

OR2102

Fabrication and Characterization of Photo- and Plasma-chemically Deposited Thiol-terminated Films

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The performance of synthetic polymers can be improved by modifying their surface properties. Polymer surfaces generally have low chemical reactivity, not capable of forming adhesive bonds, and are poorly-wetting. Among different modified surfaces, thiol-terminated ones have been progressively gaining interest over the past years. They have been shown useful for many applications, such as promoting adhesion of gold layers and nanoparticles, and for immobilizing biomolecules. In this work, thin organic films incorporating sulfur-bearing functional groups have been prepared by "co-polymerizing" gas mixtures of ethylene (C₂H₄) or butadiene (C₄H₆), as the hydrocarbon source, with H₂S, as the source of bound S in the coatings. This has been accomplished by either (i) low-pressure r.f. plasma-assisted chemical vapor deposition (PACVD); or (ii) by vacuum-ultraviolet (VUV) irradiation of the reagent gas mixtures at reduced pressure with near-monochromatic radiation from different lamps ($\lambda=112-254$ nm). Different VUV lamps have been used to investigate the wavelength dependency of the deposition chemistry and the stability of these films. All deposits were characterized by X-ray photoelectron spectroscopy (XPS) before and after chemical derivatization with N-ethylmaleimide, which serves to quantify the thiol concentrations on the surfaces. The stability of the coatings was measured as loss of thickness in water after 24h of immersion. XPS survey spectra of the deposited films at different R values reveal important amounts of bonded sulfur, the concentration, [S], being found to increase with rising R, up to [S] = 48 at. %. This analysis also shows that both deposition methods, low-pressure plasma and VUV irradiation, influence [S] in quite similar ways. After derivatization with N-ethylmaleimide, some differences between the two film types can be observed: plasma-polymers show higher [SH] values, up to 3 %. After immersion in water for 24h, all coatings remained of essentially unchanged thickness.

Keywords

plasma polymerization
vacuum ultraviolet photo-polymerization
sulfur-rich organic films