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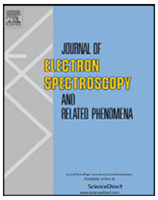

Review

Adsorbate/absorbate interactions with organic ferroelectric polymers

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ABSTRACT

We discuss the interactions of adsorbates with the organic ferroelectric copolymer poly(vinylidene fluoride (PVDF)–trifluoroethylene (TrFE)). Range of molecular adsorbates is discussed from the smaller polar molecules like water, which is small enough to both adsorb and absorb, to the larger macrocyclic metal–organic metal phthalocyanines. The changes in local dipole orientation may affect the strength of the coupling between adsorbate or absorbate and the copolymer poly(vinylidene fluoride–trifluoroethylene). The interface dipole interactions may also affect device properties. The dipole interactions are implicated at the interface between copper phthalocyanine and poly(vinylidene fluoride with trifluoroethylene) affecting the band offsets and the diode properties.

Contents

1. Introduction

Surface dipole interactions have long been implicated as important in surface adsorption and surface catalysis [1–4]. The investigation of surface dipole interactions are, unfortunately, often complicated by the influence of the substrate (including band structure effects [5]) and strong perturbations due to surface charges that induce large surface dipoles on metal surfaces [6]. Ferroelectric materials provide a great opportunity to investigate dipole interactions with adsorbates [7–32], particularly as the surface electric dipoles are “reversible” [7,8,11–18,27–29,32–46].

Our preference for crystalline polymer ferroelectric materials [19–48] as a substrate for the study of adsorbate interactions with surface dipoles stems from their surprising simplicity compared to the complex surfaces formed with the inorganic ferroelectric materials. The complexities associated with inorganic ferroelectrics include surface compositional instabilities, an abundance of lattice defects (point defects, steps and grain

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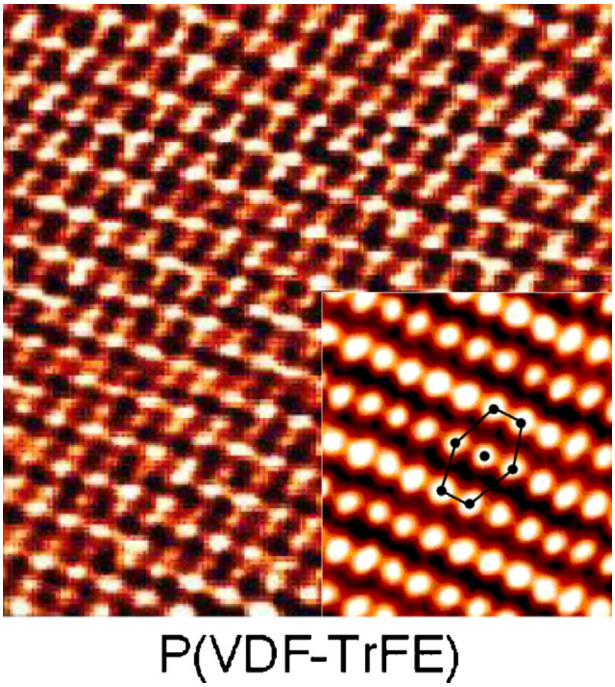

Fig. 1. The surface structure of crystalline P(VDF–TrFE) Langmuir–Blodgett films as ascertained from scanning tunneling microscopy. The scanning tunneling microscope images, recorded at 295 K, are of nominally 2 monolayer thick film on graphite substrates, with 4.4 nm × 4.4 nm image size. In the inset is the atomically resolved STM image of the surface of P(VDF–TrFE 70:30) film on graphite at room temperature, obtained at higher bias (−0.36 V instead of −0.1 V) and the surface unit cell is also indicated. Every bright spot represents a –CH_2–CF_2– or –CHF–CF_2– monomer. Adapted from [27,33,34,45].

boundaries), and considerable difficulty in preparing a stable reproducible surface with well-ordered dipoles oriented along the surface normal. We have undertaken extensive investigations of adsorbate interactions with poly(vinylidene fluoride (PVDF)–trifluoroethylene (TrFE)) copolymers, a uniquely crystalline polymer system [19–21,24–25,27,32–47].

