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Gradiently varied chain packing/orientation states of polymer thin films revealed by polarization-dependent infrared absorption

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ABSTRACT

Gradiently varied chain packing/orientation states of the polyacrylamide (PAL) thin films spin-coated on the gold (Au) substrates were found via the polarized reflection–absorption Fourier transform infrared spectroscopy (RA-FTIR). As the film thickness increases, the splitted amide I bands provide a direct evidence that the PAL thin films are of a gradiently varied bi-layered structure. In the bottom layer, most of the PAL molecules show random orientation which is induced by the non-favorable interaction from the adjacent Au surface. In the top layer, most of PAL molecules show parallel orientation to the Au surface which is induced by spin coating, evidenced by the enhanced low-frequency splitted amide I band ($\sim$1658 cm^{-1}) and N–H stretching modes of the amino groups when the light electric field vector is adjusted to be parallel to the Au surface. The observation reported in this study should be of universal significance for polymer thin films on the supported substrates, where the interfacial interaction as well as spin coating could vary the polymer packing/orientation states substantially.

1. Introduction

Polymer thin films are a kind of important materials due to their broad applications in coating, adhesive and microelectronic industries [1,2]. The long-term reliability of a polymer thin film to a large extent relies on whether the polymer chains in the film are in the relaxed state or not because the evolution of the chain conformation during usage may have negative effect on its stability. For instance, when the thickness of a polymer thin film decreases down to or lower than certain critical length, i.e. a molecular size in the scale of the mean-square end-to-end distance (R_{ee}) or radius of gyration (R_g), chain conformation of the polymer could notably be different from that of its bulk state [3–6]. Therefore the residue stress or the entropic force may evidently exist and gradually deteriorate the property of the polymer thin film [4,6–8]. It is thus of great importance to investigate the chain packing/orientation state and the related dynamic behavior for a polymer thin film. Different techniques have been applied to study this issue in the past, such as fluorescence microscopy [9–12], ellipsometry [13–16], Brillouin light scattering [16–18], X-ray reflectivity [3,19,20] and sum frequency generation vibrational spectroscopy [21–25]. It has generally been recognized that a polymer thin film is a metastable material [4] which has distinct physicochemical properties from those of the bulk polymer. For a polymer thin film on the supported substrate, besides the chain confinement effect, the interaction between the polymer and the substrate, whether attractive or non-attractive, can also have significant effect which can alter

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arrangement of the polymer chains near the polymer/substrate interface. A preliminary report on the supported polymer thin films prepared by spin coating has suggested the interaction from the substrate and spin coating can remarkably alter the chain packing states of the polymer thin films [26]. In this study, complete experimental results were present to explore the chain orientation states by analyzing the vibrational signals of the polyacrylamide (PAL) molecular groups using the polarized reflection–absorption Fourier transform infrared spectroscopy (RA-FTIR) with the grazing-angle incidence. A gradiently varied bi-layered structure of the PAL thin films on the Au substrates was confirmed. The result indicates the PAL chains in the bottom layer (adjacent to the Au substrate) and the top layer have undoubtedly different orientational orderings which lead to the polarization-dependent infrared absorption.

2. Experimental section

The Au substrates were prepared by depositing a 200-nm Au layer on top of the silicon wafers (Silicon polished wafer, N-type, Grinm, Inc.) using the high vacuum evaporator (High Vacuum Evaporator, DV-502A, Denton Inc.). The silicon wafers were pretreated by piranha solution (a mixed solution with 3:7 volume ratio of 30 wt.% H_2O_2 solution and 98 wt.% H_2SO_4) to eliminate the possible surface contamination. PAL ($M_w = 5\text{–}6 \times 10^6$) were purchased from Polysciences, Inc. The mean square end-to-end distance is estimated to be around $\sim 10^2$ nm. The PAL thin films were prepared by spin coating PAL solutions on top of the Au substrates (Spin Coater, P6700, Specialty Coating Systems Inc.). Solution concentration and spinning speed were adjusted to obtain the PAL thin films with desired thicknesses. The PAL films with thicknesses of 9.8 nm, 39 nm, 73 nm, 104 nm, 170 nm, 269 nm, 375 nm, and 559 nm were prepared. All the PAL film samples were annealed in a vacuum oven (Shel lab 1410, Shalton Mfg Inc.) at 60 °C for 24 h. Before further characterization, the samples were put in a desiccator. The Variable-Angle Spectroscopic Ellipsometer (J.A. Woollam Co., Inc.) was used to measure the thicknesses of the PAL thin films on the Au substrates.

