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New Materials and Characterization I

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Molecular Adsorption and Fragmentation of Bromoform on Polyvinylidene Fluoride With Trifluoroethylene

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ABSTRACT

Bromoform adsorption on crystalline polyvinylidene fluoride with 30% of trifluoroethylene, P(VDF-TrFE 70:30) was investigated by photoemission and inverse photoemission and found to be associative and reversible. As on other surfaces, bromoform decomposition does occur, under electron irradiation, and one possible mechanism is dissociative electron attachment.

INTRODUCTION

The adsorption of halocarbons on metal surface is an active area in surface science for more than two decades [1]. Despite the fact that the electronic structure of the haloforms is very similar [2], most of the emphasis has been on chloroform adsorption [3-8], although recently, bromoform [9,10] and chloroform [11,12] adsorption and photodecomposition on molecular films like ice have been investigated. While chloroform (CHCl₃) adsorption on calixarene molecular films has been studied [13], bromoform (CHBr₃) adsorption on the copolymer P(VDF-TrFE 70:30) provides a more compelling comparison [14] as this is a ferroelectric polymer as well as an excellent dielectric [15-17].

EXPERIMENTAL

Ultrathin ferroelectric thin films of copolymer 70% vinylidene fluoride with 30% of trifluoroethylene, P(VDF-TrFE 70:30) were fabricated by Langmuir-Blodgett (LB) deposition technique on freshly-cleaved highly ordered pyrolytic graphite (HOPG) substrates from the water subphase [16-17]. The 5 molecular layers thick films (25 Å) were annealed in ultrahigh vacuum at 110° C before and after each experiment for 30 minutes [18-21]. The Langmuir-Blodgett (LB) method produces highly crystalline films of P(VDF-TrFE) as is evident from the surface structure investigated by STM and experimental band structure mappings [18-21]. The bromoform (CHBr₃) was admitted to the ultrahigh vacuum system through a standard leak valve and the exposures are denoted in Langmuirs (1 L = 10⁻⁶ torr.sec). The combined ultraviolet photoemission (UPS) and inverse photoemission (IPES) spectra were used to characterize the molecular orbital placement of both occupied and unoccupied orbitals of the polymer substrate and the bromoform adsorbate. In both photoemission and inverse photoemission measurements, the binding energies are referenced with respect to the Fermi edge of gold or tantalum, in contact with the sample surface. The UPS data taken in this work was done with a helium lamp He I at $h\nu = 21.2$ eV and a large PHI hemispherical analyzer with an angular acceptance of ± 100 or more [14,19-21]. The IPES were obtained by using variable incident energy electrons while measuring the emitted photons at a fixed energy (9.7 eV) using a Geiger-Müller detector with an instrumental linewidth of ~ 400 meV, as described elsewhere [14,19-21].

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RESULTS AND DISCUSSION

As seen in Figure 1, the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) gap for copolymer P(VDF-TrFE) is much smaller than expected from semi-empirical method NDO-PM₃ (neglect of differential diatomic overlap, parametric model number 3) model calculations based on Hartree-Fock formalism. These differences are due to intermolecular interactions within the PVDF-TrFE film (solid state effects) and band structure, with a large band dispersion evident in the unoccupied molecular orbitals [19]. Although PM₃ is a simplistic semiempirical calculation, density functional theory (DFT) is

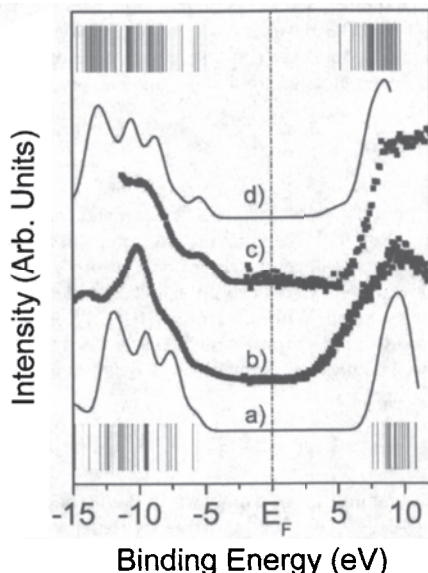


Figure 1: The combined UPS (left) and IPES (right) experimental spectra for clean PVDF-TrFE (b) and 30 L of bromoform adsorbed on PVDF-TrFE film at 120 K (c) compared to semiempirical models of the density of states for PVDF-TrFE (a) and bromoform (d). The molecular orbital eigen values are shown at the bottom and top respectively.

