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Preparation and characterization of thin films by plasma polymerization of glycidoxypropyltrimethoxysilane at different plasma powers and exposure times

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ABSTRACT

This study aims to form a functional film on the glass substrates by plasma polymerization of glycidoxypropyltrimethoxysilane (γ-GPS). Low frequency plasma generator was used to prepare plasma polymer thin films of γ-GPS (PlzP-γ-GPS) on glass substrates at different plasma powers (30, 60 and 90 W) and exposure times (5, 15 and 30 min). XPS analyses were utilized to reveal the presence of functional groups in plasma polymer films. When higher plasma powers are applied, relative amount of Si–C bonds decreases and the amount of Si–O bonds increases. Contact angle measurements were performed to evaluate surface characteristics. Atomic force microscopy (AFM) studies were carried out to elucidate morphological changes. From AFM observations, it was obtained that the surface roughness slightly increased with the increase of plasma power from 30 to 90 W.

1. Introduction

Plasma polymerization is a thin film-forming process, where thin films deposit directly on surfaces of the substrates without any fabrication. In this process, the growth of low-molecular-weight molecules (monomers) into high-molecular-weight molecules (polymers) occurs with the assistance of the plasma energy [1]. Plasma polymerization can be also used to produce polymer films of organic compounds that do not polymerize under normal chemical polymerization conditions because such processes involve electron impact dissociation and ionization for chemical reactions [2].

Plasma polymerized films are pinhole-free and highly cross-linked and therefore are insoluble, thermally stable, chemically inert and mechanically tough. Furthermore, such films are often highly coherent and adherent to a variety of substrates including conventional polymer, glass and metal surfaces [3].

Plasma polymers prepared from organo-silicone monomers are fascinating materials due to the possibility of varying the degree of organic/inorganic character and the degree of cross-linking in the material [4]. Most used monomers in this family of compounds include tetramethylsilane, vinyltrimethylsilane, hexamethyldisiloxane and hexamethyldisilazane containing Si, H, C, O or N atoms [2]. Organo-silicon plasma polymers have been assayed for a large number of applications in rather different fields such as protective coating, gas barriers, hydrophobic layers, optical coating and biocompatible films, moisture sensors and a functional interlayer [5].

In industry, silane coupling agents are applied for surface modification of glass reinforcements in order to form a functional interlayer [5]. Poly-condensed thin films of the silanes are deposited on glass substrates using a wet chemical process. However, the molecules of silane coupling agents have a tendency towards self-condensation, forming siloxane oligomers rather than complete bonding with the glass surface and the low density of siloxane bonds with the surface decreases if water molecules diffuse to the interphase [6]. The poly-condensed film is also heterogeneous [7]. On the other hand, plasma polymer films prepared from organo-silicon monomer may adhere well to glass substrates due to strong siloxane bonds at the film/glass interface, which were formed in vacuum and thus with diminished occurrence of water molecules [5]. Besides, thin polymer films may be formed as homogeneous with respect to thickness, uniformity, composition and structure [6]. Also, in our group,

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glass fibers were modified successfully by means of plasma polymerization technique using three different types of monomers, 2-hydroxyethylmethacrylate (HEMA), triethyleneglycoldimethylether (TEGDME) and ethylenediamine (EDA) [8,9].

The study examines the influence of plasma power (30, 60 and 90 W) and exposure time (5, 15 and 30 min) on the properties of thin films prepared by plasma polymerization of γ-GPS on the glass substrate. The obtained films are characterized by different techniques of surface analyses such as contact angle measurements and X-ray photo-electron spectroscopy (XPS). Also, morphologies of the plasma polymer thin films of γ-GPS (PlzP-γ-GPS) formed on the glass substrates were investigated by atomic force microscopy (AFM).

2. Materials and methods

2.1. Materials

Glass substrates were microscope slides without flaws (IsoLAB, Germany). γ-Glycidoxypropyltrimethoxysilane (γ-GPS, >98.5% purity) which was used for preparation of plasma polymerized films on glass substrates was supplied by Dow Corning Corp. Commercially available, high purity argon gas (99.995% purity) was used to remove impurities or to deactivate free radicals in a vacuum chamber. Ethanol and acetone were purchased from Merck Corp.

2.2. Preparation of glass samples

Glass microscope slides were cut into rectangular shape having sizes of $(1 \times 1)\,cm^2$. Prior to use, the glass samples were ultrasonically cleaned with ethanol, acetone and deionized water for 5 min, respectively. Then, the samples were dried at room temperature for 6 h.

