

1-17-2000

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Jaewu Choi

University of Nebraska-Lincoln, jchoi@ece.eng.wayne.edu

H.M. Manohara

University of Nebraska - Lincoln

Eizi Morikawa

University of Nebraska-Lincoln, eizi@lsu.edu

P.T. Sprunger

University of Nebraska - Lincoln

Peter A. Dowben

University of Nebraska-Lincoln, pdowben@unl.edu

See next page for additional authors

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Choi, Jaewu; Manohara, H.M.; Morikawa, Eizi; Sprunger, P.T.; Dowben, Peter A.; and Palto, S.P., "Thin crystalline functional group copolymer poly(vinylidene fluoride–trifluoroethylene) film patterning using synchrotron radiation" (2000). *Peter Dowben Publications*. 34.

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Authors

Jaewu Choi, H.M. Manohara, Eizi Morikawa, P.T. Sprunger, Peter A. Dowben, and S.P. Palto

Thin crystalline functional group copolymer poly(vinylidene fluoride–trifluoroethylene) film patterning using synchrotron radiation

Jaewu Choi,^{a)} H. M. Manohara, E. Morikawa, and P. T. Sprunger

Center for Advanced Microstructures and Devices, Louisiana State University, Baton Rouge, Louisiana 70806

P. A. Dowben

Department of Physics and Astronomy and the Center for Materials Research and Analysis, Behlen Laboratory of Physics, University of Nebraska-Lincoln, Nebraska 68588-0111

S. P. Palto

Institute of Crystallography of the Russian Academy of Sciences, 117 333 Moscow, Russia

(Received 23 July 1999; accepted for publication 16 November 1999)

The photodegradation mechanism due to synchrotron radiation exposure of crystalline poly[vinylidene fluoride–trifluoroethylene, P(VDF–TrFE)] copolymer thin films has been studied with ultraviolet photoemission spectroscopy (UPS) and mass spectroscopy. Upon increasing exposure to x-ray white light ($h\nu \leq 1000$ eV), UPS measurements reveal that substantial chemical modifications occur in P(VDF–TrFE) 5 monolayer films, including the emergence of new valence band features near the Fermi level, indicating a semimetallic photodegraded product. The photodetached fragments of the copolymer consist mainly of H₂, HF, CHF, CH₂. This x-ray exposure study demonstrates that P(VDF–TrFE) films, possessing unique technologically important properties, can be directly patterned by x-ray lithographic processes. © 2000 American Institute of Physics. [S0003-6951(00)00703-8]

The unique piezoelectric, pyroelectric, ferroelectric, and nonlinear optical properties of polyvinylidene fluoride (PVDF) have long been considered for use in many technological applications including sensors (biomedical cardiopulmonary sensors, ultrasonic transducer, radiation detector),¹ actuators (hydrophone, microphone, headphone, generator),² nonlinear optical component and fiber optics,³ and ferroelectric memory.⁴ Moreover, copolymer films of polyvinylidene fluoride–trifluoroethylene, P(VDF–TrFE), have also attracted interest due to their improved crystallinity and a lower ferroelectric critical temperature (~ 80 °C).⁵ Recently, very thin crystalline copolymer films (2–30 monolayers) of P(VDF–TrFE) have been shown to exhibit novel two-dimensional ferroelectric behavior and distinct surface pyroelectric, ferroelectric, and metallic properties largely independent of film thickness.^{6,7} These properties of the very thin crystalline copolymer P(VDF–TrFE) systems are very desirable in the production of technologically important nanoscale devices.^{1–4,8} In order to accomplish this task, a method to pattern P(VDF–TrFE) thin films is essential.⁹

In this letter, we report on an experimental study which elucidates the physical mechanism by which soft x-ray radiation is used to directly pattern thin, crystalline P(VDF–TrFE) films. Specifically, the focus here is to identify the chemical pathway, using photoemission and mass spectroscopy, of the photodegradation processes that occur when the thin-film copolymer is exposed to synchrotron white-light radiation.

