TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

On the Deposition Mechanism of the Silica Like Films in Atmospheric Pressure Glow Discharge

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contained in the exhaust gas, and formed by plasma activation, was performed by gas chromatography coupled with mass spectrometry (GC-MS). The influence of feed composition, in terms of chemical structure of the organosilicon compound and of the oxygen-to-monomer feed ratio, on the properties of the films as well as on monomer depletion and by-products concentration, was investigated.

Results show that in the absence of O_2 polymer-like coatings are deposited. Oxygen addition to the feed leads to a decrease of the carbon content of the film which is more evident when the number of methyl groups in the monomer is lower. GC-MS analyses allowed to appreciate that many linear and cyclic compounds, containing up to five silicon atoms, are formed in the plasma. As an example, in the case of HMDSO, the presence of species containing the dimethylsiloxane (-Me_2SiO-) repeating unit appears to be indicative of oligomerization processes (e.g. chain propagation, ring formation, and expansion reactions) which bring to linear and cyclic compounds with general formulas Me-$(Me_2SiO)_n$-$SiMe_3$ (n = 1-4) and $(Me_2SiO)_n$ (n = 3 - 4), respectively. The extent of unreacted monomer does not depend significantly on the feed composition even if the O_2-to-HMDSO feed ratio is varied in a wide range (i.e. 0-25). However, O_2 addition influences the quali-quantitative distribution of by-products.

The results allow to support hypotheses on the nature of films precursors as well as to clarify some aspects of the overall deposition mechanism and of plasma-surface interaction.

8:40am **PS2-TuM3 Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition by Homogeneous Dielectric Barrier Discharge**, ***N. Gherardi***, *L. Maechler, I. Enache, C. Sarra-Bournet, N. Naudé, H. Caquineau*, LAPLACE - CNRS - Université de Toulouse, France, *F. Massines*, Promes - CNRS, France **INVITED**

Low pressure plasma enhanced chemical vapor deposition (LP-PECVD) is widely used in the industry since it allows obtaining thin films without any substantial temperature increase. On the other hand, these last years, there has been an increasing interest in atmospheric pressure PECVD (AP-PECVD) since it can lead to an appreciable cost reduction. The potential cost saving is related to the suppression of the vacuum equipment and to the on-line processing capability.

In case of two dimensional materials such as rolls of thin polymer films, metal foils or glass plates, dielectric barrier discharge (DBD) appears as one of the most suitable discharges because it is a cold discharge, which is robust, and not disturbed by the motion of the substrate. DBDs normally operate in the usual filamentary mode, but it is now well-known that depending on the gas, electrical parameters, and electrode configuration, DBDs can also operate in homogeneous modes. Depending on the gas in which they are ignited, these homogeneous DBDs generally present different features. In the rare gases (helium, argon, neon…) they are known as atmospheric pressure glow discharges (APGD) as they are characterized by high current densities and an electric field profile between the electrodes showing a cathode fall, a negative glow, a Faraday dark space, and a positive column. In nitrogen, they are called atmospheric pressure Townsend discharge (APTD) as they show lower current densities and a constant high field in between the electrodes.

If AP-PECVD can be achieved using filamentary discharges, the filamentary and statistical nature of this regime leads most of the time to a lack of control of the thin film quality, deposition rate and coating uniformity on large surface. Hence this paper focuses on an AP-PECVD process using homogeneous DBDs.

More precisely, we report here on the deposition of silicon based thin films using homogeneous DBDs working at atmospheric pressure, from hexamethyldisiloxane (HMDSO) diluted either in N_2 or in He, with or without small admixture of nitrous oxide (N_2O) as the oxidizing gas. Our approach consists in studying the thin film properties as a function of the discharge type (APGD or APTD) and N_2O content in the gas phase, using various surface analysis techniques: ellipsometry, profilometry, scanning electron microscopy, Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy (XPS). The gas phase is characterized mainly through optical emission spectroscopy. Results obtained either without motion of the substrate or in a roll-to-roll configuration are discussed, showing the capability of AP-PECVD to realize multilayers.

9:20am **PS2-TuM5 On the Deposition Mechanism of the Silica Like Films in Atmospheric Pressure Glow Discharge**, ***S.A. Starostin***, Eindhoven Univ. of Technology, The Nethelands, The Netherlands, *A.P. Premkumar*, Materials Innovation Institute (M2i), The Netherlands, *M. Creatore*, Eindhoven Univ. of Technology, The Netherlands, *H. de Vries, R.M.J. Paffen*, FUJIFILM Manufacturing Europe BV, The Netherlands, *M.C.M. van de Sanden*, Eindhoven Univ. of Technology, The Netherlands

Atmospheric pressure plasma enhanced thin film deposition (PECVD) is nowadays in focus of increasing scientific and industrial interest. The benefits of this newly emerging technology are in possibilities for cost-efficient in-line roll-to-roll production without expensive and cumbersome vacuum equipment. Yet, comparing to the well studied low pressure PECVD, there is a serious lack of insights on thin film deposition mechanisms on the moving substrates at high pressure.

