Gas Jet Electron Beam Plasma CVD and CVR Method and Applications

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A new method of initiation of chemical reactions in a gas phase CVR (Chemical Volume Reactions) and on a surface CVD (Chemical Vapour Deposition) using an electron beam plasma created in a supersonic flow is presented. The method is based on the activation of initial gas molecules by electron beam and fast convective transfer of the radicals to a substrate or zone of reactions by means of a supersonic jet. In the report the description of the method and its basic technological elements (electron gun, nozzle block and additional tools) are given. The method is universal and allows implementation in a wide range of technologies, from vacuum to obtain layers and films on the surface to atmosphere to produce various chemical products. Advantages of method are described in various fields of application. The directions of the conducted developments and achievements are presented.

1. Introduction

Technologies based on the use of plasma produced by different types of discharges of various types are becoming increasingly popular in a variety of industries. The attractiveness of this technology is associated with many factors, the main of which is a low temperature process and the high rate of chemical reactions as homogeneous formation of new chemical products, and heterogeneous to form films and layers on the surface. Plasma chemistry is accompanied by complex physical and chemical reactions difficult to predict the result and moreover the end result. For example, layers of device-quality microcrystalline silicon for solar cells depends on a large number of external parameters determining the process. The search for the optimal operating conditions of plasma-chemical devices is quite challenging. Therefore, a method for efficient and manageable plasma chemistry is desired. Plasma properties created by electron beam is one of the best instruments for technologies on many reasons. The physical properties plasma created by electron beam (EBP) are considered in [1]. Degradation spectra of electrons in different gases are presented in [2]. First hybrid EB - plasma generator with external electric field for plasma chemistry (CCl_4 removal) has been developed in Plasma Fusion Center MIT and reported in [3]. In this paper we present the development of new plasma-chemical method, which allows to solve the problem of the control of plasma chemical processes and could be used for the very wide range of applications.

2. Basic principles of Gas Jet EBP CVD/CVR method

The basic principles of a controlled cold plasma chemistry are presented in Fig. 1. These principles are demonstrated on the example of the simplest binary reaction.

$$A^i + B^j \leftrightarrow AB \qquad (1)$$

The rate constant for the forward reaction is highly dependent on the quantum states (i, j) of reagents. Filling of these states occurs by collisions of plasma electrons with different states of molecules A and B, as shown in Fig. 1.

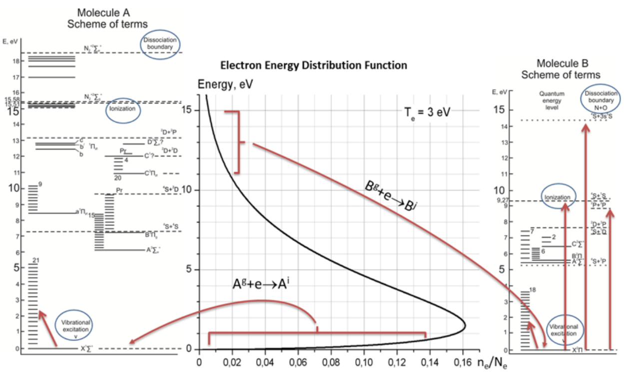


Fig.1. Basic principles of nonequilibrium controlled cold plasma chemistry.

At a relatively low energy of electrons, the vibrational excitation occurs in the ground state of molecule (A). For higher energy of electrons the excitation of other internal freedom degrees of the molecule, as well as ionization and dissociation (molecule B) become possible. In a cold plasma the rate constant of the reverse reaction is negligible, due to the Arrhenius law. Thus, the rate of a chemical process in a non-equilibrium cold plasma depends on the electron energy distribution function (EEDF). Impact of plasma parameters on EEDF can be controlled and the selectivity of chemical reactions can be handled. The possible methods of controlled plasma parameters leads to the influence on EEDF are:

a) gas flow parameters (composition, flow, temperature, density);

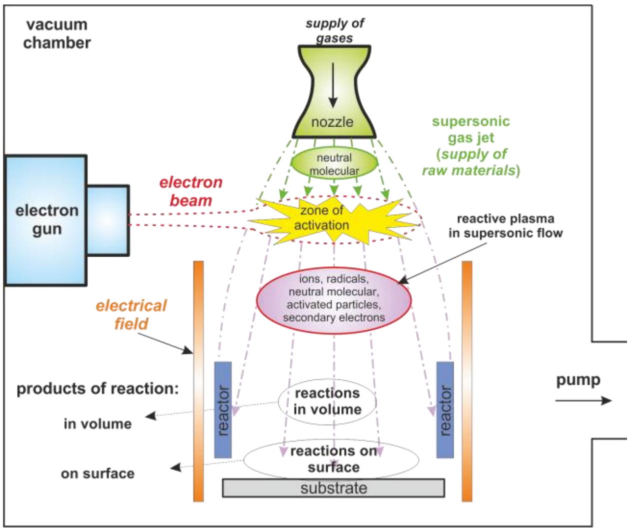
b) additional external electric and magnetic fields applied to a plasma (frequency, power, geometry);

c) electron beam parameters (energy, electric current, beam shape, modulation).