Poly(vinylidene fluoride) [PVDF, $-(CH_2-CF_2)_n-$] copolymers with trifluoroethylene [TrFE, $-(CHF-CF_2)-$] can form highly ordered crystalline ferroelectric polymer ultrathin films as has been demonstrated by X-ray and neutron scattering [19,20,22,35,37,38,40], scanning tunneling microscopy [27,33–37,39,40,42,45,46], low energy electron diffraction [36,37] and band mapping [27,36,37,46]. Although not always evident in scanning tunneling microscopy (Fig. 1), the band structure shows a characteristic super-periodicity dominated by $-(CH_2-CF_2)_2-$ or $-(CH_2-CF_2)-(CHF-CF_2)-$ “dimer” pairs [36,37,46] in the ferroelectric phase. The copolymer P(VDF–TrFE, 70:30), in spite of the low overall symmetry, does show all the characteristics of high local symmetry and symmetry selection rules, with the dipoles aligned along the surface normal [43,44]. The effects are quite significant in photoemission [43,44,47] and electron energy loss spectroscopy [38,43,44,48].

Our goal has been to obtain a detailed understanding of dipole interactions between small adsorbates and the ferroelectric polymer substrate. Fundamental surface science experiments are possible using our polymer systems because: (1) they are ultrahigh vacuum compatible, (2) the surfaces of the polymers are crystalline with a well defined structure and orientation, (3) the polymer films can be grown thin and uniform so the surface can be uniformly heated (and cooled) to well defined temperatures, and (4) the ferroelectric polymer thin films can be grown without pinholes or a large mosaic spread of different structural domains. Based on our recent results, we have good reason to believe we can now go well beyond the recently developed fundamental understanding that has come from our research efforts and construct organic multilayers systems that exhibit new phenomena like novel electronically driven phase transitions.

2. Experimental

Ultrathin ferroelectric films of copolymer 70% vinylidene fluoride with 30% trifluoroethylene, P(VDF–TrFE 70:30) were fabricated by Langmuir–Blodgett (LB) deposition techniques on graphite substrates from the water subphase [19–25,27–29,31–45,47]. The P(VDF–TrFE 70:30) films, nominally some 3–7 molecular layers thick (15–35 Å thick, as noted) were prepared in ultrahigh vacuum by annealing at 110 °C, which has proven to be an effective recipe in prior studies [19,22–29,31–41,43–45,47] and has been demonstrated to results in a surface free from impurities (including water) [48]. Thin films of short chain poly(vinylidene fluoride) were also prepared by vacuum evaporation [30,48], particularly for the fabrication of the bimolecular heterostructures (i.e. PVDF/metal phthalocyanine heterostructures), as described elsewhere [30]. Films used for this study were nominally 20 mL (10 nm) thick and grown on highly ordered pyrolytic graphite (HOPG) substrates, unless noted otherwise.

The thermal desorption spectra were obtained by annealing the graphite substrate resistively, and exploiting our ability to make films of P(VDF–TrFE 70:30) sufficiently thin to obtain the necessary thermal conductivity through the polymer thin film. Angle-resolved thermal desorption measurments were taken as described elsewhere [19,22,25–27,49,50], with a differentially pumped mass spectrometer, and the angles denoted with respect to the surface normal.

Laser-assisted thermal desorption, creating metastable excited states during thermal desorption, was also undertaken. These experiments involved obtaining thermal desorption spectra while the surface was illuminated with a pulsed nitrogen gas laser (337 nm, 3.66 eV), at 20 Hz with an intensity of 120 μJ/pulse [25,27,50]. The incident 337 nm radiation was polarized using a UV polarizer and focused onto the entire surface area of the sample (less than 2 cm^2). In our laser assisted thermal desorption experiments, we compare two different incident light polarizations: linearly polarized light with the electric field vector **E** and the vector potential **A** of the incident radiation parallel with the surface and a polarization with the electric field vector **E** and the vector potential **A** of the incident radiation perpendicular to the surface, but with the same radiation intensity/area and no change in light incidence angle, as described elsewhere [25,27,50]. The desorbing species were collected normal to the film for both thermal desorption and photo-assisted thermal desorption studies, unless stated otherwise. Because of the very low UV flux densities, we employed a very low heating rate. The heating rates for obtaining the thermal desorption spectra (TDS) were 0.5 °/s throughout this work. Faster heating rates are possible, but the concerns about thermal conductivity through the thicker polymer films precluded their use.

Inverse photoemission (IPES) was undertaken using a variable energy electron gun producing electron kinetic energies from 5 to 19 eV, incident normal to the surface. Photons were detected with a Geiger-Müller detector, as done in previous studies [22,25,27–31,35–37,41,45,50]. The instrumental line width for inverse photoemission is ~400 meV. Angle-resolved photoemission spectra were undertaken using synchrotron radiation generally at photon energies of 35 and 55 eV (unless otherwise stated), dispersed by a 3 m toroidal grating monochromator [51], at the Center for Advanced Microstructure and Devices in Baton Rouge, Louisiana [52], employing a hemispherical electron energy analyzer with an angular acceptance of ±1°. In both photoemission (UPS) and inverse photoemission (IPES) measurements, the binding energies are ref-