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High current diffuse dielectric barrier discharge in atmospheric pressure air for the deposition of thin silica-like films

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The diffuse dielectric barrier discharge in atmospheric pressure air was applied for the thin film deposition on polymeric web in industrially relevant roll-to-roll configuration. The silica-like film deposition was performed using the admixture of hexamethyldisiloxane precursor to air flow. Fast discharge imaging at 2 μs exposure time confirms plasma uniformity in a single current pulse time scale. Morphology and composition analyses indicate that the process results in ultrasmooth films (roughness comparable to initial substrate roughness) and shows the possibility to synthesize carbon-free layers. © 2010 American Institute of Physics. [doi:10.1063/1.3310024]

The dielectric barrier discharge (DBD) is a classical source of the nonthermal plasma at atmospheric pressure.[1] Nowadays DBD is also recognized as a potentially promising tool for atmospheric pressure plasma enhanced chemical vapor deposition (AP PECVD) of thin films on various substrates.[2–6] Emerging applications including encapsulation of flexible solar cells and flexible displays require large scale cost efficient production of transparent uniform dense layers with low level of surface defects. Unfortunately the common operational mode of the atmospheric pressure DBD is filamentary,[1] resulting in strong spatial nonuniformity of the dissipated power and plasma chemistry and affecting the quality of the deposited films. The rare uniform DBD modes,[7] beneficial for producing high quality films, and usually referred as low current atmospheric pressure Townsend-like discharge and high current atmospheric pressure glow-like discharge, are observed for a very restricted set of parameters such as gas mixture, dissipated power, operational frequency, etc.[2–9] Physical mechanisms leading to these homogeneous modes are still the subject of scientific discussion.[9]

Previously, we reported on AP PECVD of thin silica-like films in a glow-like plasma operating in $Ar/N_2/O_2$ +hexamethyldisiloxane (HMDSO, $(CH_3)_3-Si-O-Si-(CH_3)_3$ gas mixtures.[5,6] A further drastic improvement of the system cost effectiveness can be in the development of the deposition process assisted by the discharge running directly in atmospheric pressure air, reducing the cost of carrier gases such as argon or helium. However, sustaining of the filament-free nonthermal plasma over the large area substrate in atmospheric pressure air remains a formidable challenge within the low temperature plasma physics community. It should be noted that both oxygen and nitrogen gas in ambient air are recognized as important factors involved in the silica-like film deposition process. Molecular oxygen acts as a source of reactive oxidizing radicals formed in plasma, such as O, OH, and O_3. These radicals induce the scission of Si–C bonds in the organosilicon precursor as well as promote

the oxidation of hydrocarbon groups either in the gas phase and/or on the surface, allowing the deposition of silicon dioxide films.[10] Parallel to the role of O_2, the excited states of molecular nitrogen produced in the discharge are contributing to the fast dissociation of the oxygen via quenching reactions during the discharge and the afterglow phases.[11] Though the visually diffuse AP DBD in air was observed by several groups,[7,12–14] it appears to be not easily reproducible and was not yet applied for thin film deposition in industrially relevant roll-to-roll configuration, which is the subject of the present letter.

The experimental setup (see Fig. 1) was already described elsewhere.[5,6] The discharge area defined by the plane-parallel electrodes geometry was 40×150 mm^2 with a gaseous gap of 0.5 mm. The high voltage from a sine-wave generator at frequency of ~ 130 kHz was applied to the electrodes in a pulsed mode[5] with a pulse duration of 400 μs and a duty cycle of 20%. A 100 μm thick polymer polyethylene-2,6 naphthalate (PEN) foil treated in the discharge served the purpose of dielectric barrier. Both top and bottom electrodes were equipped with independent roll-to-roll foil transport systems. The discharge was operating in 10 slm flow of air. The HMDSO vapors were mixed with
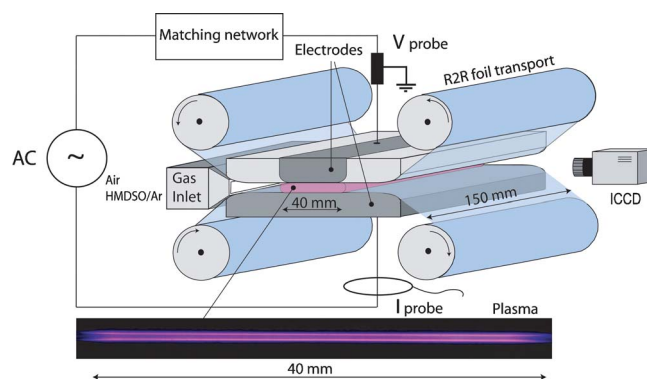

