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Comparison of crystalline thin poly(vinylidene (70%)–trifluoroethylene (30%)) copolymer films with short chain poly(vinylidene fluoride) films

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Abstract

We compare the photoemission and electron energy loss spectra of crystalline poly(vinylidene-fluoride with trifluoroethylene: 70%:30%), P(VDF–TrFE), films, fabricated by the Langmuir–Blodgett technique and annealed in vacuum, with in situ thermally evaporated films of poly(vinylidene-fluoride) (PVDF) in vacuum. The electronic structure and vibrational modes of the short chain PVDF films compare well with the crystalline P(VDF–TrFE) films indicating that vacuum annealed films prepared ex situ are free of significant surface contamination once vacuum annealed. The electronic structure for the short chain PVDF films exhibits, however, different temperature dependence than the crystalline P(VDF–TrFE) films.

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1. Introduction

Photoemission [1–6], inverse photoemission [2,3,7,8] and high resolution electron energy loss [4,6,9] spectroscopy studies have been undertaken on the crystalline surfaces of copolymer films of polyvinylidene fluoride with 30% of trifluoroethylene, P(VDF–TrFE 70:30). The experimental band structure [7,8] and band symmetries [6] of the crystalline polymer have been successfully compared with theory [10]. In addition, a surface phase transition at about 295 K [2,6–8] and a compressibility (lattice stiffening) at about 160 K [4,9], distinct from the bulk ferroelectric transition at about 350 K, are evident in these electron spectroscopies.

Since the crystalline poly(vinylidene fluoride with 30% of trifluoroethylene), P(VDF–TrFE 70:30), films are prepared ex situ by Langmuir–Blodgett monolayer deposition from a water subphase, then annealed in vacuum, one issue that is not directly addressed in such studies is the possibility of impurities at the surface. While scanning tunneling microscopy provides considerable evidence of long range order [7,8,11–13], as does the experimental band structure mapping [7,8], this is not compelling *direct* evidence of an impurity free surface layer. Impurities could include water [14] and absorbed organic species. The spectroscopic signatures of PVDF can, however, provide a benchmark of film quality, free from chemical contamination.

Comparison with evaporated short chain polymer films formed in situ by thermal evaporation provides one means for addressing the efficacy of using the very surface sensitive electron spectroscopies to crystalline P(VDF–TrFE 70:30) films prepared ex situ. We can also address whether the electronic structure of short chain PVDF films is fundamentally different than crystalline P(VDF–TrFE 70:30) films. The copolymer poly(vinylidene fluoride–trifluoroethylene, 70:30) has lower bulk ferroelectric phase transition critical temperature (~80 °C) than the melting

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point (~160 °C) while the critical bulk ferroelectric transition temperature of PVDF is higher than the melting point (~200 °C) [14,15].

2. Experimental and theoretical details

The very thin crystalline P(VDF–TrFE 70:30) films were formed by Langmuir–Blodgett monolayer deposition from water subphase, as described elsewhere [15,16]. The films were prepared by gentle annealing to 150 °C in vacuo and surface composition characterized for P(VDF–TrFE 70:30) with core level spectroscopy (XPS) and inverse photoemission (IPES) as described elsewhere [2–4,6–8]. For in situ deposition by thermal evaporation of PVDF, a commercial PVDF powder (Aldrich) was used. Although the average chain of the commercial PVDF evaporation source was quite large (approximately ~534,000 amu or about 8300 (CH_2–CF_2) monomers; average length of the polymer chain ~2.2 μm), nonetheless, the chain length of the evaporated PVDF was quite short. The mass spectra, taken in a magnetic sector mass spectrometer, of the heated PVDF vapor prepared by evaporation at 250 °C (Fig. 1a), and 350 °C (Fig. 1b), indicates few chains longer than 8 to 9 (CH_2–CF_2) monomers. On the basis of the mass spectrometer results, we undertook to fabricate our short chain PVDF films by thermal evaporation with the source at about 230 °C at 1×10^{-7} Torr. The film thickness was monitored with a quartz crystal thickness monitor. The layer-to-layer packing of the film formed from evaporated PVDF was