Experimentally, crystalline 5 monolayer films of poly(vinylidene fluoride–trifluoroethylene) [P(VDF–TrFE); 70:30], $-[(-\text{CH}_2-\text{CF}_2)_x-(\text{CF}_2-\text{CHF})_{1-x}]_n-$, were grown on highly doped *n*-type Si(111) wafers by Langmuir–

Blodgett (LB) monolayer deposition from a water subphase, as described elsewhere.^{6,7,10} The chemical composition and structure of the LB copolymer P(VDF–TrFE) films was confirmed with angle resolved x-ray spectroscopy, x-ray diffraction, and scanning tunneling microscopy.^{6,7,11}

In the present study, the exposure effects of the soft x-ray white light radiation on to the P(VDF–TrFE) films were probed with valence band and shallow core level photoemission spectroscopy (UPS). Experiments were performed at the Center for Advanced Microstructures and Devices (CAMD), using the PGM beamline. In white-light geometry used for exposures, this beamline delivers soft x-ray radiation throughout a bandwidth of 100–1000 eV. In order to probe the initial and consequent changes in the electronic structure, monochromatic light from the PGM, at an energy of 74 eV, was employed in UPS measurements. Due to the attenuated flux, photodegradation during UPS measurements were minimal, compared to white-light exposures. The emitted fragments from the P(VDF–TrFE), due to the soft x-ray irradiation were detected *in situ* using a residual gas analyzer (RGA). The “exposure values” reported are deduced from the mesh current (μA) times exposure time (min) of synchrotron radiation white light.

As can be seen in Fig. 1, the photodegradation of the crystalline 5 monolayer copolymer P(VDF–TrFE) films due to exposure of the soft x ray appears in the modification of the electronic valence band spectra. Figure 2(c) reveals that the pristine valence band spectra can be deconvoluted with five peaks, based on an *ab initio* SCF LCAO theoretical calculation.¹² Peak A corresponds to the fluorine 2*s* state. Peak B is related to the C–F band. Peaks C and D are assigned as a C–C band while peak E corresponds to a C–H band in the polyethylene.^{13,14} UPS measurements reveal that,

^{a)}Electronic mail: jchoi1@lsu.edu

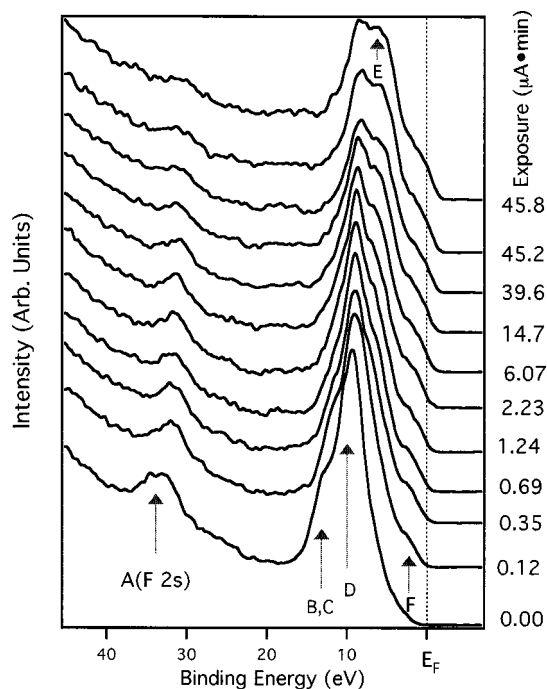


FIG. 1. The valence band photoemission spectra of 5 monolayer films of copolymer poly(vinylidene fluoridetrifluoroethylene) are taken from the normal incidence of 74 eV photon and 45° emission of the photoelectron with respect to the surface normal as a function of white light exposure [exposure=mesh current (●) exposure time].

upon subsequent exposure of white light radiation on the P(VDF-TrFE) films, each band shifts to lower binding energy and a new feature near the Fermi level develops (peak F). Based on theoretical calculations, the existence of peak F provides evidence of a π -bonding band formation in the polymer chain due to the loss of fluorine and/or hydrogen. Figure 2(a) shows that with increasing white light exposure, the intensity of peak A exponentially decreases as peak F increases. Moreover, the photodegradation process is accompanied by a rapid decrease in peak C intensity and increase in the width of peak B. With the development of the new feature F, there are rigid shifts of the binding energies (peaks A, B, D, and E) related to the metallicity change of the polymer, and consequent work function change, with increasing exposure as shown in Figs. 2(b) and 2(c). Based on these UPS observations, it is proposed that the photodegradation mechanism includes a crosslinking in-between the polymer chain (peak width broadening of peak B) increasing the white light exposure.

Figure 3 shows the evolution of photofragments observed in a RGA as a function of the exposure time to white light irradiation. Partial mass spectra were collected for H₂, F, HF, CHF, CH₂, and CF₂. With initial white light exposure, the large amounts of constituent fragments from the polymer were created and emitted. With continued exposure, all measured photoinduced defragmentation intensities decayed exponentially and then almost saturated. This suggests a propensity of surface or near surface constituent components being initially photodetached followed by limited diffusion of further components through a surface barrier.