notorious for under estimating the band gap sometimes by a factor 2 or more [23], particularly for molecular systems, and must be rescaled for comparison with experiment [24], particularly final state spectroscopies like photoemission and inverse photoemission. To compare the model calculations with experiment (Figure 1), we applied Gaussian envelopes of 1 eV full width half maximum to each calculated molecular orbital energy (eigen value) to account for the solid state broadening in photoemission and then summing. These model density of states calculations are rigidly shifted in energy by 5.3 eV (representative of work function Φ equal to the difference of vacuum energy E_{vac} and Fermi level E_F) and then compared with the combined photoemission

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and inverse photoemission data, as indicated in Figure 1. No corrections are made for final state effects or matrix element effects in either calculation, so the comparison with experiment is simplistic, but still useful [14].

Following bromoform adsorption on PVDF-TrFE at 120 K, there is a clear suppression of the PVDF-TrFE photoemission features, and new features match the expected molecular orbitals of bromoform (Figure 1). This tends to suggest that bromoform adsorption “wets” the surface of PVDF-TrFE. The HOMO-LUMO gap, as determined from the combined photoemission and inverse photoemission, for bromoform adsorbed on PVDF-TrFE at 120 K is larger than expected based on the model semiempirical molecular calculations, as seen in Figure 1. This may be due to final state effects [24,25] that become more pronounced with decreasing temperature and the increased bromoform coverages. The possible decrease of photoemission final state screening is consistent with the fact that PVDF-TrFE is a good dielectric at 120 K. Thus bromoform adsorption on PVDF-TrFE at 120 K, should more closely resemble bromoform in the gas phase than the fully screened molecular adsorbate on a conducting substrate.

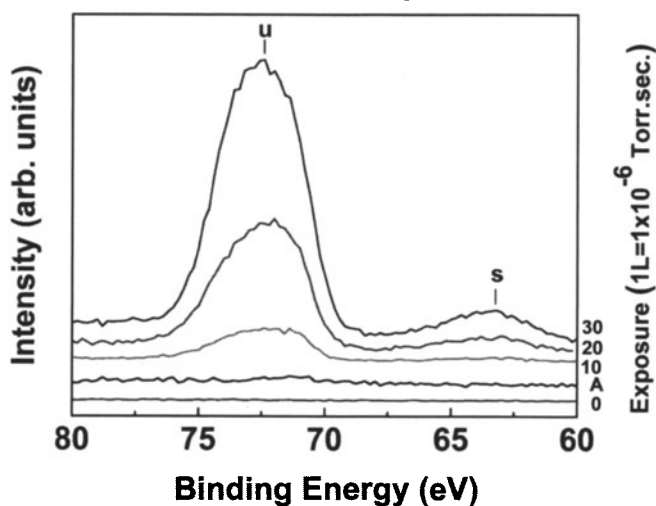


Figure 2: The sequence of photoemission spectra of a 5 monolayer thick P(VDF-TrFE 70:30) at 120 K film before and after CHBr_3 exposure (1 Langmuir (L) = 1×10^{-6} Torr.sec.). Spectrum A is after annealing to room temperature showing that molecular adsorption of bromoform on PVDF-TrFE is reversible.

Bromoform adsorption is observed in the X-ray photoemission of the bromine 3d core level as well. The intensity increases with increasing exposure, in as seen in Figure 2. The binding energy of 72.1 ± 0.1 eV at low bromoform exposure increases to 72.6 ± 0.1 eV at higher exposures to P(VDF-TrFE) at 120 K [14], as illustrated in Figure 2. In spite of our inability to resolve the $3d_{5/2}$ to $3d_{3/2}$ core levels, the bromine 3d XPS features exhibit larger binding energies than expected for the $3d_{5/2}$ core level: a binding energy of 70.3 eV has been measured for condensed bromophenol blue [26], although the binding energy for gaseous bromoform is 76.8 eV [27]. This is consistent with the higher oxidation state of bromoform although final state

effects (as mentioned above) could contribute to increased binding energies, as the polymer substrate is a nominal dielectric. The increase in core level binding energy with increasing coverage suggests a repulsive interaction between adsorbate species, so a stronger interaction with the substrate polymer is certainly possible, and indeed likely.

