THE BASIC REACTOR FOR KINETIC STUDIES OF PLASMA–SURFACE INTERACTIONS

Georgy K. Vinogradov
Department of Electrical Engineering and Electronics,
Nagoya University, Nagoya 464-01, Japan

ABSTRACT
A box-type plug flow RF reactor was proposed for kinetic studies of plasma-surface interactions. Spatial distributions of plasma parameters including "chemical activity" under different discharge conditions are discussed. The reactor can be recommended as the basic one for plasma chemical laboratories to study mechanisms of plasma-surface interactions and gas phase transformations.

INTRODUCTION
Gas discharge systems represent very complex self-consistent objects including an interacting surface. It is hopeless to change one of their parameters without corresponding variations of others. So, the preferable way to study intrinsic mechanisms must go only through a maximum possible simplification of discharge reactors in order to transfer them into well defined objects, interpretable from the point of view of basic physical and chemical methodology.

Many deposition processes have been realized under glow discharge conditions. And still several basic problems exist with processes carrying out on the reactive surface. These problems are not so rigid recently in plasma chemical etching but still far from a reasonable clarification in cases of plasma polymerization and other film depositions processes. The reasons consist of the shortage of experimental approaches and methods of diagnostics specially designed for these objects. It is now usual case when the most powerful methods of experimental investigations have being applied to such plasma chemical systems which in principle can not be treated as something definite. More than this, a lot of experimental data publishing in literature can not be used by other researchers, nor for a modelling, neither for a simple understanding of phenomena.

Any plasma-chemical object is kinetic in nature principally. A kinetic approach demands at first a careful selection of the reactor used. And the purpose of an investigation must be clearly distinguished: application and process control or a mechanistic study. This demand follows from the real situation, that the majority of industrial reactors are not suitable for mechanistic studies (excluding in some extent very low pressure discharges).

Various realizations of flow type cylindrical reactors are the most representative model systems suitable for an achievement of reproducible stationary state and well controlled kinetic conditions. And only plug flow reactors can be used for a studying of gas phase transformations and general mechanisms. DC and RF discharges in cylindrical gas flow type reactors are well developed and studied. However, recently a great variety of their realizations exist. It does not allows one to transfer experimental results and use them for a modelling of mechanisms without reasonable criteria and in the absence of a theory of similarity for plasma-chemical systems.

Some proposals exist to use an axially symmetric capacitively coupled parallel plate RF discharge under a bell jar as a referent system. The
idea of axial symmetry is going from industrial needs on a large area uniform deposition. But it is suitable within some limitations only for a very low pressure processing (in order of $10^{-3}$ Torr and lower) when it is possible to neglect for gas phase chemical reactions. In case of glow type discharges this reactor is unsuitable for investigations of mechanisms of plasma chemical processes. Different areas of such reactor are characterized with different conditions, plasma volume and real residence time are indefinite. Plasma particles and products are travelling through different zones of the chamber and possess a very wide residence time distribution function. Particulate formation in a gas phase makes the situation unpredictable at time. And the kinetic analysis is unapplicable though there are some time variations of some parameters. The presence of chemical reactions in a gas phase introduce in a physical discharge system a vast range of fast ($10^5-10^7$ s), slow ($10^3-10^5$ s), and very slow ($1-10^3$ s) processes, which inevitably change physical parameters in a great extent. Power distribution and mass transfer processes become the most influential factors.

The cylindrical geometry of the gas flow type reactors itself does not guarantee kinetic conditions. Usually, a distribution of power density from the energy source is not uniform along the gas flow.

Discharge systems were studied by several authors to find out reasonable kinetic characterization [1–7] and to select experimental conditions for most informative results. However, the more or less universal reactor suitable as a representative kinetic plasma-chemical object for comparative studies was not proposed. Here we are describing well examined and practically accomplished box-type reactor which do satisfy almost all critical points of our consideration, and which can be recommended as a referent reactor for plasma-chemical researches.