The relative emitting amounts of the hydrogen fragments due to the white light exposure is 100 times larger than fluorine fragments. As shown in Figs. 1 and 2, the fluorine 2s

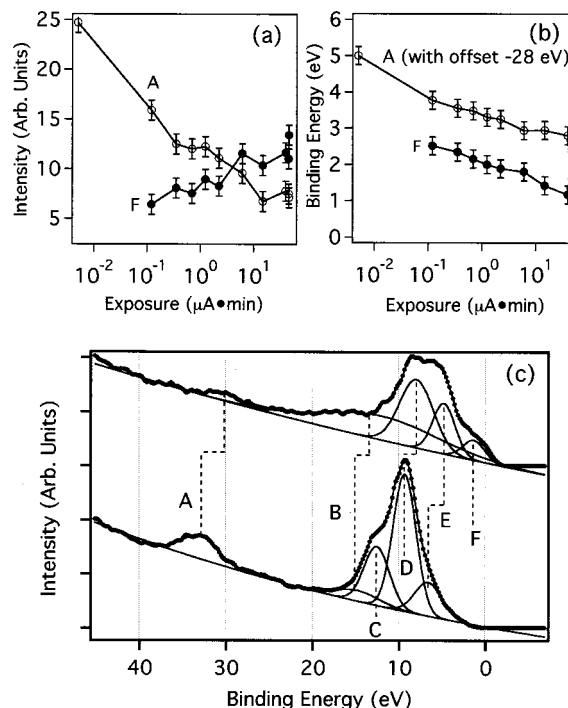


FIG. 2. Intensity changes (a) and binding energy changes (b) of peak A and peak F with respect to the synchrotron white light exposure and (c) deconvolution of the valence band spectra for pristine P(VDF-TrFE) films (bottom) and for largely photodegraded films (top).

peak intensity is relatively slowly decreased. The main photofragments from the copolymer P(VDF-TrFE) films due to the white light exposure are H₂, HF, CHF, and CH₂. Specifically, the detection of CHF mass spectra, as shown in Fig.

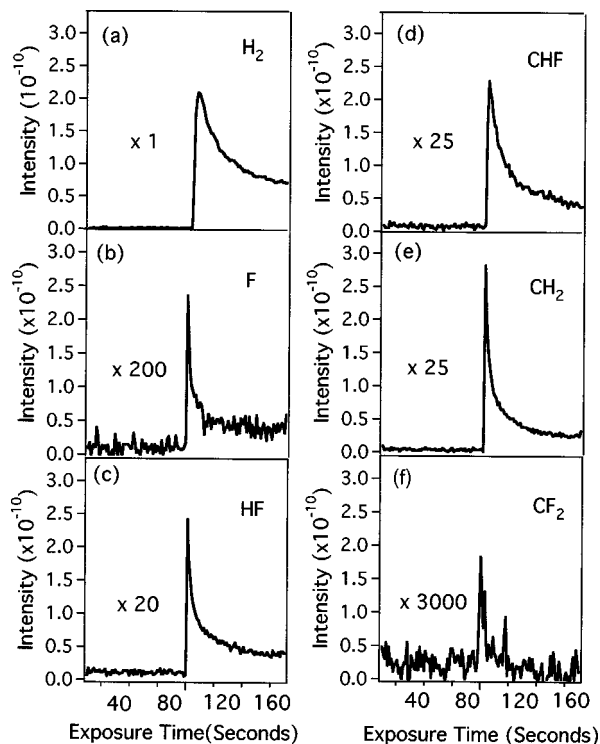


FIG. 3. Mass spectra of the photofragments with subtraction of the background from a 5 monolayer P(VDF-TrFE) film with exposure of soft x-ray white light (with mesh current=0.9 μ A) are collected at leak mode using a residual gas analyzer for (a) H₂, (b) F, (c) HF, (d) CHF, (e) CH₂, and (f) CF₂. The soft x-ray white light exposure is turned on at about 100 s.

