Workshop "Plasmas in Medicine"

BIOFUNCTIONAL PLASMA POLYMERIZED ETHYLENEDIAMINE THIN FILMS FOR IMPLANT COATINGS

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The plasma polymerization of ethylenediamine (EDA) in capacitively coupled 13.56 MHz plasma was investigated to synthesize mechanical stable thin films with biofunctional interface relevant for implant coatings. The experimental set-up consists of a stainless steel vacuum chamber with diameter and height of 400 mm, respectively, including vacuum pumps, the necessary units for gas control and rf power supply as well as diagnostic ports. The powered planar rf electrode with diameter of 100 mm forms with the grounded chamber wall an asymmetric rf discharge with negative self-bias voltage at the powered electrode. Additionally, a specific arrangement for temporal covering the substrate against the plasma is mounted above the powered electrode. This covering enables the investigation of thin film deposition after defined plasma chemical conversion of the precursor molecules without interruption of the rf plasma. Further, to ensure constant temperatures of the samples on the powered rf-electrode, its temperature can be controlled of between 10-15°C by a cooler. The rf plasma can be operate either in continuous or pulsed mode. For pulsed mode operation the pulse-delay generator was connected with the rf-generator which allows pulse frequencies up to 10 Hz. The duty cycle of the square-pulse was kept constant at 50%. The typical rf power input was in the range from 20 W to 100 W.

The plasma processing gas was a mixture of argon (4 sccm - 60 sccm) and the precursor EDA (4 sccm - 20 sccm). The gas flow rate of the EDA is adjusted by a needle valve. To ensure a constant EDA vapour pressure the storage container for the liquid EDA was kept constant at 30 °C by use of thermostat. Additionally, the EDA gas transfer units to the plasma reactor were also heated to avoid condensation. The total gas pressure was in the range from 20 Pa to 200 Pa.

The plasma chemical conversion of the precursor ethylenediamine (EDA) was studied by means of optical emission spectroscopy (OES). In particular the strong CN emission at 384 nm was applied to monitor the state of plasma chemical fragmentation of the precursor molecule, see Figure 1a. At the beginning, the rising intensity ratio CN/Ar reflects the consumption of the precursor molecule EDA due to plasma chemical reactions. Steady state condition is received after about 80 s plasma processing time at the used plasma processing parameters.

The deposited thin films on silicon and aluminium substrates were characterized using spectroscopic ellipsometry (UV-vis) for determination of thin film thickness and optical properties (refractive index, extinction), and FT-Infrared-Reflection-Absorption-Spectroscopy (IRRAS).

At steady state plasma conditions the growth rate of PPEDA thin film amounts to about 0.3 nm/s, see Figure 1a.

The FTIR absorption spectrum of deposited PPEDA thin films show characteristic broad absorption bands of N-H (3000 and 3500 cm^{-1}), C-H (2900 cm^{-1}), C≡N/C≡C (2150 cm^{-1}), and

NH_2 (1600 cm^{-1}) which indicates cross-linked plasma polymer films, see Figure 1b. The strong absorption at 1600 cm^{-1} may be the result of the overlapping absorption with the imine group (-CH=NH) as interpreted by Krishnamurthy et al. [3]. Furthermore, they found also nitrile (C≡N) groups in the FTIR spectrum.

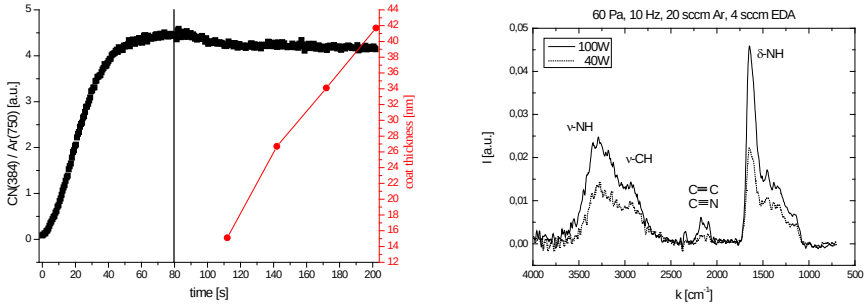

Fig. 1: (a) Ratio between the optical emission intensities of the CN molecule at 384 nm and the argon line at 750 nm (black). Growth of PPEDA thin film on silicon substrate during steady state plasma conditions (red). (b) IR absorption spectrum (IRRAS) of thin PPEDA films deposited on aluminium substrate at two different rf powers. Pulsed rf plasma: 100W (40 W), 10Hz, 60Pa, 20sccm Ar, 4sccm EDA.

For the cell adhesion tests the plasma polymerized etylenediamine thin films were deposited on biomedical substrates (TiAlV corundum blasted) relevant to endoprosthesis. The human osteoblastic cells MG-63 (ATCC) were seeded onto the sample and cultivated in DMEM at 37 °C and 5 % CO_2. The cell adhesion (10 min) on PPEDA thin films deposited in the pulsed plasma operation is significantly enhanced in comparison with the uncoated reference sample, see Figure 2.

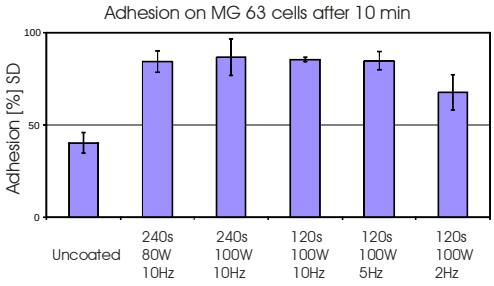

Fig. 2: Cell adhesion of MG63 cells on uncoated and PPEDA coated TiAlV substrates.

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Reference

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