**BOX-TYPE RF CAPACITIVELY COUPLED REACTOR**

Fig. 1 shows the box-type reactor. It was realized in several modifications [8–10] for plasma polymerization and etching processes. In Fig. 1 there are indications: 1 – grounded temperature stabilized electrode; 2 – copper RF shield; 3 – teflon case; 4 – gas input; 5 – gas distributor; 6 – heated electric probes with different areas; 7 – through orifices for optical spectroscopy; 8 – electrically insulated and independently temperature stabilized stage for the flat probe-substrates; 9 – copper mesh to prevent plasma from spreading outside the reactor; 10 – gas flow; 11 – mechanical shutter. The plasma volume is well defined and limited from all six sides. It gives magnitudes of specific parameters and a possibility for their uniform distribution. The spatial uniformity is well controlled by optical spectroscopy and contact methods.

The reactor was shaped as a rectangular channel limited by a copper temperature stabilized electrodes, teflon back and side walls and a copper mesh at the gas exit side. Side walls were 20 mm thick to prevent RF field distortions, heat exchange and initiations of plasma outside the reactor. Gas is supplied through a distributor with numerous small (diameter
is about 0.3 mm) orifices to produce a uniform flux just from the wall of the reactor. The uniformity of the gas flux was supported by uniform distributions of both deposition and etching profiles across the reactor under different discharge conditions.

The discharge gap was usually about 20 mm, width 60-80 mm, length 120-140 mm. The excitation frequency 40.68 MHz to avoid a strong sheath formation and to preserve organic films from energetic positive ion bombardment. This frequency is really "high" in compare with industrially used 13.56 MHz, which usually can be characterize as an transient frequency from low to high. Probe measurement also easier to carry out with this higher frequency.

Reactor walls have through orifices for an optical spectroscopy. It appears to be unacceptable to use any optical windows because of their rapid contamination or etching. The area of diagnostic orifices is much smaller than the output cross section of the reactor. So, they don't disturb too much the gas flux.

An additional advantage of the reactor consists of the possibilities to mount very easily and quickly any probes and additional movable instruments without taking care for a gas leaks. Also, the elevated pressure in the reactor in compare with a bell-jar pressure makes sure for a gas purity inside the reactor because an atmospheric air penetrating under the bell-jar does not go inside the reactor in case of high enough gas flow rates.

Plasma-surface interactions as well as gas phase transformations can be studied in this reactor under the well defined kinetic conditions. To demonstrate this possibility we consider some spatial distributions of plasma parameters, which give not only a quantitative view for it, but shows some approaches for mechanistic studies as well.

**SPATIAL DISTRIBUTIONS OF PLASMA PARAMETERS**

To control plasma and process parameters several specially designed methods were used. Traditional tools such as heated Langmuir probes, heated wire-calorimeter, thermocouples, optical emission spectroscopy, gas chromatography [9,11] etc. were used. Also, very simple express method for a spatial distributions of plasma chemical activity was used: the method of thin wires [12]. It can be easy realized in any discharge setup without special preparations. Very thin wires (metall or dielectric) satisfying in dimensions the Langmuir criteria for thin probes can be hanged up in any directions. The wires will interact with plasma as a Langmuir probes under the floating potential (in case of plasma polymerization they will be electrically insulated from plasma by dielectric film). In such case, the thickness distributions on these wires will reflect local plasma properties not distorted by the interacting surface. And there is no trouble from a shunting of electric fields. Plasma interact with thin wires (probes) through a highly resistive sheath. The sheath certainly preserve plasma from shunting by thin wires.

Kinetic probes were recog-nized as the most powerful dia-agnostic tool for plasma-surface interactions [9,13,14]. And the kinetic gas
chromatography with a gas probing along the gas flow was demonstrated as the most powerful gas phase diagnostics in case of very complex chemical systems, that is apparently for any plasma polymerization system [8, 11, 16, 17].