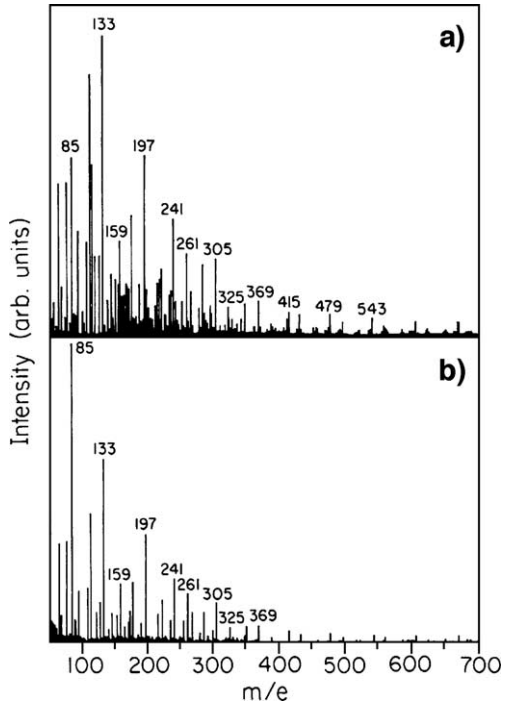

Fig. 1. Mass spectra from thermally evaporated PVDF at 350 °C (a) and 250 °C (b).

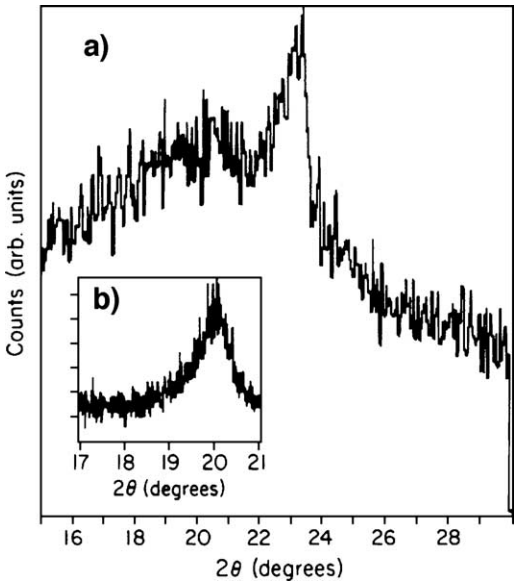

Fig. 2. X-ray diffraction spectra are taken at room temperature using Cu-Kα line for a) ~100Å thick PVDF formed by thermal evaporation, and b) a nominally 5 monolayer copolymer P(VDF–TrFE 70:30) film fabricated by the Langmuir–Blodgett technique.

characterized by θ–2θ X-ray diffraction. The reflection for the <110> layer spacing, at about 20°, is characteristic of the crystalline copolymer P(VDF–TrFE) films [4,8,15,16] (and shown as an inset to Fig. 2). This diffraction feature is also evident for the in situ evaporated short chain polymer films, though the diffraction peak is much broader than for the films fabricated by Langmuir–Blodgett techniques, as seen in Fig. 2. The X-ray diffraction of the in situ evaporated short PVDF films also exhibits an additional diffraction peak at 22.5°, not found for the films fabricated by Langmuir–Blodgett techniques.

As both PVDF and copolymer PVDF–TrFE films are insulating, very thin samples were essential for the electron spectroscopies to avoid excessive charging of the sample surface. Therefore, nominally 2 to 5 monolayer P(VDF–TrFE 70:30) films and ~100 to 150 Å PVDF films were chosen for this work. The evaporation temperature and sample temperatures were determined using a chromel–alumel thermocouples.

For the angle-resolved photoemission studies at the Center for Advanced Microstructure and Devices (CAMD) synchrotron light facility, synchrotron radiation was dispersed by a plane-mirror grating monochromator beamline described in detail elsewhere [17]. The measurements were performed in an ultra high vacuum (UHV) chamber employing a hemispherical electron energy analyzer with an angular acceptance of ±1°, as described elsewhere [18]. The combined resolution of the electron energy analyzer and monochromator was about 0.25 eV. All angles (both light incidence angles and photoelectron emission angles) reported herein, are given with respect to the substrate surface normal. The electron energy loss spectroscopy (EELS) was undertaken using an LK-2000 spectrometer at Oak Ridge National Laboratory.