

The reactivity of thin plasmopolymerized ethylenediamine films

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Nitrogen-rich plasma polymerized ethylenediamine (PPEDA) films (20 nm - 70 nm) relevant for implant coatings were deposited on different substrate materials (Au, Ag, Cu, Al, Zn, Ti, Ti6Al4V, and X2CrNiMo) in low pressure capacitively coupled 13.56 MHz plasma. The molecular composition of the thin PPEDA films was characterized by IR reflection-absorption spectroscopy. During storage of these films in ambient air, characteristic changes in the absorption spectrum were observed on a short time scale immediately after deposition, and over long-time period of 360 days. In the specific case of the combination Cu-PPEDA, new absorption bands appear which reveal additionally interface reaction of the PPEDA film with the substrate material.

A capacitively coupled 13.56 MHz plasma, pulsed with 10Hz at 50% duty cycle, was applied for deposition of thin plasma polymerized ethylenediamine films (PPEDA) relevant for human MG63 cell-adhesive implant coatings. The plasma processing gas was a 5:1 mixture of argon and the precursor ethylenediamine (EDA). To ensure a constant EDA vapour pressure the storage container for the liquid EDA was kept constant at 30 °C. The typically plasma processing parameters are the total pressure of 60 Pa, total gas flow rate of 24 sccm, as well as rf forward power of 60 W used for thin film preparation and the investigation of the film ageing during long-time storage in ambient air, and 100 W for the study of PPEDA reactions with substrate material, respectively. The molecular composition of PPEDA thin films was analysed by FTIR reflection absorption spectroscopy (FT-IRRAS). For the IRRAS measurements the thin PPEDA film was deposited on highly reflective metallic surfaces.

The FTIR absorption spectrum of the PPEDA thin film deposited on aluminium substrate shows characteristic broad absorption band of the ν -N-H stretching vibrations (3000 and 3500 cm^{-1}) as well as the ν -C-H (2900 cm^{-1}), ν -C \equiv N/C \equiv C (2150 cm^{-1}), and δ -NH₂ (1600 cm^{-1}) absorption bands which indicates cross-linked plasma polymer film, see Figure 1 left side. 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. [2]. Furthermore, they found also nitrile (C \equiv N) groups in the FTIR spectrum.

The comparison of the thin film absorption spectrum directly after preparation with that after 360 days storage under ambient conditions shows significant changes in the absorption spectrum. The difference spectrum provides information about the formation or the degradation of molecular structures and groups due to reactions with oxygen as well as the broadening and shift of absorption bands, see Figure 1 right.

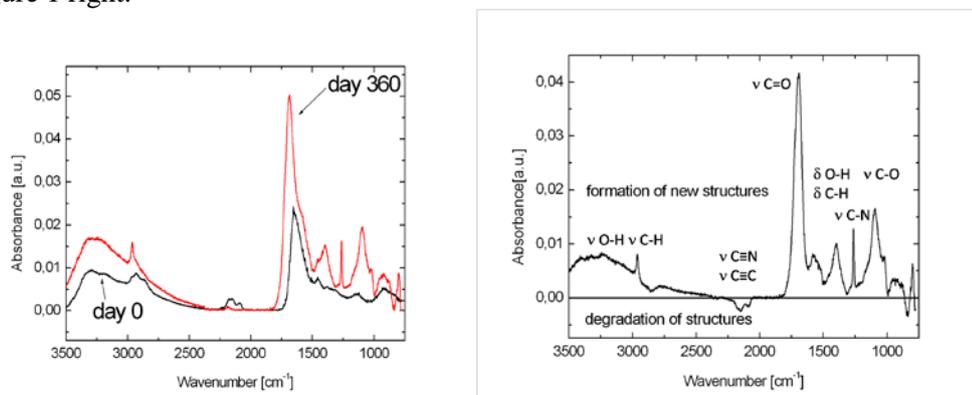


Fig. 1: Left: FT-IRRAS spectra of thin PPEDA film directly after preparation and after 360 days storage in air. Right: the corresponding difference spectrum from left shows the formation and degradation of molecular structures and groups after storage over 360 days under ambient air.

In more detail, the characteristic changes due to ageing of the thin PPEDA films results from the increasing O-H absorption (stretching vibrations at $3500\text{-}3000\text{ cm}^{-1}$), the formation of carbonyl groups C=O (stretching vibrations at $1700\text{-}1680\text{ cm}^{-1}$) which may be assigned to acid amide formation. In the fingerprint region the changes are found which are assigned to the deformation vibrations of C-H and O-H groups at $1465\text{-}1375\text{ cm}^{-1}$ as well as to the stretching vibrations C-N and C-O at about 1250 cm^{-1} and 1100 cm^{-1} , respectively. Furthermore, the loss of the $\text{C}\equiv\text{N}$ and $\text{C}\equiv\text{C}$ molecular structures is observed.

Beside the aluminium substrate, further metallic substrates are taken into consideration for studying chemical reaction of the PPEDA film with the substrate material. The metallic Cu, Ti/Cu, Ag, Zn, and Ag layers were prepared by high power pulse magnetron sputtering (HIPIMS) whereas the Al and the Au layers were deposited by thermal evaporation on glass samples. The Ti as well as the X2CrNiMo 17-12-2 samples were polished solid material. With exception of copper, all other investigated materials reveal no significant reaction with the thin PPEDA film. In the specific case of Cu-PPEDA combination significant new absorption bands are found, see Figure 2. The new absorption bands can be identified due to chemical reactions of the copper with OH groups and H_2O at $4000\text{-}3000\text{ cm}^{-1}$ [3][4][5], with NH [5], NH_2 and NH_3 at $3500\text{-}3000\text{ cm}^{-1}$ [3] and N_3 at 2000 cm^{-1} [6].

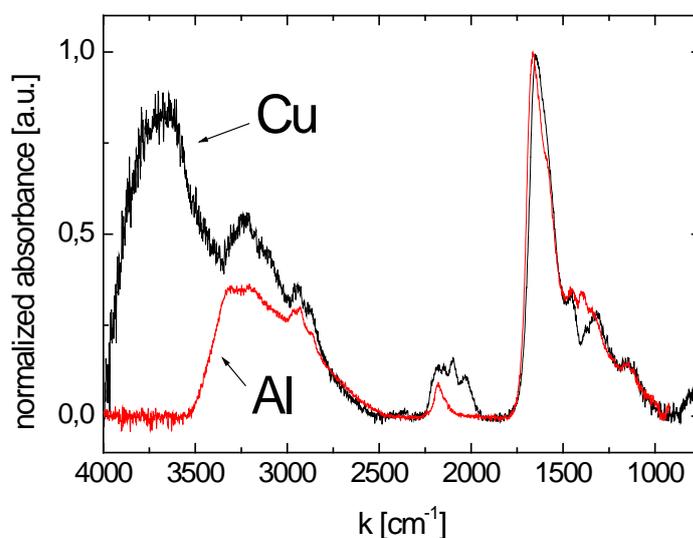


Fig. 2: Normalized IR absorption spectra (FT-IRRAS) of thin PPEDA film on copper and aluminium substrate directly after deposition.

Acknowledgments

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