In spite of possible stronger interactions with the substrate than with adjacent adsorbate species, bromoform adsorption on P(VDF-TrFE) must be weak: chloromethane, with a similar static dipole, is not seen to molecularly adsorb on P(VDF-TrFE) at all at 120 K. The adsorbed species whose signature is evident in photoemission, inverse photoemission and XPS is molecular bromoform. Following bromoform adsorption, the core level XPS bromoform signal is no longer apparent at when the substrate is annealed to room temperature, as the adsorbate bromoform desorbs below room temperature (Figure 2).

The main bromine 3d core photoemission intensity increases with coverage, but after each annealing the bromine signal is lost, indicative of bromine desorption. Following adsorption at 120 K and photofragmentation (as in [9,10,28]), the bromine 3d core level signal is persistent to room temperature and above (120° C) (Figure 3) and we must infer that dissociative adsorption is not reversible and is persistent in XPS to well above room temperature, so we attribute the core level spectra in Figure 2 to molecular, not dissociative adsorption. The photodissociation of bromoform leads to bromine 3d XPS features at 71.4 ± 0.2 and 75.1 ± 0.3 binding energies: binding energies both larger and smaller than the molecular bromoform 3d feature at 72.6 ± 0.1 eV binding energy (Figure 3.)

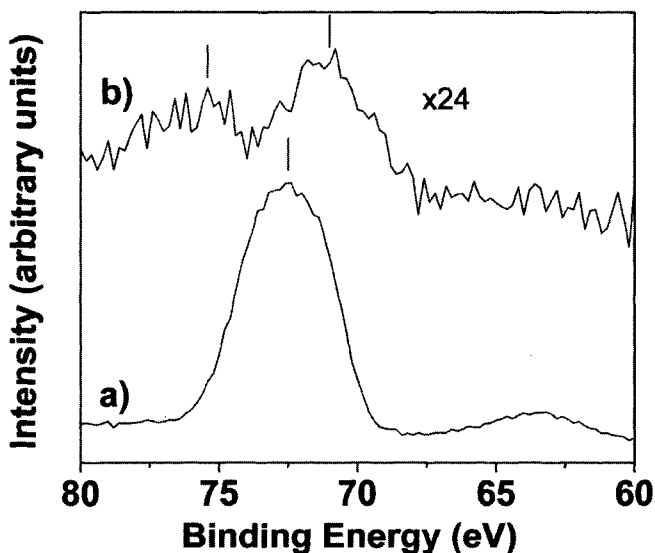


Figure 3: The photoemission spectra of photodissociated bromoform on P(VDF-TrFE) (top) leads to bromine 3d features at 71.4 ± 0.2 and 75.1 ± 0.3 binding energies: binding energies both larger and smaller than the molecular bromoform 3d feature at 72.6 ± 0.1 eV binding energy.

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This decomposition of bromoform is most efficient under electron irradiation, suggesting that a dissociative negative ion resonance may play a role. Such short lived negative ion states are known for a variety of bromoalkanes [29] and dissociative electron attachment has been identified for chlorofluoromethanes in the gas phase [30-31]. While definitive identification of such dissociation mechanisms would require careful investigation of the decomposition rates as a function of electron kinetic energy, this remains a likely scenario.

CONCLUSIONS

We find evidence for molecular adsorption of bromoform on PVDF-TrFE. Chloromethane, with a similar static dipole, is not seen to molecularly adsorb on P(VDF-TrFE) at all at 120 K and we suspect it is a more weakly bound adsorbate compared to bromoform. As with other studies of bromoform adsorption, decomposition on an insulating substrate does seem facile under electron irradiation, even at low electron kinetic energies.