FIG. 1. (Color online) Scheme of the experimental roll-to-roll DBD assisted deposition setup. The conventional macrophotograph of the discharge in air (10 slm flow) is also shown (side view).
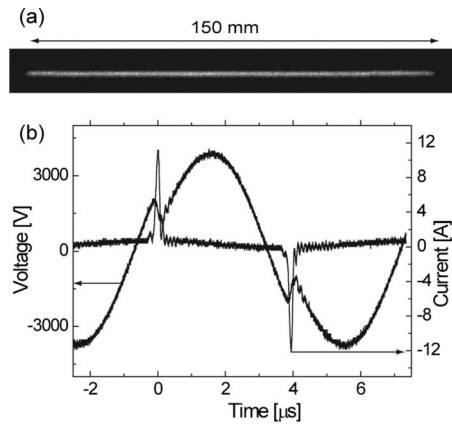
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FIG. 2. (a) ICCD image of the DBD discharge in air/Ar/HMDSO 10 slm/ 0.1 slm//0.4 g/hr gas mixture recorded at exposure time of 2 μs (front view) (b) Voltage and current waveforms of the same discharge.

0.1 slm of Ar in the mass flow controlled evaporation unit and then were added to the air flow. Note that the small admixture of argon is comparable to its natural concentration in ambient air. The deposition rate under operating condition of complete precursor consumption was in the range of 1.4–7.0 nm/s, scaling proportionally with the HMDSO mass flow (0.4–2.0 g/hr). The chemical composition of the film was studied by attenuated total reflection Fourier-transform infrared absorption spectroscopy (ATR-FTIR) and x-ray photoelectron spectroscopy (XPS). Atomic force microscopy (AFM) was used to quantitatively analyze the morphology of the deposited films. The film thickness has been determined by means of variable angle (65–70–75°) spectroscopic ellipsometry. The optical model consists of a Cauchy layer describing the polymer substrate in its transparency range (400–1000 nm) and a Cauchy layer describing the SiO_2 optical properties.

The diffuse discharge in air was observed in the absence and presence of HMDSO and argon. The discharge appears as two narrow bright sheaths next to the top and bottom dielectric surfaces with a darker central bulk region (Fig. 1). A small gaseous gap,[13,15] dielectric material properties,[16] and implemented dynamic matching[17] are contributing to the formation of the visually uniform plasma. According to Meek's criterion,[15] the streamer breakdown, which leads to the nonuniform discharge, occurs when the charge density in the electron avalanche becomes high enough to create electric field comparable with the external field value. This happens when the number of electrons in the single avalanche ex-

ceeds $\sim 10^8$ or the product of the first Townsend ionization coefficient and gap size is exceeding $\sim 19–20$. The analysis of the *I-V* characteristics shows that the breakdown takes place at voltage values lower than 3.0 kV. Using an analytical expression for the first Townsend coefficient in air,[18] the number of electrons in an avalanche in this limiting case can be estimated to be $\sim 10^4$, which is well below the Meek's criterion.

The intensified charge coupled detector (ICCD) photograph of the discharge in operating roll-to-roll conditions captured at 2 μs gate time and the corresponding voltage-current waveforms are shown in Figs. 2(a) and 2(b). The discharge image was taken without any kind of hardware or software signal accumulation and averaging. The lateral uniformity of the light emission pattern along the deposition area in Fig. 2(a) proves that within a single unipolar discharge current pulse, the plasma provides a uniform treatment of the substrate. The images recorded at exposure times shorter than the current pulse duration showed partial filling of the gaseous gap by plasma. Our previous analysis of the atmospheric pressure glow-like discharge development[19] points out that, while the high current density glow-like spot momentarily occupies only a small part of the electrode surface, it rapidly propagates over the whole electrode area and results in diffusive visual appearance. From the recorded discharge current waveform it can be calculated that the peak current density averaged over the electrode surface can reach ~ 200 mA/cm^2. This value is considerably higher than current densities which are typical for Townsend-like discharge[3,9] which usually not exceed 0.5–1.0 mA/cm^2. Although the discharge development at the submicrosecond scale was not studied here, it can be expected that, in order to provide a uniform film deposition, the plasma should be uniform at the time scale defined by the time it takes for radicals produced in the gaseous gap to diffuse to the substrate surface. For the conditions of the present work this diffusion time can be estimated to be in order of few millisecond, thus significantly exceeding the duration of a single current pulse (~ 0.5 μs).

