

Modification of polyvinyl alcohol surface properties by ion implantation



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ABSTRACT

We describe our investigations of the surface physicochemical properties of polyvinyl alcohol modified by silver, argon and carbon ion implantation to doses of 1×10^{14} , 1×10^{15} and 1×10^{16} ion/cm² and energies of 20 keV (for C and Ar) and 40 keV (for Ag). Infrared spectroscopy (IRS) indicates that destructive processes accompanied by chemical bond (—C=O) generation are induced by implantation, and X-ray photoelectron spectroscopy (XPS) analysis indicates that the implanted silver is in a metallic Ag3d state without stable chemical bond formation with polymer chains. Ion implantation is found to affect the surface energy: the polar component increases while the dispersion part decreases with increasing implantation dose. Surface roughness is greater after ion implantation and the hydrophobicity increases with increasing dose, for all ion species. We find that ion implantation of Ag, Ar and C leads to a reduction in the polymer microhardness by a factor of five, while the surface electrical resistivity declines modestly.

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1. Introduction

Polymer materials are of great interest for their widespread use in fields from medicine to aerospace [1–4]. Ion, electron beam and plasma treatment provide tools for the modification of material surface properties and are important areas of advanced industrial technology [5–7]. Ion and plasma methods are widely used for alteration of polymer surface properties, for example to modify the wettability, microhardness, conductivity, etc [8,9], and the physical processes occurring in the interaction of energetic ions with solid materials have been studied in detail [10,11]. However, the chemical and structural change mechanisms in the subsurface modified layer have been less investigated.

Polyvinyl alcohol (PVA) belongs to a class of biodegradable polymers that are widely used in modern medicine for the production of implants and immunotolerant pins, as well as blood substitute components formed by freezing and thawing of polymer solutions. PVA is a material with high dielectric strength, good charge storage capacity and dopant-dependent electrical and optical properties. It is a semicrystalline polymer, and an important feature of PVA is the presence of both crystalline and amorphous regions. The two regions are well separated by states with intermediate degree of ordering, which enhances the macromolecule and produces several crystalline and amorphous phases. PVA is

normally a poor electrical conductor; it becomes conducting upon the addition of certain dopants. Conductivity in PVA arises because of the high rate of physical interaction between polymer chains via hydrogen bonding between the hydroxyl groups and the dopant, and is primarily determined by the properties of the amorphous regions. The conductivity of these composites can be further enhanced by exposure to ionizing radiation.

Gold [12] and silver [13] nanoparticles have been formed in a near-surface layer by electron beam irradiation; greater electron beam energy and pulse duration lead to smaller nanoparticle size. PVA macromolecule ordering can be affected by implantation of gaseous ions in various ways. Helium ion implantation leads to ordered alignment of macromolecules [14], whereas chlorine ion implantation results in reduced crystallinity [15], which is caused by chemical interaction with the polymer bonds. Much work remains to be done in the investigation of ion implantation induced effects on the physicochemical, morphological and functional properties of PVA. Here we describe our studies of the surface physicochemical and mechanical properties of PVA modified by silver, argon and carbon ion implantation.

2. Materials and methods

PVA samples were prepared by dissolving polyvinyl alcohol ($[-CH_2CH(OH)-]_n$) granules in water at 90 °C in a 10% solution. Then the solvent was removed by drying at room temperature in a Petri dish to form material at a thickness of ~1 mm.

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2.1. Ion implantation

Ion implantation was realized by a facility incorporating our MevvaV.Ru vacuum arc ion source [16]. This implantation facility operates in a repetitively pulsed mode with vacuum arc discharge current 150 A, repetition rate 10 Hz and pulse duration 250 μ s. Ion species used in the present work were Ag, Ar and C. In this ion source, gaseous ions are all singly ionized and hence we used Ar⁺ ions [17]. Metal ion species are in general multiply ionized; for carbon the charge state of the extracted ion beam is essentially singly ionized C⁺, while for silver the mean charge state of the extracted beam is 2+. Thus the implantation beams were of Ag²⁺, Ar⁺ and C⁺ ions. Since the ion source extraction voltage was always 20 kV, the ion beam energies were 40 keV, 20 keV and 20 keV, respectively. The transition of the ion source discharge system to a hollow cathode glow discharge mode took place for the Ar ion generation [18]. Implantations were carried out to accumulated doses of 1×10^{14} , 1×10^{15} , and 1×10^{16} ions/cm². The implantation dose rate and average power density at the PVA target were adjusted by the ion beam current and pulse repetition rate, and were 1×10^{11} ion/(cm²·s) and 0.5 mW/cm², respectively. The samples were mounted on a water-cooled target holder whose temperature did not exceed 20 °C. Working pressure of 1×10^{-6} Torr was maintained by an oil-free high-vacuum cryogenic pump.

