

Molecular order at polymer interfaces measured by broad-bandwidth vibrationally-resolved sum frequency generation spectroscopy

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Abstract: Broad-bandwidth vibrationally-resolved sum frequency generation spectroscopy has been used to measure the molecular orientation distribution at polystyrene/dielectric interfaces. A novel microcavity structure allows isolation of the free or buried interface and reveals their opposite absolute orientations.

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OCIS codes: (190.4350) Nonlinear optics at surfaces

1. Introduction

Measurement of the structure of polymer/dielectric interfaces is crucial to an understanding of adhesion between such materials. Vibrationally-resolved sum frequency generation (VR-SFG) spectroscopy is a non-invasive, interface specific and chemical sensitive probe of the buried interfaces of transparent media [1]. The use of broad bandwidth femtosecond pulses enables the parallel acquisition of spectra across an entire resonant spectral range without laborious laser tuning [2]. The coherence of SFG allows the measurement of the phase of the VR-SFG signal relative to a non-resonant reference, which reveals the absolute orientation of the resonant molecular species [3].

2. Experiment

A polystyrene/dielectric/Au microcavity was fabricated with a ~130 nm polystyrene (PS) thin film and varying thicknesses of a commercially available spin-on dielectric [4]. The variation of the thickness of the dielectric varies the phase between the SFG generated in reflection and SFG generated in transmission and reflected from the Au substrate. Appropriate choice of the dielectric thickness can enhance the signal from either PS interface through constructive interference and null the signal from the other interface. VR-SFG spectra of the C-H stretch modes of the phenyl groups of polystyrene have been measured for these structures. As shown in Figure 1a, a 207 nm dielectric layer selectively enhances the signal from the polystyrene/air interface which attenuates upon surface degradation by ozone exposure. As shown in Figure 1b, a 340 nm layer reveals the buried polystyrene/dielectric interface, which remains robust upon ozone exposure. Fits of the spectra of these two interfaces reveal resonances of the ν_2 and ν_{7a} modes of similar amplitudes, but opposite sign relative to the non-resonant spectral envelope from the Au substrate demonstrating that the interfacial phenyl groups are oppositely oriented.

Further investigation and comparison with previous results demonstrates that the molecular orientation and degree of macroscopic ordering varies with the underlying dielectric [5].

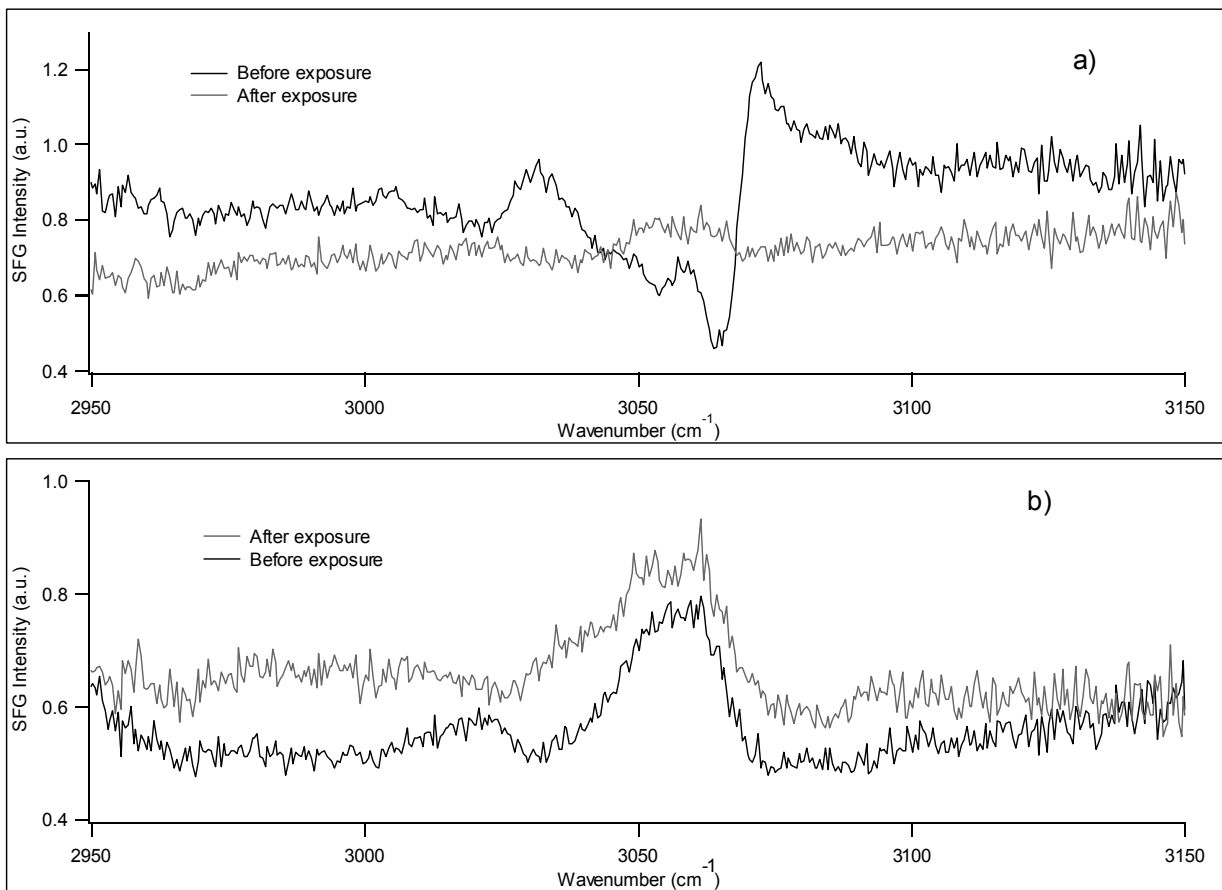


Fig. 1. VR-SFG spectra of C-H stretch modes of phenyl groups in polystyrene on a.) 207 nm dielectric layer and b.) 340 nm dielectric layer before and after exposure to ozone.

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