COMPREHENSIVE STUDY OF REACTION KINETICS OF SIMPLEST UNSATURATED FLUOROCARBONS IN NON-EQUILIBRIUM PLASMA. MECHANISM OF HETEROGENEOUS STAGES OF PLASMA-SURFACE INTERACTIONS.

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INTRODUCTION

The gas discharges reaction kinetics of saturated simplest fluorocarbons (**CF4, C2F6, C3F8**) has been deeply studied because of their significance for the dry etching processes. However, in the opposite case of thin fluorocarbon film growth (plasma polymerization) the mechanisms of reaction kinetics still remain unclear.

Assuming that plasma chemical reaction kinetics in complicated mixtures of organic compounds can be understood only as a multi-channel multi-stage self-consistent process, we put to the forefront here the heterogeneous stages of reaction kinetics of unsaturated fluorocarbons: **C2F4, C3F6, c-C4F8, C8F16** with respect to the roles of electrically charged and neutral particles. The complexity of the object makes the problem strongly adhered to speculative modeling in circumstances of the lack of reliable experimental data on the particular effect of each particle fluxes. This kind of experimental data has been obtained in the resent study. Here we present the most credible generalizations justified by the experimental data.

KINETIC CONDITIONS AND APPROACHES

Among the reactors utilizing glow type discharges there are only a few interpreatable in terms of chemical kinetics. Such reactors possess well defined gas dynamics and uniform distribution of physical parameters, main of which is the specific discharge power. It is common knowledge that only two types of ideal flow chemical kinetic reactors exist. They are the ideal mixing and ideal replacement or plug flow reactors. The only second one can be characterized by the kinetic residence time parameter and represents the most definite kinetic object.

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Traditional DC discharge tubes represent the simplest reactors operating under the plug flow conditions which are determined by the ratio between a linear gas velocity and longitudinal diffusion. They should be the most favorable objects for the detailed studies of reaction mechanisms. However, they have two general experimental imperfections: 1) it is very difficult, if possible, to maintain a steady state DC discharge in electronegative gases; 2) initial chemical transformations proceed in the plasma zone with indefinite entrance boundaries.

The box-type RF discharge reactor [1], being the tubular shaped reactor accomplished by the strictly limited entrance plasma boundary, meets the majority of experimental demands for kinetic investigations. It is the next step in the development of the plug flow reactors proposed earlier [2-4]. The reactor admit real time steady state kinetic observations beginning from about 2 *ms*. In each experiment it can give a wide range distance (time) resolved kinetic distributions. Such distributions are the most informative kinetic data concerning the mechanism of chemical transformations.

It is important to note that, for example, typical kinetic time for a 20% monomer conversion is about 15-25 ms (≈0.2 W/cm^3) depending on a monomer and other conditions. The much longer residence times typical for the majority of glow discharge reactors, especially for the bell-jar types, are not favorable for kinetic investigations of the most informative initial stages of chemical transformations. A non-uniform longitudinal distribution of the specific discharge power, hence, the plasma density, typical for the long tubes with local discharge excitation, disguises the chemical kinetic phenomena as well.

The method and several techniques of surface kinetic probing have been developed to distinguish and study separately the surface phenomena affected by plasma electrically charged particles and electric fields [5]. An idea of the kinetic probe is simple [6]. The probe is a small electrode-substrate, contacting with plasma by the strictly defined area, and connected in series with a high impedance electric current stabilizer. Additional reference electrode having small sheath impedance must be immersed into the plasma to complete the electric circuit. The small size of the probe means that the probe does not perturb the neutral plasma components which are determined mainly by the bulk plasma. Well controllable constant electric current flowing between the plasma and the probe surface across the deposit allows one to set and keep constant during the process (deposition, etching, surface modification) any ratio between the neutral and electrically charged fluxes thus using the bias current as independent internal parameter of plasma-surface interaction. It is the only one principal possibility in case of dielectric deposits. This condition is necessary and enough to control the true surface potential. Hence, there is no other way to do it.

Since it is impossible to reveal the deposition or etching mechanisms without understanding of the gas phase condition, determining the neutral particle fluxes onto the surface, the use of kinetic probes was accomplished by corresponding analysis and arrangement of the gas kinetic conditions. The generalizations presented here have been verified by corresponding modeling and explain other the results known in literature. Any incontestable experimental data contradicting to the generalizations have not been found.

Kinetics and mechanisms of heterogeneous stages of plasma polymerization of **C2F4, C3F6, c-C4F8, C8F16** in **RF** capacitively coupled discharge (**40.68 MHz**) have been systematically studied. The pressure range was **0.1-1 Torr**, linear gas velocity **0.1-3 m/s**, specific discharge power **0.01- 0.5 W/cm^3**, gas kinetic residence time **0.002-1 s**.

