Metal/conjugated polymer interface probed by SFG spectroscopy

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Polymeric optoelectronic devices (PLEDs and photovoltaic cells) have expressive technological interest for their potential application in consumer electronics. At the same time, a few outstanding technological problems, such as limited device lifetime and low emission efficiency, have sparked a tremendous scientific effort to understand the physics of these materials and to optimize their properties. In the recent literature, it is becoming evident that interfacial issues are critical to the performance and lifetime of the devices [1]. For example, chemical reactions and/or other physical interactions (metal diffusion into the polymer, packing and orientation differences, etc) may occur at a metal/polymer interface, affecting the electronic structure of the interfacial region and determining the charge injection and trapping at the interface. In this work we have used surface vibrational spectroscopy by Sum-Frequency Generation (SFG spectroscopy) to investigate the interface between Aluminum and poly[2,7-(9,9-dihexylfluorene)-*co*-alt-2,5-(decylthiophene)] – PFT. In the SFG technique [2], two laser beams of frequency ω_1 and ω_2 overlap at an interface and a third beam is generated at a frequency $\omega_3 = \omega_1 + \omega_2$. This second-order nonlinear optical process is allowed only in media with broken inversion symmetry, so that the technique is inherently sensitive to interfaces. In particular, it is possible with SFG spectroscopy to study the polymer layer in contact with the metallic electrode without contributions from the bulk polymer film. With ω_2 as an infrared beam tuned through molecular vibrations, the changes in the intensity of the sum-frequency signal yield the vibrational spectrum of the interface. Changing the polarization of the input and output beams also allow the determination of molecular orientation at interfaces. To investigate the effect of the sample preparation procedure, we have investigated both the PFT/Al interface, with the polymer spin-coated over the metal, and the Al/PFT interface, with the metal evaporated on top of PFT spin-cast films. The SFG spectra of the PFT spin-cast film on glass is also shown for comparison. A qualitative analysis of our preliminary results shows that all samples are inhomogeneous on the mm length scale (in terms of average chain orientation), since both the intensity and polarization dependence of the SFG spectra vary from spot to spot on the sample. The PFT glass and PFT/Al interfaces show the same vibrational spectrum in the 1000 to 1800 cm^{-1} range, with several peaks attributed to the fluorene and thiophene backbone. However, an additional very strong peak at ~1400 cm^{-1}, with particular polarization dependence, appears in the SFG spectrum of the Al/PFT interface. This appearance suggests that a doping process occurs when the Al is evaporated at elevated temperatures over the PFT film. The high intensity of this new peak could be explained by a shift in the electronic structure of the polymer, in the presence of the charge from doping process, leading to a doubly resonant SFG signal (vibrational and electronic resonance).

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