2.3. Plasma polymerization

Plasma polymerization was carried out in low frequency (LF) plasma generator (operating at 40 kHz with a maximum power 200 W), Model Pico, from Diener Electronic GmbH + Co. (Germany).

Cleaned and dried glass samples were subjected to plasma polymerization treatment. In a typical plasma treatment, at first, the chamber containing the samples was evacuated to a pressure of 0.12 mbar. Then, argon gas was introduced into the chamber for 10 min at a pressure of 0.3 mbar before generation of the plasma to remove impurities and to ensure a uniform gas environment. After that, the chamber was re-evacuated to approximately 0.12 mbar again. Thereafter, monomer gas inlet was opened and the monomer gas was allowed to flow through the chamber for 5 min at a pressure of 0.16–0.17 mbar. Then, the generator was turned on and the samples were exposed to LF-generated γ-GPS plasma at different plasma powers (30, 60 and 90 W) and exposure times (5, 15 and 30 min). At the end of the process, the generator was turned off automatically and monomer inlet was closed manually. Argon gas was introduced into the chamber for 10 min at a pressure of 0.3 mbar to deactivate free radicals.

2.4. Characterization of plasma polymer films

2.4.1. X-ray photoelectron spectrometer (XPS)

XPS was used to determine the surface elemental compositions of the glass samples and to investigate the changes in the chemical functionality of the glass sample surfaces at different plasma powers and exposure times. The XPS spectra were obtained with a Specs ESCA instrument (Germany), equipped with a non-monochromatic Mg Kα radiation source at a power of 200 W (10 kV, 10 mA) and EA 200 hemispherical electrostatic energy analyzer. The base pressure in the XPS analysis chamber was about 10^{-9}–10^{-10} torr. The analyzer was operated in constant analyzer energy (CAE) mode with pass energy of 96 eV for elemental quantification purposes and 48 eV for C1s peak shape comparison purposes. The concentrations of different chemical states of carbon and silicon in the C1s and Si2p peaks were determined by fitting the curves with Gauss–Lorentz functions.

2.4.2. Contact angle measurements

In this study, the captive bubble technique was used for contact angle measurements. This method also provides reliable contact angle values for quantification of surface free energy (SFE) of a material. The advantages of the captive bubble technique over the other techniques are explained in details elsewhere [10].

In this technique, a special microscope (QX3 computer microscope, 60X, Intel) and a computer system were used to measure contact angles in a three-phase system consisting of water, solid surface, and bubbles of air or liquid *n*-octane. The glass cell was filled with ultra pure water and the glass samples (1 cm^2) were placed in it. A special L shaped syringe needle containing *n*-octane (purity, 99%, Acros Organics, Belgium) or gas (air) releases bubbles beneath the sample. The volume of these bubbles did not exceed 5 μL. A computer screen provided an image of the captive bubble. The supporting computer software (Wettability Pro Classic, version 2.0.0 from Czech Republic) used these data to calculate the contact angles between *n*-octane and the solid surface, θ_o, and between air and solid surface, θ_a. Contact angle experiments were repeated for five times for each sample surfaces. The SFE of the each sample was determined by contact angle measurements. Contact angle results of air and *n*-octane from captive bubble experiments were used to find the polar and dispersive interaction components of surface energy [10].

2.4.3. Atomic force microscopy (AFM)

The atomic force microscope (AFM) was used to examine the morphology of glass surfaces and to determine surface topography and roughness of the plasma polymerized glass samples. AFM measurements were performed in contact and tapping modes at room temperature and in the air using MultiMode SPM (AFM/STM) Nanoscope IV from Digital Instrument. Roughness parameters (R_a and R_{ms}) calculation and image processing were performed using Nanoscope IV software. Silicon nitride probe in contact mode and silicon probe in tapping mode were employed. Sample surfaces were scanned without any surface modification. Measurements were made twice or thrice on different zones of each sample. Surface roughness values were determined in three random areas per sample, scanning across areas of $2 \times 2\ \mu m^2$.

3. Results and discussion

3.1. XPS analysis

Elemental compositions from XPS spectra were at different plasma powers and plasma exposure times were given in Figs. 1 and 2, respectively. As can be seen from Fig. 1, C content of PlzP-γ-GPS films decreases with increasing of power from 30 to 60 W. However with the increasing of plasma power from 60 to 90 W, C content increases. From the viewpoint of oxygen content, it was obtained that firstly increase and later decrease, which is also in opposite to C regime from 30 to 90 W, was observed. Yue and Padmanabhan indicated that the surface oxygen content is crucial for good wetting and bonding of the resin [11]. Lai et al. also reported that the ratio of oxygen atom on the surface increases due to fact that the number of oxygen-containing groups rises up [12].