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Application of atmospheric pressure glow discharge (APGD) for deposition of thin silica-like films on polymeric webs

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Silica-like films were deposited on PEN and PET polymeric foils in atmospheric pressure glow discharge (APGD) in a roll-to-roll reactor open to ambient air. APGD was ignited in a mixture of inexpensive carrying gas argon and nitrogen with oxygen and hexamethyldisiloxane (HMDSO) precursor. The uniform diffuse glow in various gas mixtures was sustained by utilizing electronic stabilization network. APGD operation in air for a present setup was demonstrated. The contribution of different deposition mechanisms to the resulting silica-like film is discussed. The dependence of film structure and chemical composition on the conditions during deposition process was studied by means of SEM, ATR-FTIR and XPS analysis. The influence of oxidant concentration on the deposited film properties is analyzed and discussed.

1. Introduction

Atmospheric discharges are nowadays in focus of serious research activity. This is mainly induced by the new promising applications possibilities for high pressure non-thermal plasmas. One of the traditional and successful fields of gas discharge application is plasma enhanced chemical vapour deposition of thin films (PECVD). Implementation of the atmospheric pressure discharges for PECVD can be advantageous, but also imposes scientific and technological challenges.

Atmospheric pressure surface processing, including thin film deposition or surface modification, is primarily attractive because it allows a considerable cost reduction by avoiding usage of vacuum equipment and by offering a possibility of in-line roll-to-roll production. However, treatment of large area substrates requires creation of considerable volumes of uniform non-

thermal plasma, which is not a trivial task at atmospheric pressure.

One of the ways to produce non-thermal atmospheric plasma, allowing direct treatment of the large surface areas, is dielectric barrier discharge (DBD). Unfortunately, the most common form of high-pressure dielectric barrier discharge is a non-uniform filamentary mode, when discharge splits in many tiny current channels. The existence of uniform diffuse mode of DBD (suitable for high pressure PECVD) is usually strongly restricted by gas mixture composition, dissipated power and operation frequency. Often this rare uniform mode of atmospheric DBD is referred to atmospheric pressure glow discharge or APGD [1].

Despite apparent potential of the APGD for high pressure PECVD, till now there are not many reports about successful implementation of this promising technology for deposition of silica-like films. This is directly related to the difficulties of sustaining uniform mode of the discharge at atmospheric pressures in arbitrary gas mixture. Gas mixtures for deposition of oxide films usually should contain electronegative oxidant which is easily triggering transition to a filamentary mode. It is known that APGD can be obtained in pure gases for instance N₂ [2] and Ar or gas mixtures with high He content [3]. In the last case high costs of the gas mixture are making industrial application difficult. In a recent article [4] authors are utilizing uniform Townsend mode of the atmospheric DBD for deposition of silica-like coatings. The difference between Townsend DBD and APGD, studied here, is in that atmospheric glow discharge is characterized by higher current and specific power