Sustaining the diffuse filament-free plasma can be considered as an important, though not necessarily sufficient condition for the deposition of smooth inorganic thin films with low level of surface defects.[5] The deposition process described here results in visually transparent and well adherent films. The AFM scan image of the reference PEN substrate and of the 330 nm thick film web-roll deposited at HMDSO flow rate of 1.2 g/hr are shown in Figs. 3(a) and
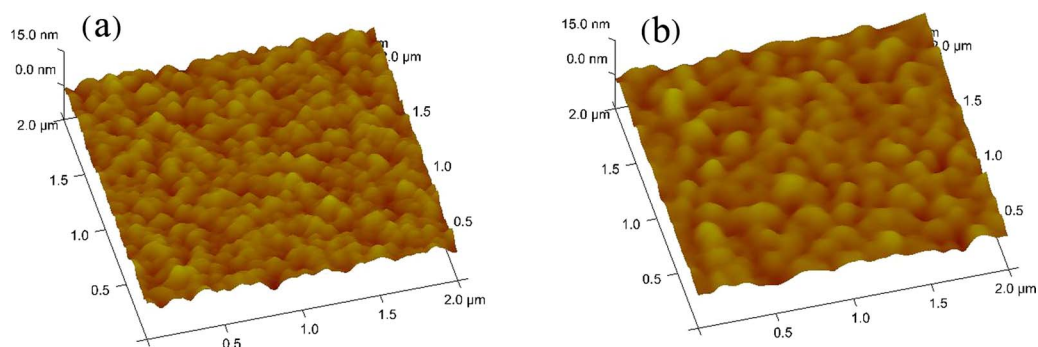

FIG. 3. (Color online) AFM scan images of (a) bare PEN substrate, rms roughness: 1.38 ± 0.07 nm (b) 330 nm thick silica-like film deposited at 1.2 g/hr of HMDSO mass flow rate in air discharge, rms roughness: 1.33 ± 0.09 nm.
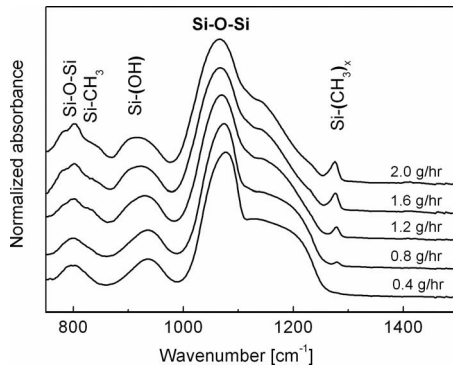
FIG. 4. ATR-FTIR spectra of the silica-like films deposited at different HMDSO precursor mass flow rates.

3(b), respectively. The RMS roughness value of the deposited film remains low with thickness $(1.33 \pm 0.09$ nm), being close to the one of the pristine polymer foil $(1.38 \pm 0.07$ nm), indicating a specific growth mechanism without any roughness development. The smooth film morphology and roughness development under air discharge conditions are very similar to the film deposited under argon-rich gas mixture conditions, which we reported earlier.[5,6]

The ratio between the oxidizer (molecular oxygen) and organosilicon precursor content in the gas mixture as well as energy delivered per precursor molecule are important parameters, influencing the deposited film chemical composition. The variation of the film composition as a function of HMDSO mass flow (0.4–2.0 g/hr) at fixed discharge power $(2.3$ W/cm^2) is shown in the ATR-FTIR spectra presented in Fig. 4. The main absorption bands in the $1000-1150$ cm^{-1} region can be assigned to the asymmetric stretching of the Si–O–Si group.[20,21] The Si–OH stretching at 930 cm^{-1} is often seen in the spectra of silica-like film deposited at atmospheric pressure without additional heating of the substrate.[3,22] The carbon content variation in the coating can be traced by observing the absorption peak at $1280-1260$ cm^{-1} (corresponding to Si$-$(CH$_3$)$_n$ groups with $n=1,2,3$).[20,21] This absorption peak shifts[20,21] toward higher wavenumbers with decrease in n. At HMDSO mass flow of 0.4 g/hr no carbon related absorption was observed in the infrared spectrum. The quantitative XPS analysis of the film stoichiometry (HMDSO mass flow rate of 0.4 g/hr) confirms the inorganic character of the deposited silica-like layer with O/Si ratio of 2.16, indicating the presence of silanol groups, and a residual atomic carbon content of 1.5%. No nitrogen incorporation into the film was detected by means of XPS.

