Nuclear Instruments and Methods in Physics Research B 360 (2015) 54–59

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Ion irradiation as a tool for modifying the surface and optical properties of plasma polymerised thin films

Daniel S. Grant [a], Kateryna Bazaka [a,b], Rainer Siegele [c], Stephen A. Holt [d], Mohan V. Jacob [a,*]

[a] College of Science, Technology and Engineering, James Cook University, Townsville, Queensland 4811, Australia
[b] School of Chemistry, Physics, and Mechanical Engineering, Queensland University of Technology, Brisbane, Queensland 4000, Australia
[c] Institute for Environmental Research, Australian Nuclear Science and Technology Organisation, Lucas Heights, New South Wales 2234, Australia
[d] Bragg Institute, Australian Nuclear Science and Technology Organisation, Lucas Heights, New South Wales 2234, Australia

ARTICLE INFO

Article history:
Received 1 June 2015
Accepted 24 July 2015
Available online 15 August 2015

Keywords:
Plasma polymerisation
Thin films
Swift heavy ions
XRR
Ellipsometry

ABSTRACT

Radio frequency (R.F.) glow discharge polyterpenol thin films were prepared on silicon wafers and irradiated with I^{10+} ions to fluences of 1×10^{10} and 1×10^{12} ions/cm^2. Post-irradiation characterisation of these films indicated the development of well-defined nano-scale ion entry tracks, highlighting prospective applications for ion irradiated polyterpenol thin films in a variety of membrane and nanotube-fabrication functions. Optical characterisation showed the films to be optically transparent within the visible spectrum and revealed an ability to selectively control the thin film refractive index as a function of fluence. This indicates that ion irradiation processing may be employed to produce plasma-polymer waveguides to accommodate a variety of wavelengths. XRR probing of the substrate-thin film interface revealed interfacial roughness values comparable to those obtained for the uncoated substrate's surface (i.e., both on the order of 5 Å), indicating minimal substrate etching during the plasma deposition process.

1. Introduction

Swift heavy ion (SHI) irradiation (energies above 1 MeV) is known to induce a number of characteristic radiation-chemical processes in polymeric materials. In common with other types of ionising radiation (e.g., gamma rays, electrons, etc.), SHIs can produce cross-linking, chain scissions, free radicals, and unsaturated bonds in hydrogenated polymers [1]. Unique to SHI irradiation however, is that as the ion traverses the polymeric medium (with penetration depths that can be tailored in the order of tens of micrometres) its large deposited energy density produces a latent track of well-defined dimensions [2,3]. Furthermore, the energy and species of the ion employed in the irradiation process exert considerable influence on the extent of cross-linking or chain scissions within the structure of the polymer in question [4]. Many of the aforementioned radiation-chemical processes are confined to occur within the penumbra of this track [5]. The capacity for SHIs to modify physical and chemical properties of polymers has fostered a number of studies aimed at developing and enhancing commercial applications. These include lithography processes, the fabrication of nanotube templates, and nanoporous membranes [6–8].

Radio frequency (R.F.) glow discharge is a well-established dry process for the fabrication of organic thin films [9]. Typically, energy is supplied to a process gas (such as helium, argon, or atmospheric gas) leading to the formation of a non-equilibrium cold plasma within either an internal, external, or electrodeless reactor vessel [10]. Monomer units are then introduced to the plasma glow, where they are subjected to fragmentation, excitation, and ionisation by the energetic plasma. The resulting species subsequently adhere to the substrate material via either physical absorption or chemical bonding processes. The result is the formation of highly cross-linked and structurally disordered films possessing a number of advantageous physical and chemical properties, including strong substrate adhesion, pin-hole free surface topologies, and chemically functionalised surfaces. Furthermore, a large variety of deposition parameters (including vacuum pressure, precursor selection, R.F. power, reactor geometry, monomer flow rate, plasma gas, deposition time, etc.) can be varied to achieve polymer films with specific properties or combinations thereof [11]. For these reasons, R.F. glow discharge polymers have found numerous current and prospective applications as conformal coatings for inorganic electronic assemblies [12], encapsulation films for organic electronic devices [13], and

* Corresponding author.
E-mail address: Mohan.Jacob@jcu.edu.au (M.V. Jacob).

http://dx.doi.org/10.1016/j.nimb.2015.07.109
0168-583X/

coatings for various other substrate materials (exhibiting an assortment of tailored anti-fogging, corrosion resistant, and abrasion resistant properties) [14].

In this research, we focus on the application of 50 MeV I^{10+} SHIs to polyterpenol thin films fabricated using an R.F. glow discharge polymerisation technique. The precursor monomer for these films, terpinen-4-ol, is a non-synthetic monocyclic terpene derived from the distillation of tea tree oil. Studies undertaken by our group have demonstrated that in addition to possessing the aforementioned generic plasma polymer properties [15,16], polyterpenol thin films demonstrate rectifying electron-blocking hole-transport behaviour [17], and the retention of terpinen-4-ol functional groups within the polymerised film imbues this polymer with antibacterial properties [18]. The primary objective of this research is to characterise the effects of iodine SHI irradiation on the surface and optical properties of polyterpenol, and, to the extent that it is possible to do so, to interpret these property changes in the context of the elementary ion energy loss mechanisms. These findings will tailor the direction of future investigations into coupling polyterpenol's attractive material traits with SHI irradiation's capacity to modify polymeric material properties.