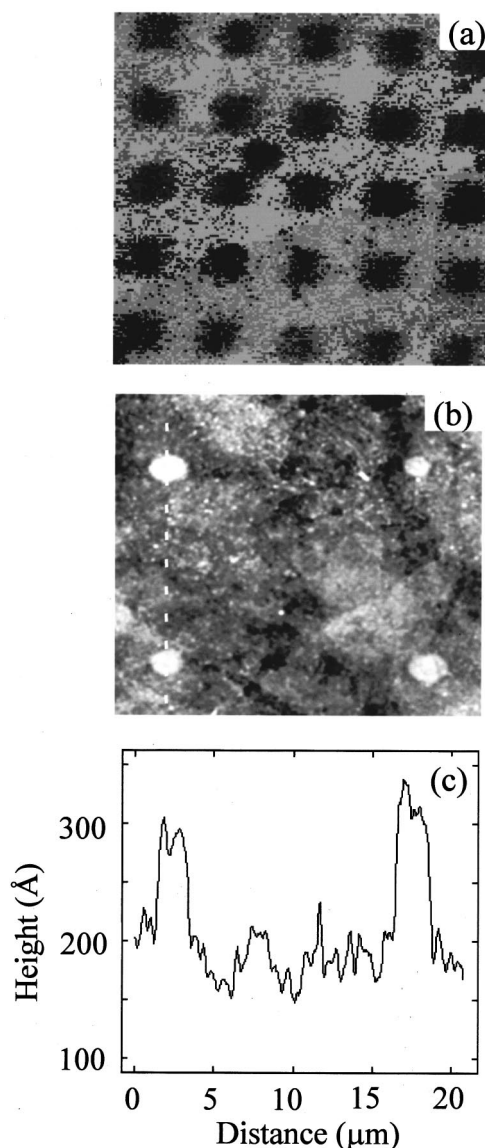


FIG. 4. Patterned crystalline 30 monolayer copolymer P(VDF-TrFE) films which are patterned using a nickel wire mesh mask ($15\ \mu\text{m}\times 15\ \mu\text{m}$ squares) with $\sim 3\ \mu\text{m}$ sputtered tantalum. Exposure was conducted using hard x rays (2–10 keV) with $\sim 100\ \text{J per cm}^3$ exposure at the bottom surface. The pattern size is about $16\ \mu\text{m}\times 16\ \mu\text{m}$; (a) optical microscopic data; (b) atomic force microscopic data; and (c) line profile across the pattern.

3(d), was not detected in the pure PVDF films.¹⁵ This indicates that the observed CHF mass spectra can be ascribed to photofragmentation of the trifluoroethylene monomer components. The CF_2 fragments are nearly absent at the initiation of the white light exposure, as shown in Fig. 3(f). Overall, this indicates the residual material upon exposure is carbon rich (carbonic or graphitic). As detailed above, this proposal is in agreement with the evolution of the UPS spectra with increasing exposure, namely the development of the π -bonding band and attenuation of the F-derived core band intensities.

Based on these observations, it is easily recognized that, employing standard lithographic methods, this photodegradation mechanism can be utilized to produce micro- and nanostructured devices. As a demonstration of this capability of the functional group polymer, Fig. 4 shows both optical and atomic force microscopic images of a directly patterned

30 monolayer crystalline functional group copolymer P(VDF-TrFE) film, produced upon direct exposure of white light through a nickel wire mesh mask. The photoetched area represents regions that could be used as metallic electrodes, as suggested by the Fermi level crossing described above, due to the white light exposure. The unexposed areas, or pristine crystalline P(VDF-TrFE), could be used as a function generator by its own physical properties, such as pyroelectric, piezoelectric, ferroelectric, and nonlinear optical properties. Switching the dipole moment in this type of patterned very thin crystalline ferroelectric films (2–30 monolayer films) can be activated using standard transistor-transistor logic (TTL) bias and thus can be directly utilized in the ferroelectric-based memory devices.⁴

In summary, we have shown that the very thin crystalline functional group copolymer P(VDF-TrFE) films can be directly photoetched and patterned using a white light synchrotron radiation. Moreover, UPS and *in situ* mass spectroscopy have been utilized to characterize the photodegradation mechanism. The photofragments consist of mainly H_2 , HF, CHF, CH_2 . The residual material is carbon rich and chemically more carbic or graphitic. A Fermi level crossing in the valence band electronic structure of the residual material is observed and indicates a metallicity change. The change of the valence band structure is strongly related to the formation of double bonds in the polymer chain and crosslinking between interchains. Combining the observed properties of the metallicity change in the residual material and direct pattern transferring in the functional group polymer P(VDF-TrFE) suggests that a strong potential for future use in integrated micro-(lateral) and nanoscale (vertical) devices.

This work was supported by the Office of Naval Research and the Air Force Office of Scientific Research through Contact No. 30602-98-C-0105, Subcontract No. SU 3531141. The authors acknowledge the AFM assistance of K. Lian.

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