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Physical Properties and Structure of Thin Conducting Ion-Beam Modified Polymer Films

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Summary: In this work, a complex investigation of the film surface composition, chemical bonding, conductivity, optical properties, density, hardness and Young's modulus of ion-beam-modified polyimide films was carried out. It was shown that the partial destruction of chemical bonding under ion bombardment leads to the formation of graphite-like, amorphous carbon islands, which increase the surface film conductivity by several orders of magnitude, from an insulating to a semiconducting region. Strong enhancements of both the conductivity and the optical absorption coefficient occur when the fraction of amorphous carbon clusters dispersed in a polyimide matrix reaches 40 %. The values of hardness, Young's modulus and density at high irradiation doses reach the values typical of a hydrogenated amorphous carbon.

Keywords: conductivity; density; ion implantation; polyimide; XPS

Introduction

Thin films of aromatic polymers such as polyimides (PI) find extensive use in electronics. For particular sensor applications, physical properties of these films must be tailored. In this case, PI films are used as water vapor-uptaking layers for bimorphic humidity sensors. It was shown that ion implantation improves sensoric properties of polyimides.[1-3] In this work, the changes in structure and physical properties of polymer films are discussed in dependence on the dose and energy of implanted ions and irradiation conditions for PI films, which lead to optimal sensor properties.

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Experimental

The polyimide considered in this study is DuPont's polyimide PI2566 obtained from 4,4'-(1,1,1,3,3,3-hexafluoropropan-2-yl)bis(phthalic anhydride) and 4,4'-oxydianiline, Figure 1a). The samples were obtained by spin coating of Si substrates with PI precursor solutions (polyamic acids / *N*-methyl-2-pyrrolidone). The PI films were soft-baked at 90 °C for 20 min to remove the solvent and then they were cured in nitrogen at 400 °C for 1 h. The final film thickness was typically between 500 and 600 nm. The PI films were irradiated with a B^+ ion beam (energy 180 keV, dose 10^{13} - 10^{16} B^+/cm^2).

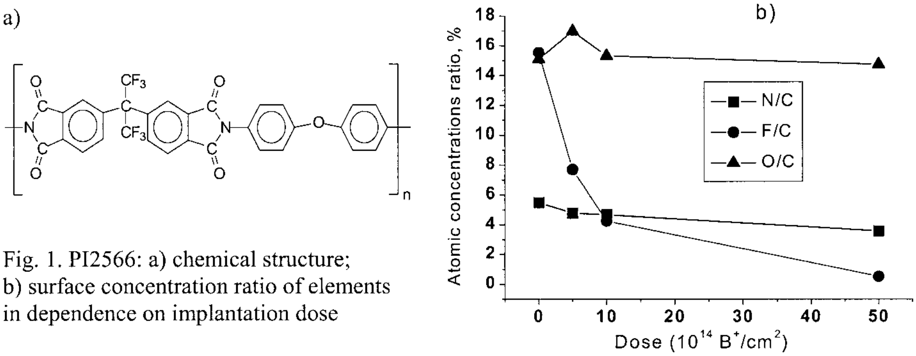

Fig. 1. PI2566: a) chemical structure; b) surface concentration ratio of elements in dependence on implantation dose

The chemical structure of the modified polyimide layers was investigated by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics PHI 5702 electron spectrometer. The sampling depth of this technique amounts to 2 - 5 nm at a take-off angle of 45°. The atomic ratios of the elements were estimated using tabulated sensitivity factors. The spectra were referenced to the C 1s line at 284.8 eV arising from C-C or C-H bonds. The core level peaks have been analyzed by means of a Gauss-Lorentz best-fit computer program with background subtraction. The curve-fitting quality was evaluated by chi-convergence. Volume and surface conductivity measurements were performed using electrode configurations consisting of an evaporated NiCr bottom electrode, pressure-measuring and guard electrodes as described in IEC 93.[4] Refractive index and extinction coefficient spectra were calculated from the main ellipsometric angles Δ and Ψ measured in the spectral range 400-900 nm with a Woollam spectral ellipsometer working in the rotating analyzer mode. Hardness and Young's modulus *E* of modified PI films were investigated by the Hysitron depth-sensing nanoindentation technique with a Berkovich indenter. The nanoindentation analysis was carried out by the Oliver and Pharr method.[5] Density and *E* modulus were determined by a surface-acoustic-waves (SAW) technique as described in [6].

