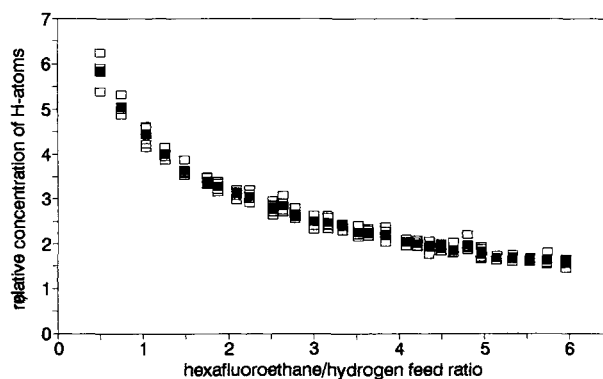


Figure 5 Relative concentration of hydrogen atoms in the plasma calculated by AOES as a function of hexafluoroethane/hydrogen ratio in the feed gas. Hollow symbols: single measurements; filled symbols: mean values.

In a further step, combination reactions of the carbon-bearing radicals cause the deposition of highly crosslinked plasma polymers containing fluorine and hydrogen:



Since atomic hydrogen is one of the most frequent radicals in the gas phase and since it is probably to be found in a steady state with the other plasma particles, its amount in the plasma seems to be a suitable standard to check the reproducibility of chemical and physical plasma conditions. In Figure 5, the relative concentration of atomic hydrogen calculated by AOES vs. the mixture ratio of the feed gas is depicted. As expected, the content of atomic hydrogen in the plasma decreases as the amount of molecular hydrogen in the feed gas is reduced. The single measurements show only trifling deviations

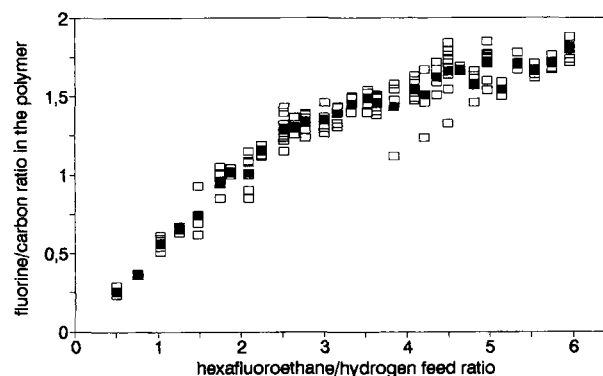


Figure 6 Fluorine/carbon ratio from X-ray analysis of the plasma polymers as a function of hexafluoroethane/hydrogen ratio in the feed gas. Hollow symbols: single measurements; filled symbols: mean values.

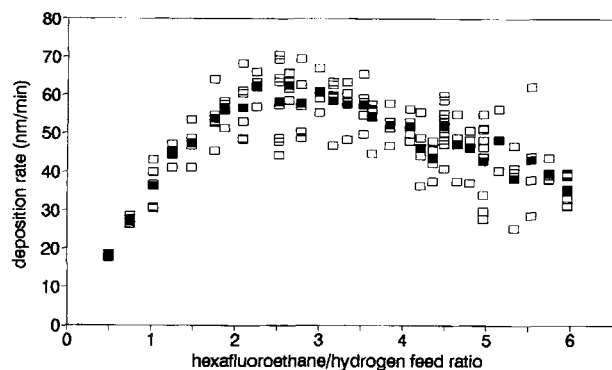


Figure 7 Deposition rate of the plasma polymers determined by SEM as a function of hexafluoroethane/hydrogen ratio in the feed gas. Deposition time: 2 h; hollow symbols: single measurements; filled symbols: mean values.

from the mean values, demonstrating in this manner very good reproducibility of plasma conditions.

If the chemical and physical plasma parameters are reproducible, the same should be found out concerning the composition of the plasma polymers. Figure 6 represents the fluorine-to-carbon ratio of the plasma deposition as established by X-ray analysis vs. the mixture ratio of the feed gas. Except for three or four single measurements (out of 150), the deviation from the mean values is shown to be small.

Deposition Rate

Figure 7 shows the deposition rate of plasma polymer as stated by SEM vs. the feed gas ratio. In comparison with values cited in the literature,² the deposition rate is sufficiently high. The curve displays a maximum, indicating at this point an optimum concentration of polymer-forming species in the plasma.