Fig. 2 shows spatial distributions of film deposition rate across the gas flow in parallel to electrodes. The distribution along the silicon plate has a uniform part except of the presheath area of about 10-15 mm from both walls. Very interesting features of local maximums of the deposition rate on the thin RF discharge. This distribution is formed under the influences of several discharge parameters. Two of them determine the appearance of maximums: gas temperature distribution, which suppress film formation, and the distribution of positive ions bombarding the surface and activating surface sites. The mechanism of film formation is discussed elsewhere [9, 15]. However it is clear, that variations of the reactor width will extend the central uniform part of deposition keeping practically the same near wall areas.

Shape and position of maximums depends on discharge parameters. Next Fig. 3a, b shows a similar distribution in case of a poor 1% mixture of octa-fluorocyclobutane with argon. In this case maximums are more apparent and perhaps indicate also higher dissociation and excitation rate in a movable sheath area of RF power pumping.

Distributions across the discharge gap also have been measured (Fig. 3b). Their shape is practically the same as for ones shown above. An asymmetry of the growth rate demonstrates very insignificant difference between RF and grounded electrode sheaths.

Fig. 4 demonstrates clearly that chemical transformations of initial organic compound were completed just near the gas entrance. It means that to study kinetics and mechanisms of plasma chemical transformations of poor mixtures one need very short residence time measurements. Otherwise the most informative initial stages of decompositions would be completely lost and their mechanism can not be reproduced from the later stages. More than this. In the last case initial chemical transformations practically were completed in a sheath area. It means that any use of uniform plasma characteristics for the description of the process would be incorrect as well. It was interesting to note, that such strong chemical transformation can proceed under very stable and uniform plasma conditions as one can see from the distributions of the ArI and even CF2 carben
emission. It is clear that correlations between CF2 emission and the growth rate does not exist here, so that the polymeric film is growing without a direct participation of CF2 carben, it was shown definitely elsewhere [8,11,16]. The possibility to control plasma uniformity is important to guarantee from wrong interpretations. In case of non-uniform power distribution, for example, "full glow" and "non-full glow" [7] process parameters can not be addressed to some definite object.

In case of different substrates size and location one can not compare kinetics of film growth or etching without taking into account a whole distributions in space, and dependencies of the process kinetics on substrate size or geometry. Only corresponding distributions can be considered as an adequate representation of plasma chemical objects. Fig.4 demonstrates a variety of distributions obtained in a comparatively low pressure discharge. These conditions are not precisely plug flow. Some longitudinal mixing still exist. However the mixing dose not suppress too much longitudinal variations. And here again, in spite of uniform plasma density, that is determined from an Ar emission, the film growth rate is changing more than one order of magnitude on the wire-substrate, and it is comparatively small smooth changing on the silicon plate. And both profiles have no correlations with a CF2 emission. In this case longitudinal kinetic variations demonstrates complicated combinations between several discharge parameters. This combinations are controllable and very informative under the stationary state conditions.

To distinguish real plug flow conditions one need to control longitudinal distribution of some representative chemical kinetic parameters. It can be only sometime deposition or etching rate, but the adequate parameters can be derived only from the gas composition. In the box-type reactor we studied the gas phase composition of a series of fluorocarbons beginning from few milliseconds. Initial parts of kinetic curves describing chemical transformations easily prove the vicinity of plug flow conditions: practically all kinetic curves are going from the zero time point and look like straight lines. Along with an increasing residence time kinetic curves elucidate well interpretable gas phase chemical synthesis. Any models of mechanism of plasma-chemical transformations or can be examined on the basis of such definite and detailed data without too wide speculations and unfounded implications.

**CONCLUSION**

Both gas phase and heterogeneous plasma chemical kinetics of glow type discharges are too complex to be studied without necessary experimental simplifications. It means the necessity to transform investigated system close to the well defined physical and chemical objects which can be really treated as well defined kinetic objects. Very simple and convenient "box-type" reactor discussed above may be recommended for research studies of deposition and etching processes with gas phase reactions as
a representative type of a plug flow reactor with a wide range of residence time. This reactor was developed not for the uniform deposition or etching, but for a studying of origins of non-uniformities.

REFERENCES