In this contribution we present a study of the deposition process of silica-like films in the diffuse high power variety of the dielectric barrier discharge referred as atmospheric pressure glow discharge (APGD) [1, 2]. This process is capable to produce uniform carbon-free silica-like films on the polymeric webs in low cost gas mixtures [2]. Considering deposition mechanisms in a roll-to-roll atmospheric PECVD reactor with a moving polymer substrate and gas flow, three different pathways which are simultaneously contributing to the film formation can be identified: a) ionic deposition, where ionized products of the decomposed precursor drift in the electric field towards the surface; b) diffusive deposition of neutral radicals produced in plasma and afterglow phases and c) deposition of large particles or dust. Due to the gas flow and depletion of the precursor, each of these mechanisms leads to layers characterized by a specific composition, morphology and location within the discharge area. In this contribution we will address the influence of the different mechanisms on film deposition, supported by space-resolved spectroscopic ellipsometry, XPS, SEM and water contact angle measurements. The experimental profiles of the deposition rate along the gas flow were analyzed with a 2D numerical convection-diffusion deposition model.

[1] S. Okazaki, M. Kogoma, M. Uehara, Y. Kimura, J. Phys. D: Appl.Phys., **26**, 889, (1993)

[2] S.A. Starostin, M.A. ElSabbagh, E. Aldea, H. de Vries M. Creatore, M.C.M. van de Sanden, *IEEE Trans. Plasma Sci.* **36**, 968 (2008)

[3] S. Starostine, E. Aldea, H. de Vries, M. Creatore, M. C.M. van de Sanden, Plasma Process Polym, **4**, S440 (2007)

9:40am **PS2-TuM6 Industrial Scale Pulsed Atmospheric Dielectric Barrier Discharges**, ***B.D. Schultz***, *W.M. Hooke, W.F. Hargrove, A.R. Martin*, International Technology Center

Atmospheric dielectric barrier plasma glow-like discharges over 1 meter in length and 500 square centimeters in area have been generated in air with a custom high voltage driving source. Pulse peak currents well in excess of 1 kiloampere at atmospheric pressure with total charge transfer up to 90 microcoulombs have been repeatedly generated in homogeneous discharges at frequencies up to 100 hertz. A rapid voltage rise time at 20-30kV is readily achieved by the source and is sufficient to produce a voltage across the electrodes in excess of the DC breakdown voltage prior to the onset of breakdown. The overvoltage condition plays an important role in determining the uniformity of the plasma discharge. Electrical modeling of the discharge characteristics show the resistivity of the plasma to change over the course of an individual pulse causing the discharge characteristics to switch from an oscillatory state to a critically damped state. Charge transfer and power densities in dielectric barrier discharges are limited by the electrode size and the intrinsic material properties of the dielectric used to distribute the space charge. It will be shown that the charge transfer of each pulse scales proportionally with the size of the electrodes for a given dielectric as should be expected for a complete homogeneous discharge. This paper will emphasize the correlation between overvoltage conditions, dielectric material properties, and electrode size to the electrical charge transfer of the glow-like discharge. The impact of the charge transfer scaling behavior on the scaling of other critical parameters like current density will also be discussed.

10:40am **PS2-TuM9 Optical Emission Spectroscopy of an Argon DC Microdischarge: Electron Density and Gas Temperature Profiles**, ***S.G. Belostotskiy****, *T. Ouk, V.M. Donnelly, D.J. Economou*, University of Houston, *N. Sadeghi*, Université Joseph Fourier de Grenoble, France

Optical Emission Spectroscopy was employed to study a high pressure (100s of Torr) DC microdischarge in argon, with traces of N_2 and H_2 present and acting as optical tracers. Spatially resolved measurements of gas temperature across the 600 μm slot-type discharge were obtained from analysis of the rotational structure of two transitions of the first positive band of N_2: $B^3\Pi_g(v{=}4) \rightarrow A^3\Sigma_u^+(v{=}1)$ and $B^3\Pi_g(v{=}5) \rightarrow A^3\Sigma_u^+(v{=}2)$. Gas temperature profiles peaked at the cathode side of the discharge and slowly decreased towards the anode. Such behavior is consistent with the physics of DC discharges, where most of the power dissipation occurs in the cathode layer. The gas temperature increased with increasing current, reaching a maximum of T_g = 1200 K at I = 30 mA and P = 600 Torr. Electron densities were extracted from the spectral profile of the H_β line. The profile was fit with a Voigt function, which included Doppler, pressure, instrumental and Stark broadening. The electron density was estimated from the contribution of Stark broadening. The spatial profile of electron density

***** PSTD Coburn-Winters Student Award Finalist