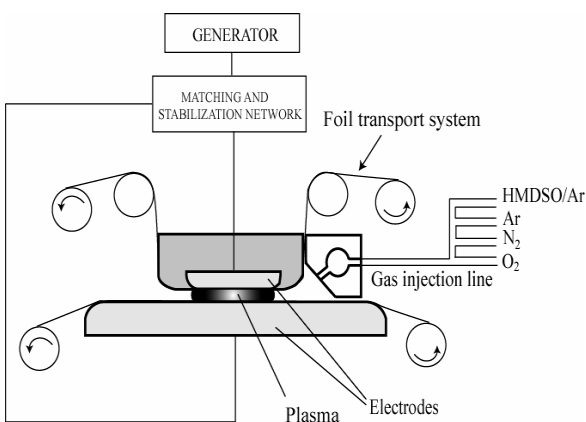


Figure 1. Schematic drawing of the experimental setup

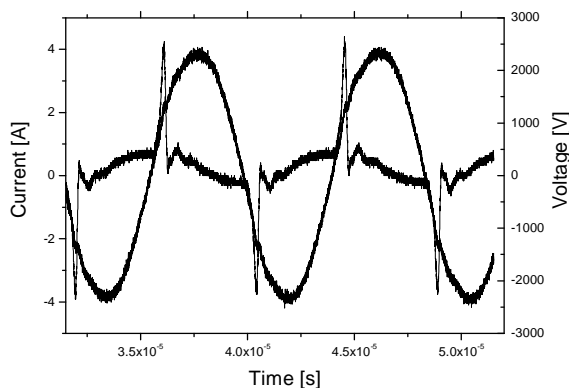


Figure 2. Voltage-current waveforms for APGD in air

densities, considerable space charge and formation of the electrode sheaths.

In the present work we focus our studies on the APGD deposition of thin (~ 100 nm) SiO_2 -like films on polymers. One of the most known applications of these inorganic films is for gas/moisture diffusion barrier layers on polymers, but also other applications are very much appealing, e.g. scratch resistant coatings and optical coatings. Here it is our aim to investigate how the properties of the deposited films depend on the discharge conditions.

2. Experimental setup

Schematic picture of the experimental setup is shown in Fig.1. The dielectric barrier discharge was ignited between two plane-parallel electrodes made from stainless steel and covered with dielectric barrier. The dimension of the discharge area was 40×150 mm². The electrode gap was 1 mm. A polymer foil (100 μm thick) treated in the discharge served the purpose as dielectric barrier. Both top and bottom electrodes were equipped with independent roll-to-roll foil transport systems. Two different polymer foils were tested as a substrate material in the present investigation: polyethylene terephthalate (PET) and polyethylene-2,6 naphthalate (PEN).

The DBD was powered by a RFPP LF-5 generator. Electrical circuit included matching elements together with discharge stabilization subcircuit. Discharge stabilization allows to sustain a uniform discharge avoiding transition to filamentary regime [5-7]. The operation frequency of the RFPP generator was tuned in the range of 100-200 kHz to achieve better power coupling into discharge. A typical voltage amplitude between the electrodes was 1.5 - 3 kV and the maximum value of

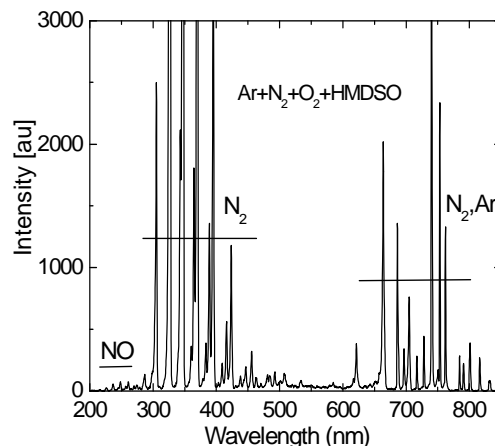


Figure.3 Optical emission spectrum of the APGD in $\text{Ar:N}_2\text{:O}_2\text{:HMDSO}$ mixture

discharge current peak was in the range of 4 – 8 A. The electrical characteristics of the discharge were monitored by a Tektronix TDS 3034B oscilloscope equipped with Tektronix P6015A voltage and Tektronix P6016 current probes.

The gas mixtures used in present investigation contained argon (80%), nitrogen (20%), oxygen and hexamethyldisiloxane (HMDSO) as a precursor. Mixture of argon and nitrogen as carrier gas was used in this work to reduce the breakdown voltage and to allow operation of the system at 1 mm inter-electrode gap with voltage amplitude of approx 2 kV. Operation of the APGD in pure nitrogen and air is also possible in the studied reactor if discharge gap is reduced. The total gas flow rate was 12 slm with a fixed precursor content of 50 ppm. The flow rate of the carrier gas and oxygen was controlled by mass flow meters (Bronkhorst). HMDSO precursor was injected using an evaporation unit (Bronkhorst).

APGD discharge uniformity was monitored by a Dalsa EC-11-05H40 sensitive array camera with 13 μs frame integration time. Deposited coatings were analyzed by attenuated total reflection Fourier transform spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM). Film thickness was controlled by spectroscopic ellipsometry (SE).