ELECTRICALLY CHARGED AND NEUTRAL PARTICLES, ELECTRIC FIELDS

Positive ions have been traditionally considered as the most important particles in plasma-surface interactions. Their energetic contribution to the surface stages has two different portions: 1) kinetic energy and mechanical momentum transfer; and 2) internal potential energy which can be efficiently consumed in non-elastic processes due to an ion neutralization. A side effect of ion bombardment consists of electric charging of dielectric surfaces contacting plasma. Surface mechanisms involving positive ions, especially on the polymer like surfaces, are still not well understood.

Several independent effects of low energy (from a few to about fifty electronvolts) positive ion bombardment on the surface are well known each:

- excitation of collision cascades equal to the local temperature increase, stimulating the bulk and surface diffusion (mixing) and desorption of surface adsorbates;
- mechanical momentum driving the weakly bonded surface particles into the bulk (mainly generates the compressive strength in the deposited films);
- scission of chemical bonds, i.e. generation of the top layer surface free radicals (surface activation in plasma polymerization);
- deposition of positive electric charge in the top surface layer.

In case of plasma polymerization all these effects work at the surface. It explains a great variety of experimental data and hypothesis published in literature.

It is well proved that the low energy positive ion bombardment is always a ***destructive factor*** by itself. For example, in poor mixtures of fluorocarbons, when positive ion and neutral fluxes on the surface are on the same order of magnitude, the film deposition rate on the Langmuir probe was measured to be remarkably decaying down to zero while the only positive ion flux was increasing. Positive ion bombardment (surface activation) takes an essential portion of mass away from the growing film surface. But this mass decrease is covered by the following mass gain provided in other processes.

The efficiency of positive ions in surface activation depends on the gas phase neutral composition. If to count such efficiency as a number of monomer units (starting molecule) incorporating into the film per one incident ion then one can get a wide range from the *negative values* (sputtering, etching) up to about *ten*. Positive ions activate only the top surface of the deposited macromolecule or oligomers. An immediate incorporation of positive ions into the film structure can hardly affect the growth rate magnitude under the typical plasma polymerization condition. However, it can not yet be excluded from consideration in case of very low deposition rate condition ($\approx$0.1 nm/s) and in a case when an initial organic monolayer layer is been forming on an inorganic surface, especially metal.

Electrons have not been considered as a *competitive* counterpart to positive ions in plasma polymerization. However, namely electron activation was firstly discovered to produce thin polymer films under the vacuum condition of electron microscopes.

Accelerated electrons crosslink the surface adsorbate. We have shown by the kinetic probe method, that electrons do contribute to the surface stages of plasma polymerization, moreover, such contribution can be stimulated by positive electric bias even to compete with the ion activation.

The mechanism of electron activation is different from that of ion. Electrons can penetrate inside the surface dielectric deposit providing non-elastic collision. Electrons do not transfer any appreciable mechanical momentum to the surface, hence they do not stimulate the desorption of physical adsorbate in comparison with positive ions. Plasma electrons bombarding the surface can easily crosslink the surface layer up to about 100 nm thickness. The efficiency of surface activation by plasma electrons derived from our kinetic probe measurements is as high as about **0.03-0.1** from that of positive ions depending on the conditions.

From the above consideration it must be clear that electrons never contribute to the surface activation simultaneously with positive ions because they need comparatively thick layer of adsorbed which is usually removed by positive ions. The deposition rate under the stimulated electron bombardment can be as high as that of the ion bombardment under the same discharge condition and depends strongly on the substrate temperature. The absolute value of apparent activation energy of the film growth in such a case is about 3 times higher than that under the ion bombardment.

Properties of the films deposited under the stimulated electron or ion activation are different. The electron bombardment promotes a cross-linking of fluorocarbons (or other surface adsorbates) preserving the monomer functional groups while the ion bombardment tends to destroy, randomize them, and densify the film structure. For example, films deposited under the *same discharge condition*, the *same deposition rate* but different bias activation possess different optical refractive indexes: films with lower indexes have been deposited under the stimulated electron activation.

Negative ions never reach the surface under the condition of non-biased substrates because of the positive plasma space charge. They flow on the surface when the surface potential is shifted above the plasma potential (anode condition). However, their contribution to the surface stages of plasma polymerization of fluorocarbons even under such exotic conditions was never found.

CF2 carben is usually suggested in literature as a main precursor for the plasma polymer film formation. In contrast, in chemical kinetics CF2 carben is well known as very low reactive particle. There have been no one correlation found between the film growth rate and CF2 density during the plasma polymerization. Its contribution to the *surface stages* of film formation under the typical plasma polymerization condition, if exist, is negligible. However, as it is known, it can not be excluded as a probable film precursor under the condition of very low deposition rates like the "side wall formation" conditions in Si dry etching or initial layer formation on some inorganic surfaces.