2.2. Characterization

The structural characteristics of implanted PVA were investigated by infrared spectroscopy using a single attenuation total reflection attachment to IR-spectrometer Nicolet 5700. Surface elemental composition was analyzed by X-ray photoemission spectroscopy (XPS) using a PHI X-tool automated XPS microprobe with a K_αCu source.

Surface morphology was studied by atomic force microscopy (AFM) using a scanning probe microscope NTEGRA Aura in tapping mode. Structural analysis was carried out by scanning electron microscopy using a Quanta 200 3D dual-beam scanning electron microscope (SEM) and focused ion beam (FIB) instrument. Before SEM study the samples were coated with a conducting graphite film of 2–5 nm thickness by magnetron sputtering so as to alleviate charge build-up on the surface. PVA wettability with ethylene glycol and glycerol were measured by a sessile drop technique using a Kruss Easy Drop instrument. Ethylene glycol was applied as polar liquid since polyvinyl alcohol is water soluble. The surface energy calculation was done using the Owens-Wendt equation:

$$\sigma_{s-l} = \sigma_s + \sigma_l - 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^P \cdot \sigma_l^P}) \quad (1)$$

where σ_s is the solid/gas surface tension, σ_{s-l} the liquid/solid surface tension, σ_l the liquid/gas surface tension, and σ^D and σ^P the dispersive and polar parts, respectively, of the surface tension or surface free energy [19].

Microhardness was measured with a Nanotest 600 hardness testing instrument at a load of 0.5 mN. Surface electrical resistivity (also called sheet resistance) was measured using an E6-13A teraohmmeter and calculated by the formula

$$\rho = Rb/l, \quad (2)$$

where R is the measured resistance, b the sample width, and l the sample length [20]. Surface resistivity is measured in units of Ohms/square (Ohm/ \square) [21].

3. Results and discussion

Ion beam irradiation leads to irreversible changes in polymer materials. Energy ions are slacked into the target material by

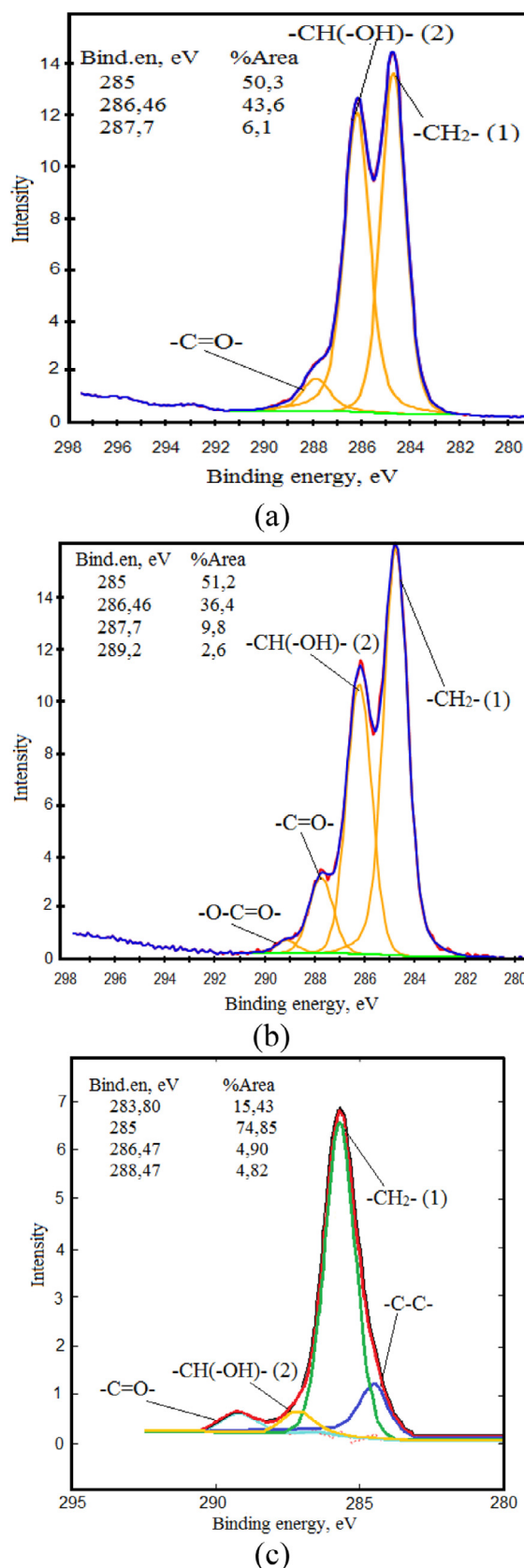


Fig. 1. C 1s core level XPS spectra of PVA, (a) unimplanted, (b) Ag implanted to 1×10^{16} ion/cm², (c) Ar implanted to 1×10^{16} ion/cm².

momentum transfer to target atoms (nuclear stopping) and by exciting the electronic system of the target (electronic stopping)

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