Plasmachemical Synthesis in Low-Temperature Atmospheric Pressure Plasma

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Abstract—Pesicular features of various types of electrical gaseous discharges used to generate and sustain low-temperature plasma at atmospheric pressure have been considered. Applications of dielectric barrier discharges (DBD), corona, radiofrequency (RF), and microwave (MW) discharges for the synthesis of different materials have been discussed.

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INTRODUCTION

Nonequilibrium low-temperature plasma is characterized by significantly higher electron energies compared to the energies heavy plasma components: ions, neutral atoms, and molecules. Collisions of high-energy electrons with atoms and molecules result in their dissociation, excitation, and ionization. It is worth to mention that these processes are not accompanied by a considerable increase of the temperature of heavy plasma component. Due to the fact that ionized and neutral plasma components remain to be relatively low energetic plasma does not cause the thermal effect on the substrate surfaces.

Nonequilibrium low-temperature plasma is easily generated in electrical discharge at low pressure. However, this technology has a serious disadvantage, namely, the need in a costly vacuum equipment.

In this connection, beginning in mid-1990s, much effort has been made all over the world on the development of low-temperature plasma sources stably working at atmospheric pressure. Since this time the number of publications on low-temperature atmospheric pressure plasma (LTAPP) sources has become to grow exponentially. Most LTAPP sources are relatively simple and have fairly low operating costs. The use of sources operated at high partial pressures of precursors (about three orders of magnitude higher compared to low-pressure plasma), brings great advantages to plasmachemical processes involving homogeneous chemical reactions, for example, plasma enhanced chemical vapor deposition (PECVD) of nanopowders or cleaning from toxic organic compounds. However, certain problems with LTAPP sources arise in plasma assisted processes based on heterogeneous chemical reactions (PECVD of thin films or etching of materials) due to the necessity to prevent homogeneous reactions leading to vapor phase depletion or by-product formation. At the same time, recent research has shown that LTAPP holds promise for practical applications: film deposition, synthesis of new compounds, surface modification, removal of highly toxic organic pollutants from air, surface etching, synthesis of nanopowders, etc.

Most LTAPP sources are based on arc discharges characterized by high heat release. Arc discharge plasma is widely used in technology (welding, sawing, sputtering, and high-temperature chemical synthesis). However, such thermal strains might be reasonable high for many applications, because the temperature of the treated surface can reach 2000°C. In this connection, over the past twenty years active R&D work has been done on plasma sources with different types of electrical gaseous charges (corona, barrier, radiofrequency, and microwave), with lower temperatures of heavy plasma components (600–800°C).

In present review work we will demonstrate the great horizons of using low-temperature atmospheric pressure plasma processes for plasma stimulated synthesis of different materials.
Specific Features of Electrical Gaseous Discharges at Atmospheric Pressure

The gaseous discharges at low pressures (0.5–200 Pa) are widely used for generation of low-temperature plasma and can sustain over a long time. It happens due to the fact that the characteristic time of the discharge instability development which induces to transition of the glow discharge to arcing is indefinitely long. The usage of atmospheric pressure leads to shortening the time of discharge instability development up to nanoseconds [1].

Abundant evidence is available [2–26] to show that any processes that tilt balance between generation and lack of charge carriers can cause instability and the transition from volume discharge to channeling. This transition results in a change of the temperature regime and in spatial inhomogeneity of plasma, which is critical and highly undesirable for many technological applications. Furthermore, another reason for the instability of the atmospheric pressure plasma during the nanomaterial synthesis is the accumulation of plasmachemical reaction products having lower ionization potentials and, consequently, higher ionization rates [27].

Discharge instability is the main limiting factor to the design of sources of low-temperature nonequilibrium volume discharges at atmospheric pressure, and this prompts research into the reasons for their generation and mechanisms of development [4, 5, 7].

The main problem that must be solved when developing LTAPP sources is to stabilize and sustain discharge in the reaction gas mixture. A general approach is either the usage of an inverse feedback for the discharge current–voltage or restriction of the discharge sustainability time.

Most modern plasma sources use self-sustained atmospheric pressure gaseous discharge. As the largest amplitude of electric field in self-sustained plasma is in the cathode region, the instabilities are associated with field fluctuations initiated in this region. Several methods to suppress electric field fluctuations have been reported [28–35]. The simplest one [28] is the use of a segmented cathode with each segment connected to power supply source via a ballast resistor. The fluctuations of the discharge current (for example, increase), induced by developing discharge instabilities, lead to fluctuations (increase) of the voltage, which drops on the ballast resistor, and, consequently, changes (decrease) the discharge voltage. Another approach to avoid instabilities in the cathode region is establishing such discharge sustainability conditions that prevent plasma formation in this plasma region. For this purpose, another discharge region, which plays the role of the cathode region for the main volume plasma zone, were added [29–35]. Plasma cathodes are efficient in terms of suppression of cathode potential drop and are capable of ensuring reliable contact with plasma, because they are not damaged by secondary processes on their surface. However, the processes that occur in the double layer at the plasma boundary, can induce instabilities as well [28].

A fairly simple approach to preventing the transition of the volume discharge to channeling can be realized in the case of corona discharge [36]. Corona discharge takes place when a high electric field with a potential gradient (strength) is created near at least one of the electrodes. This condition is fulfilled when an electrode contains prickly parts with a small curvature radius (tip or needle). The corona discharge current is confined by the space charge of carriers in the strength region. The charge carriers drift to the second electrode (ideally, at infinity) in the gas under the action of the electric field. The corona discharge can be generated and sustained both at a dc and ac over a wide range of frequencies. Pulsed corona discharges, where nonequilibrium plasma is formed due to streamers propagating from a needle electrode, are also used [37, 38].

The use of such gas discharges in the plasmachemical technology is limited by a strong spatial inhomogeneity of plasma. The region, where the most intense gas ionization and excitation processes take place, is localized in the vicinity of the tip electrode. In the case when a substrate to be treated is placed close to a high-voltage corona-producing electrode, special measures should be taken to prevent short-circuiting the discharge current to the substrate and discharge sparking or arching (depending on the power supply source).

An alternative approach to prevention of discharge instabilities consists in limiting the time of discharge current flowing less than the transition time from the volume discharge to channeling [7, 28, 39–65].

The discharge time can be limited by using a dielectric barrier on the electrode surface. The dielectric