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Plasma 2D modeling and diagnostics of DLC deposition on PET

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Abstract

The possibility to apply two dimensional (2D) emission spectra of short-lived excited species for estimating the uniformity of production of ions and radicals that have an important role in the deposition of diamond-like coatings on polymeric substrates was investigated. Images of the α-balmer line of atomic hydrogen in CH_4/H_2 discharges were recorded under various total gas pressures and substrate bias voltages to reveal that the increase of the total gas pressure enhances radial non-uniformities of the electron population with energy higher than 16 eV. A comparison between these images and the results of a 2D simulator of CH_4/H_2 discharges shows that the most abundant ions (H_3^+, CH_5^+) and radicals with high reactivity in the gas phase (CH_2, CH, C) present similar axial and radial distribution with these emission maps.

Keywords: Plasma CVD; Bias growth; Reactor modelling; Gas phase reactions

1. Introduction

Recently, the deposition of DLC on polymeric substrates has attracted particular attention for application in plastic optics [1] as well as in food packaging [2] and in biomedical products [3]. Different polymeric substrates as Polycarbonate (PC), Polymethylmethacrylate (PMMA), Polyethylene terephthalate (PET) and Polyvinyl chloride (PVC) substrates have already been coated with amorphous carbon films leading to a significant improvement of their chemical and mechanical surface properties [4–6]. Plasma Enhanced CVD has a definitive advantage for the growth of these films, because it permits the deposition on these sensitive polymer substrates even at room temperature [7]. However, a drawback of this technique is the rather high complexity as a number of physical and chemical processes take place simultaneously, which in turn makes process understanding and its effective control and reproducibility more difficult.

In this sense, there is an emerging need for suitable in situ and non-intrusive plasma diagnostics that can support in an easy and fast way control and optimization of such processes. In this direction, the present work is focused on the implementation of 2D emission spectroscopy as a diagnostic tool for the fast estimation of production and axial/radial distribution of ions and radicals that have an important role in the DLC growth on PET in CH_4/H_2 discharges. The work was performed under well controlled discharge electrical conditions and for different total gas pressures and PET substrate bias voltages and it was complemented by the use of a 2D fluid model of CH_4/H_2 RF discharges.

2. Experimental

The experiments were performed in a cylindrical stainless steel parallel plate chamber with 5.5 mm in diameter electrodes and adjustable electrode separation. The interelectrode space for this series of experiments was kept constant at 25 mm. The chamber is equipped with four quartz windows suitable for optical measurements. The RF electrode is powered by an ENI ACG-3 13.56 MHz RF generator via an L-type matching network, while the substrate electrode is biased using an ENI AT3200 variable frequency generator tuned at 30 KHz. The amount of RF power actually fed into the discharge chamber was determined using an accurate method, employing Fourier transform analysis of power and phase from current and voltage waveform measurements. The excitation voltage and the discharge current signals were measured on the powered electrode lead, using a high impedance 1 : 100 attenuation voltage probe (Hameg, model AZ92) and a 0.1 Ω transfer impedance RF current probe (FCC model F-35-1). The measured voltage and current waveforms were then transformed to the ones at the surface of the powered electrode using an equivalent circuit comprising only experimentally

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determined components [8]. The substrate bias voltage was measured using another high impedance 1:10 attenuation voltage probe (Hameg, model AZ92).

The setup used to record the emission spectra and 2D emission images consists of a cylindrical or a focusing achromatic lens, an imaging spectrograph and an iCCD detector (Andor, iStar734). The dimensions of the quartz window were higher than the discharge area allowing the recording of the emission from the whole discharge area either in the axial or the radial direction. Emission spectra of CH_4/H_2 discharges were obtained for the wavelengths between 200 nm and 700 nm. Emission 2D images were recorded for the CH radical ($A^2\Delta \rightarrow X^2\Pi$, 431 nm), H_2 ($d^3\Pi_u \rightarrow a^3\Sigma_g^+$, 612 nm), H_α ($n=3 \rightarrow n=2$, 656 nm) and H_β ($n=4 \rightarrow n=2$, 486 nm) by using suitable interference filters.

3. Model

The 2D self-consistent model has been described in detail in Refs. [9,10]. Briefly, the model uses the particle, momentum and energy balances obtained from moments of the Boltzmann transport equation, coupled with Poisson's equation for a self-consistent calculation of the electric field.