In summary, it was demonstrated that diffuse high current dielectric barrier discharge can be sustained directly in atmospheric pressure air over large electrode area. Furthermore, it can be applied for the deposition of high quality silica-like films on polymeric substrates in a web roll reactor with air being the process gas. The film composition can be tuned by the variation of organosilicon precursor partial pressure, allowing production of low carbon content SiO$_2$-like layers or carbon-rich polymerized films. It was shown that the silica-like films deposited under atmospheric pressure air discharge conditions are characterized by an ultrasmooth surface morphology and low defects level, comparable to that of the untreated substrate.

[1]U. Kogelschatz, Plasma Chem. Plasma Process. **23**, 1 (2003).
[2]A. Sonnenfeld, T. M. Tun, L. Zakickova, K. V. Kozlov, H.-E. Wagner, J. F. Behnke, and R. Hippler, Plasmas Polym. **6**, 237 (2001).
[3]F. Massines, N. Gheradi, A. Fornelli, and S. Martin, Surf. Coat. Technol. **200**, 1855 (2005).
[4]S. E. Alexandrov and M. L. Hitchman, Chem. Vap. Deposition **11**, 457 (2005).
[5]S. Starostine, E. Aldea, H. de Vries, M. Creatore, and M. C. M. van de Sanden, Plasma Processes Polym. **4**, S440 (2007).
[6]P. Antony Premkumar, S. A. Starostin, H. de Vries, R. M. J. Paffen, M. Creatore, T. J. Eijkemans, P. M. Koenraad, and M. C. M. van de Sanden, Plasma Processes Polym. **6**, 693 (2009).
[7]S. Okazaki, M. Kogoma, M. Uehara, and Y. Kimura, J. Phys. D **26**, 889 (1993).
[8]E. Aldea, P. Peeters, H. de Vries, and M. C. M. van de Sanden, Surf. Coat. Technol. **200**, 46 (2005).
[9]F. Massines, N. Gherardi, N. Naude, and P. Segur, Eur. Phys. J.: Appl. Phys. **47**, 22805 (2009).
[10]D. Magni, Ch. Deschenaux, Ch. Hollenstein, A. Creatore, and P. Fayet, J. Phys. D **34**, 87 (2001).
[11]F. Kaddouri, G. D. Stancu, D. A. Lacoste, and C. O. Laux, J. Phys.: Conf. Ser. **157**, 012005 (2009).
[12]J. R. Roth, J. Rahel, X. Dai, and D. M. Sherman, J. Phys. D **38**, 555 (2005).
[13]Z. Fang, Y. Qiu, and Y. Luo, J. Phys. D **36**, 2980 (2003).
[14]J. Ráhel and D. M. Sherman, J. Phys. D **38**, 547 (2005).
[15]J. M. Meek and J. D. Craggs, *Electrical Breakdown of Gases* (Wiley, New York, 1978).
[16]M. Li, C. Li, H. Zhan, J. Xu, and X. Wang, Appl. Phys. Lett. **92**, 031503 (2008).
[17]E. Aldea, J. Bastiaan, M. C. M. van de Sanden, and H. W. de Vries, US2007210721 (2007).
[18]Yu. P. Raizer, *Gas Discharge Physics* (Springer, Berlin, 1991).
[19]S. A. Starostin, P. Antony Premkumar, M. Creatore, E. M. van Veldhuizen, H. de Vries, R. M. J. Paffen, and M. C. M. van de Sanden, Plasma Sources Sci. Technol. **18**, 045021 (2009).
[20]D. R. Anderson, *Analysis of Silicones* (Wiley, New York, 1974).
[21]P. J. Launer, *Silicon Compounds Register and Review* (Petrarch Systems, Bristol, 1987).
[22]V. Raballand, J. Benedikt, and A. von Keudell, Appl. Phys. Lett. **92**, 091502 (2008).