The RA-FTIR spectroscopy (RA-FTIR, FTS-6000, Bio-Rad Inc.) were applied to capture the polarized infrared spectra of the PAL thin films on the Au substrates. The polarizer was mounted before the infrared light shot at the sample surface. The s- and p-polarized lights with the grazing-angle (85°) incidence were used, as shown in Fig. 1. With this grazing-angle incidence, the transition dipole moments of molecular groups parallel and normal to the Au surface can be separately detected simply by using s- and p-polarized lights respectively, as demonstrated by the selection rules for RA-FTIR on the reflected metal surfaces [27–29]. The ZnSe polarizer (Tydex J.S. Co., spectral range from 1.5 μm to 14 μm or 6667 cm^{-1} to 714 cm^{-1}) was used to obtain the light with >95% polarization. The orientation of a certain PAL molecular group can thus be analyzed based on its polarization-dependent infrared absorption. During the infrared experiment, the sample chamber of the infrared spectrometer was vacuumized for at least 1 h before collecting the background and the sample spectra. Otherwise the interference from humidity and carbon dioxide in the sample chamber would lead to the low signal-to-noise ratio.

3. Results and discussion

3.1. Polarization-dependent spectra and splitting of amide I band

The normal infrared spectrum for a PAL bulk sample has been reported previously [30]. The amide I mode and the N–H stretching modes from the amide groups (—CONH_2) are the strongest modes. Here as shown in Fig. 2, using RA-FTIR, the collected spectra for a series of PAL thin films spin-coated onto the Au substrates show strong characteristics depending on the light polarization and film thickness. Fig. 2 shows the RA-FTIR spectra of the PAL thin film

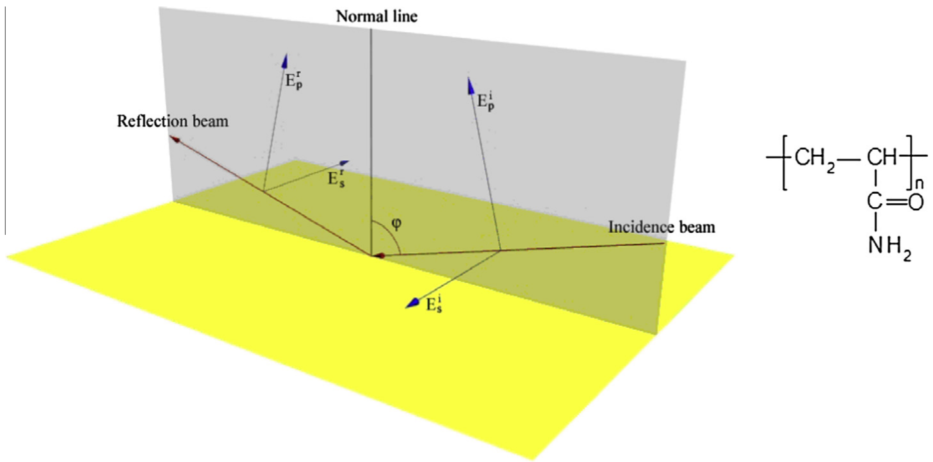

Fig. 1. Optics of RA-FTIR with a grazing-angle incidence (left panel). For a certain molecular group, with this grazing angle incidence, the infrared transition dipole moment parallel to the Au substrate surface is detected when the light polarization is adjusted to be “s” and the infrared transition dipole moment normal to the Au substrate surface is detected when the light polarization is adjusted to be “p”. The monomer unit of PAL is also shown (right panel).