Special attention was given in the detailed gas phase chemistry and the DLC growth by including in the model 27 species (radicals, ions, neutrals, excited species), 5 surface species (physisorpted sites and bulk material), 58 gas phase reactions (electron – molecule, radical – molecule, radical – radical, ion – neutral) and 44 surface reactions (physisorption, chemisorption, desorption, sputtering and stitching). The required collision cross-sections were taken from Refs. [11,12] and the set of reaction rate constants from Ref. [13]. For the plasma – surface interaction it was assumed that all radicals reaching the surface are initially physisorpted with probabilities taken from Ref. [14]. Then a number of reactions were considered which can lead to spontaneous desorption, chemisorption, sputtering and ion enhanced chemisorption. The rate constants of these reactions, the sputtering yields and the ion sticking probability were taken from Refs. [14,15]. For the spatial discrimination of the transport equations a Sharfetter – Gummel scheme was applied and in order to avoid instabilities the distance between the two electrodes was divided to 40 grid points whereas the radial direction was divided to 50 grid points.

4. Results and discussion

Experimental measurements of the power dissipation in the discharge and 2D optical emission spectra together with the fluid model were applied at different CH_4/H_2 total gas pressures (0.25 to 1 Torr) and for different substrate bias voltages (0 to 350 V peak to peak). The fraction of CH_4 in the gas mixtures was set at 8% in all cases, the total gas flow rate at 50 sccm and the distance of the RF electrode from the PET surface at 2.5 cm. In these conditions, previous work of this group [16] has shown that the decrease of pressure or/and the increase of the substrate bias for the same applied voltage (400 V peak to peak) results in an enhancement of the power dissipation in the discharge. This trend was also reproduced by the simulation and an excellent agreement was found between the model calculations and the experiment concerning the electrical properties of the discharge. For instance, in the case of 0.25 Torr and unbiased conditions the calculated power was 4.1 W and the measured 3.8 W. For the same pressure but for 350 peak to peak substrate bias the calculated power was 7.2 W and the measured 6.9 W. This agreement, which is very important for a reliable application of the model, was achieved only after the introduction of almost all the electron collision reactions that can take place with CH_4 and H_2 but also with higher homologues as C_2H_2, C_2H_4, C_2H_6 and C_3H_6 that are produced in the discharge. The use of simplified gas phase chemistry schemes always led to model underestimation of the total power dissipated in the discharge.

In the same work [15], time-averaged 1D spatially resolved optical emission spectroscopy of CH excited species ($A^2\Delta - X^2\Pi$) and α-balmer line of atomic hydrogen were found to be rather sensitive in the variations of either the total gas pressure or the substrate bias voltage. However, no information was obtained on the radial distribution of the species, which will affect the uniformity of the deposited layers. Thus, Fig. 1(a), (b) and (c) presents the time-averaged 2D images of the H_α line

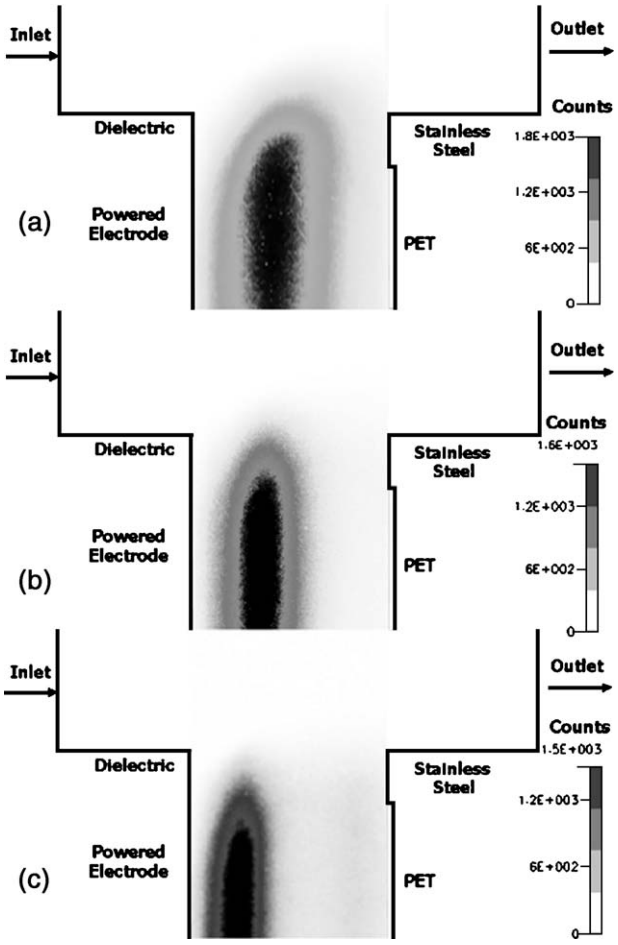

Fig. 1. 2D emission images of α-balmer line of atomic hydrogen in 8% CH_4 in H_2 discharges, 400 V peak to peak RF voltage, and 350 V substrate bias voltage and for total gas pressures of (a) 0.25 Torr (b) 0.5 Torr and (c) 1 Torr.