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Tailoring of the PS surface with low energy ions: Relevance to growth and adhesion of noble metals

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Abstract

Ion–polymer interaction induces different phenomena in the near surface layer of polymers, and promotes its adhesion to metals. Using XPS, TEM and AFM, polystyrene surface was examined after 1 keV ion-beam treatments with oxygen, nitrogen and argon ions in the ion fluence range from 10^{12} to 10^{16} cm^{-2} to clarify the following points: chemical reaction after treatment in vacuum and after exposure to air, identification of adsorption-relevant species for metal atoms, formation of cross-links in the outermost polymer layer. The early stages of metal–polymer interface formation during metallization play a crucial role in the metal–polymer adhesion. Therefore, the influence of the ion fluence and ion chemistry on the condensation of noble metals, film growth and peel strength were measured. The peel strength showed a maximum at a certain fluence depending on ion chemistry. For example, the surface treatment with very low fluence of oxygen ions improved the adhesion between copper and polystyrene by two orders of magnitude without significantly increasing the surface roughness measured with AFM. The locus of failure changed at the same time from interfacial failure for untreated polymer surfaces to cohesive failure in the polymer for modified surfaces. A multilayer model of the metal–polymer interface after ion treatment is suggested.

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Keywords: Ion irradiation; Polymers; Glass transition; X-ray photoelectron spectra–surface analysis

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1. Introduction

Metallized polymers are used widely in many products. The metallization of polymers with noble metals is of interest for various applications [1]. However, due to the chemical inertness of

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noble metals, a surface treatment of the polymers is necessary before metal deposition in order to improve the metal/polymer adhesion. It is known that irradiation of polymer surfaces with low energy ions promotes adhesion to metals [2]. This paper provides new results concerning the correlation between the adhesion strength and the early stages of metal/polymer interface formation after surface treatment with low energy ions (1 keV). The early stages of metallization (emphasis is put on Cu and Au) are far from thermodynamic equilibrium conditions since isolated metal atoms impinge on the polymer surface. Therefore, various competing processes (adsorption, surface diffusion and nucleation after encountering of metal adatoms, metal atom reemission into vacuum, etc.) have to be taken into account to understand how the metal–polymer interface is formed. Some details on nucleation and growth of noble metals on non-treated polymer surfaces as well as some new techniques for investigation of these phenomena were presented elsewhere [3–5]. The strong metal–polymer adhesion in the case of more reactive metals such as Cr, Al or Ni, as a rule, is accompanied by higher condensation coefficients (the ratio of the number of adsorbed metal atoms to the total number of metal atoms arriving at the surface) and nucleation densities compared to noble metals. These tendencies should be taken into account when studying the influence of ion irradiation on adhesion properties of noble metals on polymer surfaces. Recently [6,7], we have investigated the enhancement of the adsorption probability of metals on polymers by ion irradiation. In this paper, a number of new details are discussed, in relation to the earlier studies. Chemical processes occurring in the outermost layers (0–5 nm) of the polymer surface during ion irradiation with a low ion fluence between 10^{12} and $10^{16}\,\mathrm{cm}^{-2}$ are taken into account.

Like low-pressure plasma treatment, irradiation of a polymer surface with low energy ions promotes its adhesion to metals [8–10]. Due to the complexity of the plasma–polymer interaction there are still many unresolved questions regarding the contribution and the efficiency of the surface modification by different particles generated in the plasma. In order to achieve the reproducibility of the plasma treatment for practical applications, numerous parameters such as gas flow and gas mixture, discharge power density, electrical potential, working distance, etc. must be carefully controlled. In contrast, irradiation with low energy ions allows one to define exactly the process conditions of ion bombardment: ion type, energy and dose. Moreover, the ion irradiation of a polymer surface can be followed by the post-irradiation chemical modification in a reagent gas. Therefore, the influence of the treatment parameters such as fluence or ion energy on the polymer surface modification, which result in the formation of different functional groups, polymer degradation and crosslinking, can be studied independently. A significant increase in the polymer surface energy has been obtained by the so call ion-assisted reaction (IAR), in which the polymer surface was irradiated with energetic ions (~1 keV) in a reactive gas environment [10]. High energy (in MeV range) ion-beams have been used to study the structural changes induced in polymers [11] and the formation of hydrogenated carbon layers [12].

However, a poor understanding still remains concerning the processes that occur in a polymer pre-surface layer during ion bombardment, as well as concerning the kinetics of post-bombardment chemical processes. In this paper, the results of the ion-beam treatment of polystyrene (PS) is discussed. PS is an example of structurally simple polymer that contains a phenyl ring, which is used to determine the effect of the aromatic system on the rate of modification and the population of ion-induced species. Using surface sensitive techniques, polymer surfaces are examined after ion treatment in order to evaluate the following: identification of adsorption-relevant species for metal atoms, stability of aromatic rings and crosslinking in the outermost polymer layer, as well as post–treatment reaction after exposure to atmosphere. Results obtained on changes of the polymer structure induced by ion irradiation and its influence on the metal–polymer interface formation are summarized. Emphasis is put on the study of dependence of peel strength between the polystyrene film and evaporated copper on the ion fluence and ion chemistry.