Results and discussion

The changes in the polymer surface composition after ion implantation (determined by XPS) are shown in Fig. 1b. The N/C, F/C and O/C atomic composition ratios were estimated from the ratios of integrated net intensities of the N 1s (at binding energy 400.15 eV), F 1s (688.26 eV) and O 1s (532 eV), respectively, to C 1s (285 eV) spectra with a correction for the atomic sensitivity factor. The chemical modifications observed at ion doses higher than $5 \cdot 10^{14}$ B^+/cm^2 are caused essentially by the drastic depletion of F and N, the modification of the residual O and the enrichment of C. The virgin C 1s core level spectrum deconvoluted into Gaussian components consists of five distinct peaks. The lowest binding energy peak at about 284.9 eV, which is the most intense, is attributed to emission from aromatic C atoms not linked to O or N.[7,8] The peak at 286.8 eV is due to C atoms linked to nitrogen (C-N) and oxygen (C-O-C), with a possible extra contribution of C atoms of the 6FDA ring.[7-9] The peak at 288.3 eV is due to carbonyl bonds (C=O) of the imide groups[7-9] and CF_3-C-CF_3 bonds[10]. The peaks at 291 eV and 292.8 eV are respectively assigned to an energy loss effect (shake-up satellite due to the $\pi \rightarrow \pi^*$ transitions of the benzene rings), very common in aromatic structures[7,11], and to CF_3 bonds[10,11]. The O 1s band is resolved into two components at 532 eV and 533.1 eV. They are assigned to imide carbonyls C=O and C-O-C linkages[7,12,13]. The relative quantity of each bonding component can be estimated from the area it covers divided by the total area of the C 1s and O 1s spectrum. Changes of the C 1s and O 1s peak areas after ion bombardment are depicted in Fig. 2. Figure 2a shows the decrease in the aromatic C component at 284.9 eV, the C-N bonding component at 286.8 eV and the CF_3 bonding component at 292.8 eV indicating that the aromatic, imide and $C(CF_3)_2$ groups are partly destroyed. The broken C-N and C-C bonds between benzene and imide rings result in the formation of polar amide groups (-CO-N-) at low doses up to 10^{15} ions/cm^2. The further fragmentation process leads to the formation of nonpolar phenyl groups starting at doses higher than 10^{15} B^+/cm^2.[7] Simultaneously, the low binding energy peak appears at 284.2 eV, in a position which can be assigned to graphite-like, amorphous carbon (a-C) rings.[7,9,14] The residual oxygen is present as ether (C-O-C), carboxylate (O-C=O at 534.17 eV [11]),

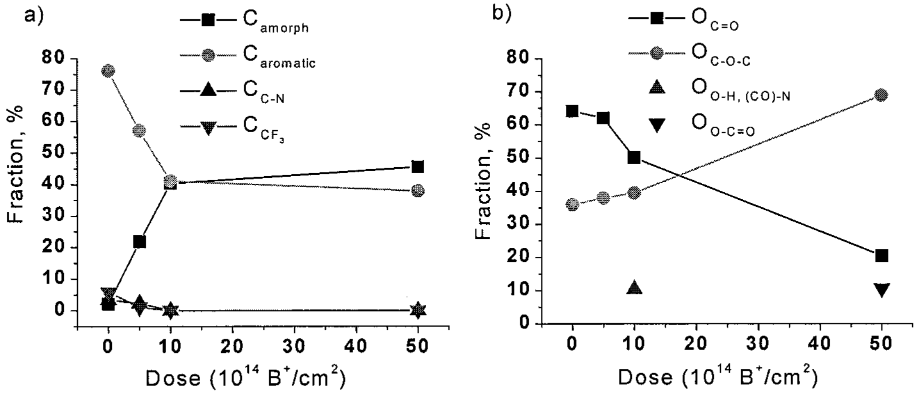

Fig. 2. Changes of XPS peak fraction in dependence on implantation dose: a) C 1s; b) O 1s