CF radical was also suggested as a film precursor. However, no correlation with the film growth rate was found. Moreover, CF absolute density is far below the level necessary to

explain the observed film growth even supposing the sticking probability was equal to 1. It should be considered as a film precursor under the etching condition.

Unsaturated monomers and C2-C5 products including double bond and cyclic structures practically don't contribute to the surface stages under usual conditions of plasma polymerization, their density never correlate with the deposition rate. Direct surface contribution of stable **C6-C8 fluorocarbons** can be supposed in some extent when the degree of monomer dissociation and the film growth rate are low at short residence times on the order of a few milliseconds. **C2F4** deposition kinetics in the range of about **5-75** ***ms*** was not changed due to the **0.5 mol. %** **C8F16** heavy additive to the gas flow in spite of the fact, that this level corresponded to the total **C8** product concentration characteristic for about **50** ***ms*** of the gas phase synthesis in a **C2F4** discharge.

Gas phase and surface free radicals

It is well proved that the gas phase monoradicals are the main precursors for film formation. Since the adsorption characteristics of different monoradicals are different, their efficiency in a film formation is also different. Generally, the heavier is a free radical, the higher is its contribution to the film growth rate. The deposition rate is determined not by the total radical density but rather by their molecular mass distribution function. The most important radicals are **C4-C8**. **C1-C3** radicals have low sticking probability, and radicals heavier than about **C8** have too low production rate. The efficiency of gas phase monoradicals in a film formation depends on several factors.

The film growth rate is determined by both the gas phase free radical flux and the density of surface free radicals. The activity of the last depends on the surface coverage or the density of physically adsorbed molecules shielding surface radicals. Positive ion bombardment affects both parameters: the surface free radical density and the density of surface adsorbate as it was described above. Surface radicals, belonging to the surface bulky macro- and/or oligomeric molecules, must be distinguished from the light radicals just incorporated into the layer of adsorbate. The last are not efficient in a film formation.

Gas phase monoradicals arriving onto the surface quench surface radicals recombining with them. Hence, the polymer film should be permanently activated to be growing. Such activation can be done only by the double action: mechanical momentum transfer cleaning the surface from the adsorbate, and by the scission of chemical bonds in the top layer of the film's bulk. Only positive ions combine both necessary actions. Excited heavy particles (metastables, vibrationally excited molecules) were not found to compete with positive ion surface activation.

Gas phase free radicals may be not necessary in case of electrically positive biased surface (anode regime). Positively biased surfaces repel positive ions. Hence, the probability of incorporation of free radicals into the film structure falls down. Then the electron flux, increasing with the bias increase, come into effect in the case of comparatively thick adsorbed layer and crosslink it. Gas phase free radicals are not necessary for film formation in this case.

Electric fields, adsorption

It was firstly revealed by the surface kinetic probes, that near surface electric fields

can strongly affect the kinetics of plasma-surface interaction. There are two origins of near surface electric fields. The plasma space charge creates the field strength on the order of 10^3 - 10^4 *V/cm* in the plasma-surface sheath. Much stronger fields on the order of 10^6 - 10^7 *V/cm* can appear in the surface *dielectric* layer when the substrate is electrically biased or even without any external bias [7]. Both fields affect surface electronic states and can strongly change the so called electro-adsorption effect [8], and hence, the rate of either deposition or etching. A competition exists between the temperature and field effects. Direct field effects can be revealed by the surface kinetic probes in any kind of plasma-surface interactions.

CONCLUSION

The majority of hypothetical models of plasma polymerization published in literature more than 15-20 years ago has already included almost all imaginable physical and chemical stages in different combinations. However, those models could not be definitely justified or falsified at that time.

The short residence time box-type plug flow reactor with a strictly limited input plasma boundary provided a way for a set of kinetic data suitable for the foolproof discrimination of the role of neutral particles in the surface stages of plasma polymerization of fluorocarbons. The role of electrically charged particles and fields was revealed by means of the method of surface kinetic probes. These current bias probes represent the unique tools specially designed to study the effects of electrically charged particles and fields on the dielectric surfaces contacting with plasma.

"Plasma polymerization" of fluorocarbons does not seem to have any specific surface chemical reaction which could be assigned to polymerization type reactions neither for ions, nor for free radicals. The Activation-Chemisorbtion Model developed earlier for plasma polymerization of light hydrocarbons [9] is valid for fluorocarbons as well. The heterogeneous stages of typical plasma polymerization process can be well described quantitatively on the basis of this model supplemented by the surface electric field effects. We did not find in literature any experimental data contradicting to the concepts presented.

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