3. Results and discussion

The implementation of the electronic stabilization network allows achieving a diffusive atmospheric plasma glow discharge (or APGD) in a large variety of gas mixtures, including ambient air. During the breakdown phase the plasma has a negative dynamic resistance and is very prone to the

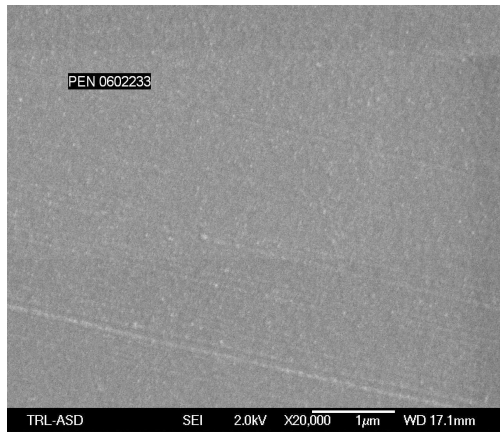


Figure 4. SEM image of the APGD deposited silica-like film on PEN substrate

development of instabilities and the filamentation growth. However, the filament current can be damped and the current of the stable plasma variety enhanced via drop of the displacement current. In the studied reactor a fast falling displacement current was generated at the plasma breakdown and plasma cut-off using a LC parallel circuit with a saturated inductance [5-7].

The observation of the discharge with the sensitive array camera, was demonstrating uniform glow without visible filaments for all regimes of deposition under investigation. Another fingerprint of the APGD is the discharge current waveform, which was showing only one relatively broad current peak per half-period of the voltage between the electrodes. An example of the voltage-current waveforms for APGD in air (0.5 mm discharge gap) can be seen in Fig.2.

Considering deposition mechanisms in a roll-to-roll reactor with moving polymer substrate and gas flow, one can distinguish three different pathways which are simultaneously contributing to the film formation: a) ionic deposition, when ionized products of decomposed precursor drift in electric field towards surface; b) diffusive deposition of neutral radicals produced in plasma and afterglow phases and c) deposition of large particles or dust. Each of these mechanisms leads to coatings with characteristic composition, structure and location in the discharge area (due to the gas flow). The fastest of the mentioned processes is ion drift. For the electric field, corresponding to experimental conditions, and atmospheric pressure ion drift time to the surface can be estimated as few μs . However because of the relatively low current density in APGD, this mechanism can not contribute significantly to the growth of the film bulk, although it may be responsible for the formation of interfacial

layer between polymeric substrate and film. Characteristic time for diffusion of the radicals in our experimental conditions is in order of several ms. Radicals diffusion to the substrate can be considered as a main pathway for formation of dense films [4]. The rate of large particles growth in gas phase depends strongly on plasma chemistry and specific input power [4]. The deposition of particles is generally undesirable, because it leads to porous, powder-like coatings.

As a result of above mentioned processes in a roll-to-roll system with a moving foil a film is formed which consists of mixed layers with different properties. Variation of the discharge conditions can change contribution of the mentioned processes and therefore affect characteristics of the resulting film.

For deposition of silica-like coatings in high pressure discharge, the gas mixture typically contains the precursor, the oxidant and the carrier gas. Molecular oxygen can be used as an oxidant or O-containing molecules, N_2O , can be used [4]. Atomic oxygen radicals and excited oxygen molecules formed in the discharge plasma are necessary to produce stoichiometric silica film. Moreover, atomic oxygen is promoting precursor decomposition and carbon elimination both in gas phase as well as from the growing film. Thus, the ratio of precursor to oxygen flow rates controls in many ways the plasma chemistry and the resulting properties of the deposited film.

Typical optical emission spectrum of the APGD in the gas mixture of $\text{Ar}:\text{N}_2:\text{O}_2/\text{HMDSO}$ is shown in Fig. 3. As one can see the spectrum is dominated by the molecular nitrogen bands and atomic Ar lines. Molecular bands attributed to NO can be seen in UV part. It can be noted that CO and CO_2 bands are not easily detectable. Comparing to the spectra of the low pressure HMDSO containing discharges [8], features attributed to the molecular or atomic hydrogen are not pronounced in APGD spectrum.