hydroxy or amide group (O-H and -CO-N- at 531.4 eV[10,15]), while the imide carbonyl (C=O) component becomes negligible (Fig. 2b). With increasing irradiation dose, the formation of amorphous and graphite-like structures is promoted which increases the surface conductivity σ_S by several orders of magnitude from an as-prepared value of $10^{-15}\,\Omega^{-1}$ to a value of $10^{-7}\,\Omega^{-1}$ at a dose of 10^{16} B^+/cm^2 (Fig. 3). The ion-beam irradiation destroys the anisotropy of the refractive index of polyimide layers.[16-18] This isotropization of the surface-near part of the polymer layers and the increasing values of their optical constants also indicate the formation of a-C islands due to the ion bombardment. In Fig. 3, the absorption coefficient k at a wavelength of 670 nm is presented in dependence on the a-C fraction. A strong enhancement of σ_S and k occurs when the fraction of a-C clusters dispersed in the PI matrix reaches 40 %. This value corresponds to the percolation threshold for the appearance of three-dimensional hopping conductivity in the thin surface-near part of the polymer layer.[8,19] In addition, the carbonization and partial graphitization and the radiation-induced crosslinking play an important role in the enhancement of electric conductivity.[19] The crosslinking is responsible for the formation of three-dimensionally-connected, rigid networks, and improves the carrier mobility, which is one of the most important parameters that govern the conductivity in implanted polymers. The degree of crosslinking of the polymer matrix can be estimated by the values of hardness and *E*-modulus, because the *E*-modulus of polymer is directly proportional to the crosslink density (or inversely proportional to the average molecular weight beetween crosslinks).[20] The radiation-induced crosslinking results in an enhancement of hardness and Young's modulus of the polymer layers up to 10 and 6 times, respectively (Fig. 4a). Here, it can be concluded that the strong enhancement of hardness and *E* modulus occurs at ion doses higher than 10^{15} B^+/cm^2 in consequence of increasing crosslinking. The modification of the polymer microstructure during irradiation with energetic ions involves the emission of volatile molecules.[2,19]

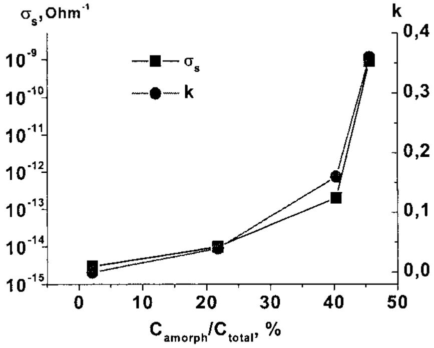

Fig. 3. Conductivity and optical extinction coefficient in dependence on the amorphous carbon fraction

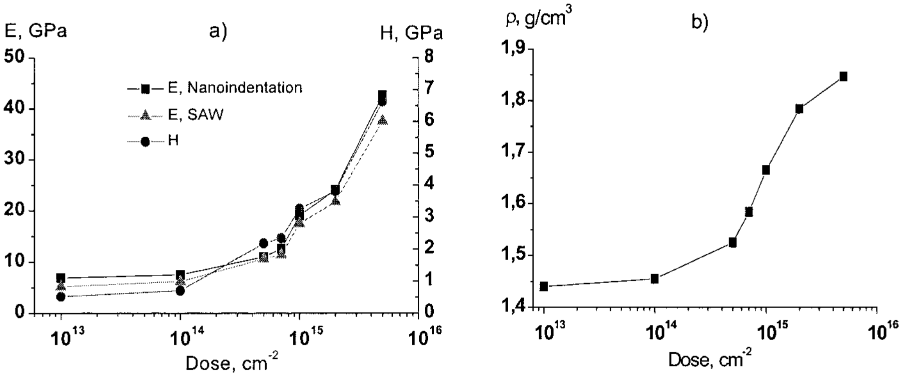

Fig. 4. Impact of ion implantation: a) on hardness and elastic modulus; b) on density

The thickness of the polymer films decreases due to the loss of material as volatile decomposition products and due to polymer shrinkage at ion doses higher than $5 \cdot 10^{14}$ B^+/cm^2.[18] The outgassing increases the density of the modified layer in comparison with the virgin PI from a value of 1.44 g/cm^3 (as-prepared) up to 1.85 g/cm^3 (Fig. 4b). The values of hardness, *E* modulus and density at high irradiation doses reach those typical of a hydrogenated amorphous carbon.[21,22]

Conclusions

All surface changes of ion-beam-modified PI films strongly depend on the implantation parameters. Electric conductivity, values of optical constants, density, hardness and *E* modulus of PI layers increase with increasing boron ion energy and dose. The PI2566 layers have the maximal moisture uptake after ion implantation with a dose of 10^{15} B^+/cm^2 at ion energy 180 keV, as it was shown in [3]. The observed increase in moisture uptake up to a dose of 10^{15} B^+/cm^2 is related to the formation of polar hydroxy and amide groups at the surface and correlated with the destruction of the hydrophobic $C(CF_3)_2$ groups. The small wettability of a-C islands and the increasing crosslinking result in a decrease in the moisture uptake of PI layers at ion doses higher than 10^{15} B^+/cm^2. Thus, irradiation at medium doses between 10^{14} and 10^{15} B^+/cm^2 results in optimum sensoric properties of ion-beam-modified polyimide films in humidity sensors.

Acknowledgments

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