For practical implementation of the principles outlined above the non-equilibrium controlled cold plasma chemistry gas-jet plasma-chemical method with the activation of an electron beam has been developed.

3. Gas Jet Electron Beam Plasma CVD/CVR (EBPCVD, EBPCVR)

The method of creation cold nonequilibrium plasma controlled by electron beam with selective reactions in a supersonic gas flow [4] is shown in Fig. 2.



Fig, 2. Cross geometry method of selective chemical reactions initialization by electron beam plasma.

To create a non-equilibrium plasma in a cold gas the electron beam generated by electron gun was introduced into the jet formed by a nozzle unit. The primary electron beam interacts with molecules in the jet and due to elastic and inelastic collisions it dissipates to form secondary electrons, ions, radicals, molecules, and particles in different excited states. The area of this degradation of electron beam in the crossed gas jet is called "the activation zone". The interaction of the primary electrons with the gas flow leads to the formation of chemically active non-equilibrium cold plasma. The electron-beam plasma creates a large number of secondary electrons with energies sometimes not sufficient to provide the processes of dissociation and ionization. External electric field could increase energy of secondary electrons to the required energy and provide the stability of electric discharge. External magnetic field allows the influence on the trajectories of the ionized particles and to form desired shape on the substrate. Chemically active particles are produced in the activation zone and then they are moving towards the substrates together with a neutral gas flow. During their path to the substrate in the flow they undergo into physical and chemical reactions with other particles (ions and neutral molecules). Products and their types are controlled by selection of frequency and power of the external fields and other parameters. The interaction of the plasma gas flow with the substrates occurs in different heterophase surface reactions leading to the formation of the layers on the substrate surfaces as in CVD. In the absence of the substrate in the flow path in the plasma are formed novel compounds (reaction products) in the volume (CVR), then they could be separated from the gas flow and can be collected in the form of gases, liquids or solids (G2L, G2S technologies).

The main elements of plasma chemical gas-jet equipment include an electron gun with hollow cathode, the nozzle unit and the device for supplying the external fields. These elements form a compact unit (cold EB plasma hybrid generator - CEBPHG) for generating gas plasma flows, shown in Fig. 3.

Fig. 3. Cold Electron Beam Plasma Hybrid Generator.

The combination in the cold generator supersonic gas flow to supply the working gas in a plasma produced by an electron beam and supported by additional external electric field provides the requirements for controlled plasma-chemical processes.

4. Gas Jet EBP CVD/CVR Applications

The following represent the advantages of the new plasma-chemical method in two different areas of application:

A. Plasma chemical deposition of layers and obtaining nanopowders under low pressure with preferences [5]:

- record rate of layers deposition on large area of substrates.
- ability to obtain a predetermined particle size and chemical composition in a free state and on the surface.
- reproducibility, controllability and manageability of the process.
- ability of the method to produce thin films of gas, solid or liquid.
- possibility to use the method for etching and surface modification.
- suppression of unwanted gas phase reactions.
- high availability of raw materials.
- ability to implement the «roll-to-roll» process technology.
- ability to use two parallel substrates during the deposition of layers (two-fold increase in performance).
- modular technology.

B. Low-tonnage plasma gas chemistry with the net preferences [6]:

- ability of industrial productive use jet of plasma chemical technique.
- versatility for raw materials.
- high service life of the equipment.
- ability to create compact, modular, transportable plants for the processing of raw materials to the final product in remote areas.
- low specific energy consumption for a healthy product due to a combination of electron-beam plasma and effective external field.
- minimum residence time in the feed gas in a jet reactor.
- small plants and small equipment costs (smaller investments at times).

5. Conclusion

At the report we present the next issues.

1. A more complete description of the gas-jet plasma chemical activation method with an electron beam;
2. Areas of ongoing developments;
3. The results of research and development for different applications.

6. References

[1] E.E.Son, *Plasma Technology, Ed. By M.Capitelli. N.-Y.: Plenum Press*, (1992) 45.

[2] V.P.Konovalov, E.E.Son, *Plasma Chemistry, Atomizdat (in Russian)*, **14** (1988) 235.

[3] L.Bromberg, M.Koch, D.Cohn, D.Patrick, E.Son, P.Thomas. *Proc.10 Int. Conf. on Gas Discharge and Applications. Swansea, Wales, UK*, **2** (1992) 769.

[4] R.G. Sharafutdinov, S.Ya. Khmel, V.G. Shchukin, M.V. Ponomarev, E.A. Baranov, A.V. Volkov, O.I. Semenova, L.I. Fedina, P.P. Dobrovolsky, B.A. Kolesov, *Solar Energy Materials & Solar Cells*, **89** (2005) 99.

[5] Konstantinov V.O., Sharafutdinov R.G., Shchukin V.G., *Proc. Int. Conf. Physics of low temperature plasma Kazan, Russia, (in Russian)*, **2** (2014) 159.

[6] Konstantinov V.O., Sharafutdinov R.G., Shchukin V.G., *Proc. Int. Conf. Physics of low temperature plasma, Kazan, Russia, (in Russian)*, **2** (2014) 143.