SEM image of APGD deposited silica like film on PEN substrate is shown in Fig. 4. It shows that smooth particle-free and pinhole-free coatings can be obtained in atmospheric discharge.

By means of ATR-FTIR and XPS analysis we observe that, in the absence of oxygen, HMDSO-like organic films (polymer-like) are deposited. Addition of oxygen leads to increase progressively in the silicon dioxide character of the film and to the decrease in carbon content in the deposited film. This can be seen in Figs. 5 and 6, which show ATR-FTIR spectra and XPS data for the coatings deposited at different oxygen concentrations in the

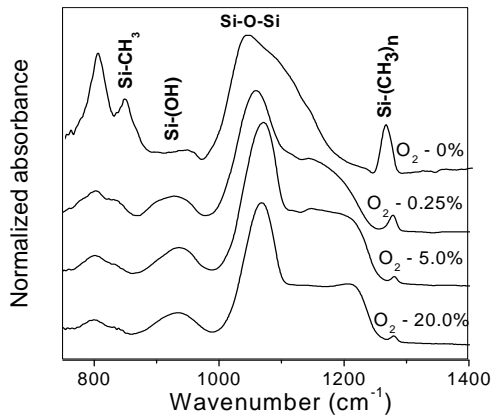


Figure 5. ATR-FTIR spectra of the films deposited at various oxygen content in the gas mixture

gas mixture. The reduction in carbon content in the coating can be traced by observing absorption peaks corresponding to Si-CH₃ at 840 cm⁻¹ and at 1280-1260 cm⁻¹ (corresponding to Si-(CH₃)_n groups with n = 1,2,3) in ATR-FTIR spectra. It is known that the absorption peak assigned to Si-(CH₃)_n groups shifts towards higher wavenumbers with decrease in n, which also implies an increase in -SiO_x(CH₃)_{3-x} (cf. for instance [9]). In our experiments such shift is observed with an increase in oxygen percentage in the gas mixture. Both XPS and ATIR-FTIR analysis shows that a limited increase in oxygen up to 20 % in gas mixture cannot totally eliminate carbon from the deposited film. Similar behavior of the residual carbon content in the film as a function of oxidant to precursor ratio (N₂O/HMDSO) was observed in [4]. According to our experimental observations, the carbon content in the film can be decreased even further with increase in specific power deposition in APG discharge.

4. Conclusion

Uniform large area silica-like coatings on the polymer substrate in roll-to-roll configuration were deposited at atmospheric pressure utilizing an APG barrier discharge configuration. The atmospheric discharge deposition system works at relatively low flow rate of the Ar/N₂ carrier gas and it is open to ambient air. This makes the system inexpensive for industrial applications.

By changing HMDSO/oxygen ratio in the gas mixture it is possible to tune the composition of the deposited film from organic polymerized HMDSO-like to inorganic silica-like coatings with negligible residual carbon content.

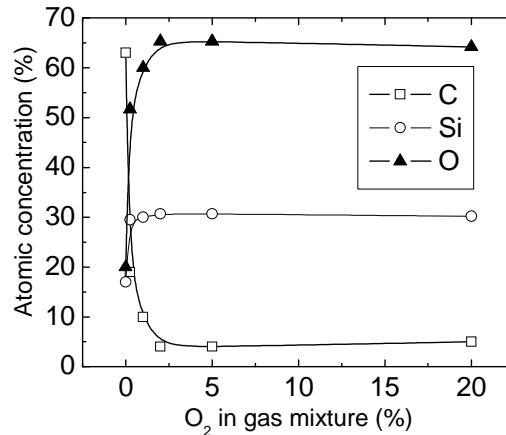


Figure 6. Composition of the APGD deposited film as a function of oxygen content in the gas mixture. Data of XPS analysis.

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