Gas phase products and kinetics in ethylenediamine plasma polymerization

J. Meichsner(*) and H. Testrich

University of Greifswald, Institute of Physics, Felix-Hausdorff-Str. 6, 17487 Greifswald

(*)meichsner@physik.uni-greifswald.de

Plasma polymerized thin films from ethylenediamine deposited on Ti-6Al-4V implant material have been shown enhanced adhesion and spreading of human osteoblastic cells MG-63 (ATCC). Beside the film deposition the stable gas phase products and their macroscopic kinetics were studied by FTIR spectroscopy and mass spectrometry to achieve fundamental knowledge about the dominant plasma chemical reaction channels in conversion of the precursor gas. The gas phase products and kinetics are also important for process control, upscaling and exhaust gas handling.

Ethylenediamine (EDA, $C_2H_8N_2$) was applied as precursor for deposition of plasma polymerized thin films with deposition rate up to 15 nm/min relevant for cell-adhesive implant coatings [1]. Here, the plasma chemical consumption of ethylenediamine (EDA) as well as the formation of stable gas phase products in low pressure rf plasma is studied. The investigations were performed using an unconfined asymmetric capacitively coupled rf discharge configuration consisting of a water cooled planar rf powered electrode of 10 cm in diameter, whereas the electrode shielding and chamber wall were grounded. The 10 Hz pulsed capacitively coupled 13.56 MHz plasma (CCP) was driven at forward rf power between 40 W and 100 W. A mixture of argon and ethylenediamine (5:1) was applied as plasma processing gas at initial total gas pressure of typical 60 Pa. For studying different states of plasma chemical gas conversion no gas flow through the reaction chamber (total volume about 50 l) was used, and gas samples were taken from the chamber after defined plasma processing time. The gas samples were analysed both by FTIR spectroscopy [2] and neutral gas mass spectrometry [3].

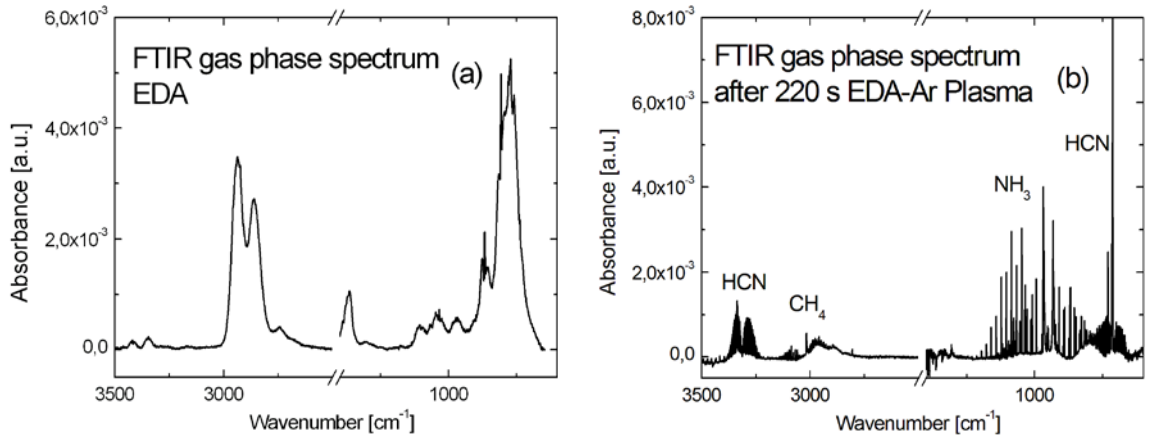

Figure 1: Gas phase FTIR absorption spectra from ethylenediamine (a) and gas sample taken from the reaction chamber after 220 s plasma processing time (b).

Generally, the precursor gas EDA mainly dissociate by electron impact in the active plasma zone, and the following reactions of fragment species at surfaces and in the gas phase result in thin film deposition and formation of neutral transient and stable gaseous reaction products. For example, the figure 1 presents FTIR gas phase absorption spectra from the precursor EDA (a) and the gas sample taken from the reaction chamber after about 220 s plasma processing time (b). It is clearly seen, that the precursor EDA is almost consumed and the stable reaction products NH_3, HCN and CH_4 could be identified in the FTIR spectrum. In similar way the mass spectrometric analysis was performed. The

typical positive fragment ion pattern are used to select characteristic positive fragment ions in the mass spectrum of the gas sample and to identify the precursor molecule and different neutral reaction products NH_3, HCN, CH_4 and H_2. Thereby, data are involved from NIST and calibration measurements using separate mass spectra from the precursor EDA and available gases (NH_3, CH_4, H_2). Thereby, the positive ion spectra reveal the characteristic positive fragment ions to indentify the EDA content as well as NH_3, HCN, CH_4 like that in FTIR analysis, and additionally H_2 as stable gaseous reaction products.
Furthermore, the gas samples taken from the reaction chamber were analysed in dependence on the plasma processing time and rf power. As an example, the Figure 2 presents the macroscopic kinetics of plasma chemical conversion of the precursor EDA in stable gaseous compounds.

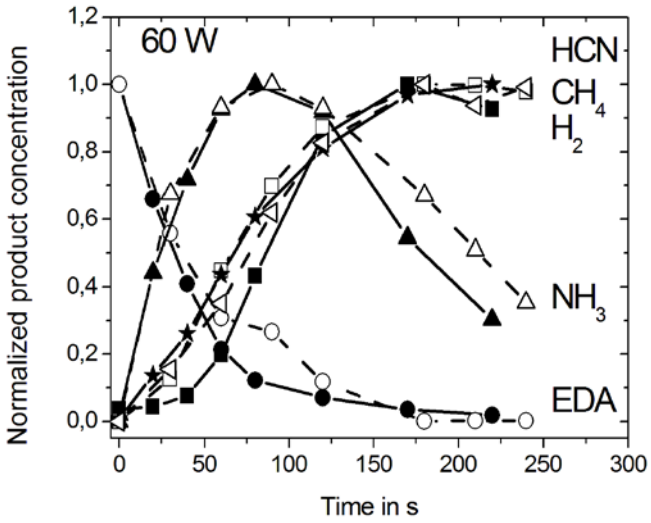

Figure 2: Normalized product concentration in dependence on the plasma processing time in pulsed rf plasma (t=0: 60 Pa, Ar:EDA=5:1; 60 W) from mass spectrometry (solid symbols and lines) and FTIR spectroscopy (open symbols and dashed lines).

The kinetics of stable gaseous reaction producs reveals a consecutive reaction in gas phase by consumption of the precursor molecule EDA, the formation of the intermediate product NH_3 and finally the end products HCN, CH_4 and H_2. The large time scale results from the gas exchange between the active plasma volume and large buffer volume in the 50l reaction chamber. Furthermore, the reaction at reactor walls may be considered, too.

Acknowledgments

The investigations were realized within the BMBF collaborative research project “Campus PlamaMed”, part PlamaImp, grant no 13N11182.

References

[1] B. Finke, F. Hempel, H. Testrich et al., Surface & Coatings Technology 205 (2011) S520–S524, doi: 10.1016/j.surfcoat.2010.12.044
[2] S. Kaledat, Diploma thesis, University of Greifswald, 2011
[3] M. Dünnbier, Master thesis, University of Greifswald, 2011