With regard to the atomic hydrogen concentration as well as to the plasma polymer F/C ratio, the poorer reproducibility of the deposition rate is a little surprising. These irregularities are more likely to be due to inaccuracy of SEM measurements rather than to actual deviations, because the plasma polymers often exhibited a very rough surface, thus making the determination of layer thickness fairly difficult. Moreover, even if the values represent correct deposition rates, for many applications (as in the present case for gas permeability measurements), reproducibility may be high enough.

SUMMARY AND CONCLUSIONS

The described plasma polymerization reactor system displays high and easy reproducibility of results as

well as simplicity of construction. It permits control of process parameters such as feed gas composition, electric power, flow of feed gas, pressure of the plasma gas, and temperature at the substrate position. In addition to that, operating voltage can be measured. The reactor works at 27.12 MHz, a frequency often used for plasma polymerization. The configuration of the reaction chamber is selected so that chemical homogeneity of the produced plasma polymer should be the best. The components of the reactor system are resistant to the plasma polymerization conditions. A spectroscopist allows one to monitor the plasma process nonintrusively on the basis of optical plasma emissions. In some cases, even relative concentrations of reactive plasma species may be determined by means of AOES.

In the case of hexafluoroethane/hydrogen mixtures, the reproducibility of the physical and chemical plasma parameters can be demonstrated by calculation of the relative concentration of atomic hydrogen in the plasma. The reproducibility of the composition of the plasma polymers is revealed by X-ray analysis.

The deposition rate is sufficiently high. At first glance, it seems to be less reproducible than the atomic hydrogen concentration and plasma polymer F/C ratio. On the other hand, irregularities of single measurements are attributed more probably to difficulties in the determination of the layer thickness by SEM than to actual deviations of the deposition rate.

F. H. gratefully acknowledges the generous financial support by the Deutsche Forschungsgemeinschaft and the Technische Universität Berlin, without which this publication would not have been possible.

REFERENCES

1. H. Biedermann and Y. Osada, *Plasma Polymerization Processes*, Elsevier, Amsterdam, 1992.
2. R. d'Agostino, *Plasma Deposition, Treatment, and Etching of Polymers*, Academic Press, San Diego, CA, 1990.
3. H. Yasuda, *Plasma Polymerization*, Academic Press, Orlando, FL, 1985.
4. A. T. Bell, *Top. Curr. Chem.*, **94**, 43 (1980).
5. R. W. Dreyfus, J. M. Jasinski, R. E. Walkup, and G. S. Selwyn, *Pure Appl. Chem.*, **57**, 1265 (1985).
6. R. A. Gottscho and T. A. Miller, *Pure Appl. Chem.*, **56**, 189 (1984).
7. B. E. Cherrington, *Plasma Chem. Plasma Proc.*, **2**, 113 (1982).
8. R. M. Clements, *J. Vac. Sci. Technol.*, **15**, 193 (1978).

9. J. Röpcke and A. Ohl, *Contrib. Plasma Phys.*, **31**, 669 (1991).
10. R. D'Agostino, F. Cramarossa, and F. Illuzzi, *J. Appl. Phys.*, **61**, 2754 (1987).
11. R. d'Agostino, S. De Benedictis, and F. Cramarossa, *Plasma Chem. Plasma Proc.*, **4**, 1 (1984).
12. R. d'Agostino, F. Cramarossa, V. Colaprico, and R. d'Ettole, *J. Appl. Phys.*, **54**, 1284 (1983).
13. R. d'Agostino, F. Cramarossa, and S. De Benedictis, *Plasma Chem. Plasma Proc.*, **2**, 213 (1982).
14. J. W. Coburn and M. Chen, *J. Appl. Phys.*, **51**, 3134 (1980).
15. U. Freyer, *Nachrichten-Übertragungstechnik*, 2nd ed., Carl Hanser, Munich/Vienna, 1988.
16. K. Köhler, J. W. Coburn, D. E. Horne, E. Kay, and J. H. Keller, *J. Appl. Phys.*, **57**, 59 (1985).
17. A. A. Radzig and B. M. Smirnov, *Reference Data on Atoms, Molecules and Ions*, Springer, Berlin, 1985.
18. A. N. Zaidèl, V. K. Prokofèv, S. M. Raiskii, V. A. Slavnyi, and E. Ya. Shreider, *Tables of Spectral Lines*, 3rd ed., Plenum Data Corp., New York, 1970.

Received February 13, 1996

Accepted April 23, 1996