2. Material preparation methods

2.1. Substrates

Plasma polymerised polyterpenol thin films were deposited on highly polished 500 μm thick 1 × 1 cm ⟨100⟩ photoresist coated single crystal silicon wafers (n-type Sb doped), sourced from Fondazione Bruno Kessler.

Prior to plasma deposition the wafers were rinsed in acetone to remove the photoresist coating. The wafers were then washed in a solution of Extran and distilled water, ultrasonically cleaned in a sonicator (distilled water, 50 °C, 30 min), and rinsed in isopropanol to remove inorganic contaminants. Residual organic contaminants were then removed using piranha solution (3:1 mixture of 25% H_2SO_4 in concentrated H_2O_2). The wafers were then subjected to a final rinse in distilled water and blown dry. The cleaning procedure produced a hydrophilic surface and led to no variation in surface roughness.

2.2. Plasma polymer deposition

Plasma polymerisation of terpinene-4-ol (99%, Australian Botanical Products) was carried out using a custom-made cylindrical glass reactor chamber, with an approximate volume of 0.0029 m^3, a length of 0.75 m, and internal diameter of 0.07 m. Radio frequency power was supplied to the chamber at 13.56 MHz via two externally coupled copper electrodes spaced 0.07 m from one another and 0.11 m from the monomer inlet. Prior to plasma formation, the chamber was flushed with argon gas for 60 s to dislodge loose contaminant particles and displace atmospheric gas. Films were fabricated at 25 W over a deposition time of 15 s, yielding film thicknesses of less than 500 Å.

2.3. Iodine ion irradiation

The polyterpenol thin films were irradiated under vacuum with 50 MeV I^{10+} ions, generated using the 10 MV ANTARES tandem accelerator (ANSTO). Specimens were irradiated at <20 nA over a 2 cm^2 area to minimise macroscopic heating, and irradiation time was varied to achieve total fluences of 1×10^{10} and 1×10^{12} - ions/cm^2. Beam current was ascertained before and after each irradiation run using a Faraday cup, and irradiation was undertaken at a temperature of 293 K and a pressure of 10^{-5} mbar.

The choice of ion energy and species employed in this study is liable to influence a number of interaction processes between the radiation and the polymeric material. These include the large number of nucleons (relative to say, H or He) leading to an increased prevalence and importance of nuclear stopping (i.e., atomic displacements and phonons) in the ion–specimen interaction as a result of the larger Rutherford cross-section and momentum transfer. The high ion energy also results in an ion velocity well in excess of the Bohr velocity, leading to a shorter interaction time between the ion and its surrounding medium, and a reduction in electronic stoppage (i.e., reduced electron excitation and ionisation) [1].

3. Characterisation

3.1. Surface properties

XRR (Cu-K_α) measurements were performed at the air–solid interface using a PANanalytical X-Pert PRO reflectometer (high tension = 45 kV, current = 40 mA). These measurements were performed as a function of incident angle (θ), observing the specularly reflected beam as a function of the momentum change perpendicular to the surface ($Q_z = 4\pi\sin\theta/\lambda$).

The XRR data was modelled using the Motofit [19] reflectivity analysis software package running in the IGOR Pro environment. These data were fitted as $\log(R)$ vs. Q using a Differential Evolution [20] algorithm, with corrections for a linear background, resolution smearing, and Gaussian roughness at each interface. As a reflectivity instrument, XRR measures the square of the amplitude. Consequently, phase information is lost, and this presents the possibility of being able to develop multiple different models that produce similar reflectivity curves. Given that the wrong physical model is unlikely to provide agreeable fits to different specimens, this issue was mitigated to some extent by measuring and co-refining multiple specimens, and through cross comparison with values provided by ellipsometry. The lack of well-defined stoichiometry in plasma polymers (and the difficulties associated with determining chemical structure of plasma polymers) precluded the use of XRR for determining film density.

Optical methods of surface feature interrogation of pristine and irradiated polyterpenol-coated silicon substrates were supported by AFM (NT-MDT NTEGRA Prime), with subsequent data analysis undertaken using the Nova software package. The instrument was fitted with an NSG10 probe (255 kHz cantilever resonant frequency, 11.5 N m^{-1} force constant, 3:1 tip aspect ratio and 10 nm curvature radius). Scans were undertaken in tapping mode to eliminate lateral tip-sample forces and limit the formation of inelastic specimen deformations. No AFM-specific specimen preparation was performed prior to undertaking the measurements, and scans were obtained at 3 × 3 μm resolution to reveal nano-scale features.

3.2. Optical properties

A J.A. Woollam variable angle spectroscopic ellipsometer (VASE) was used to probe specimen optical properties, including the complex refractive index $N(\lambda) = n - ik$. Data was collected across the 250–1000 nm wavelength region and at five angles of incidence (50–70°, in increments of 5°). Data analysis and modelling was carried out using the WVASE32 software package, following supplier recommended procedures outlined within the software package manual. Specifically, specimens were modelled using a stratified model consisting of si_jaw, sio2_jaw, and Cauchy components to model the silicon substrate, oxide, and polyterpenol thin film layers respectively. The optical constants of the silicon substrate and oxide layer were approximated using literature values contained