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Application of a Chemically Adsorbed Monolayer and Polypyrrole Thin Film for Increasing the Adhesion Force Between the Resin Substrate and the Plated Copper Layer

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ABSTRACT

A chemically adsorbed monolayer containing pyrrolyl group (Pyrrolyl-CAM) was prepared between a plated copper layer and a resin substrate for increasing the adhesion force without roughening a surface of the resin substrate. Although it was not enough to increase the adhesion force between the resin substrate and the copper layer by using only Pyrrolyl-CAM, the sufficient adhesion force was obtained by preparing a polypyrrole thin film between Pyrrolyl-CAM and the copper layer.

Pyrrolyl-CAM and the polypyrrole thin film on the substrate were evaluated by an automatic contact angle meter and auger electron spectroscopy in order to analyze the condition of the films between the resin substrate and the copper layer.

The peel strength test was carried out in order to evaluate the adhesion force. The best adhesion force was 0.98 [N/mm], and the target value of 0.60 [N/mm] was sufficiently achieved.

INTRODUCTION

In recent years, high density integrated circuit, miniaturization of electronic components and improvement of printed-wire board play roles as high functionalizing and weight saving of electronic devices. The printed-wire board is made of a resin substrate and a copper film laminated, and patterned by an etching technique. Although the adhesion force between the copper film and the resin substrate is important in this process, the adhesion force between the organic and inorganic materials is not usually good.

Therefore, oxidative solutions are traditionally used for roughing the surface of the resin substrate to increase the anchor effect. But if the surface of the resin substrate is roughened, the clock frequency used will be decreased and making the copper wires with fine pitches will be difficult. In addition, the oxidative solutions, such as dichromic acid and permanganic acid, are harmful for the human and the earth's environment.

Consequently, a new technology has been studied for increasing the adhesion force between the copper layer and the resin substrate without roughening.

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In this study, a chemically adsorbed monolayer (CAM) [1-4] containing pyrrolyl group and the polypyrrole thin film were introduced between the copper layer and the resin substrate for increasing the adhesion force without roughening the resin surface.

When the oxidative solutions are used for roughing the surface of the resin substrate in order to increase the anchoring effect, the values of the peel strength force were 0.3~0.6 [N/mm] in our test results. These values satisfied the safety and efficiency of the wiring. This is the reason why the target value of 0.60 [N/mm] was determined.

EXPERIMENTAL DETAILS

Materials

The resin substrates, 50 [mm] × 20 [mm] × 2 [mm] composed with the mixture of polyphenylene sulfide (PPS) and cylindrical glass filler $\phi = 10$ [μm], $h = 100$ [μm] (PPS : glass = 60 [%] : 40 [%]), were supplied from Alps Electric Co., Ltd.

N-[11-(trichlorosilyl)undecyl] pyrrole (PNN), which has a pyrrolyl group at the molecular end, a trichlorosilyl group at the other end, and a hydrocarbon chain group at the middle portion, was synthesized and supplied by Shin-Etsu Chemical Co., Ltd. and used as the adsorbent molecule in order to prepare PNN-CAM on the resin substrate.

Procedure

The experimental procedure is summarized in Fig. 1. (i) The resin substrates were previously cleaned by the oxygen plasma treatment at 600 [W] for 60 [s] by using RMD-150 (UL-VAC, inc.) in order to obtain the organic contamination free substrate, to increase hydroxyl groups on the substrate surface and to activate the substrate surface [5]. (ii) PNN was adsorbed monomolecularly by immersing the resin substrate in the adsorption solution containing PNN (concentration: 5×10^{-3} [mol/L]) in a mixed solvent of the dehydrated chloroform of 33 [%] and the dimethyl-silicone of 67 [%] for 2 [h] at room temperature according to the recommendation by Ogawa et al [6, 7]. This procedure was carried out in a dry air atmosphere below the humidity of 10 [%]. (iii) The substrate was taken out from the solution, and washed with chloroform and acetone. (iv) The resin substrate covered with PNN-CAM was immersed in the acetonitrile solution containing the pyrrole monomer (concentration: 0.2 [M]) for 3 [min] at room temperature. (v) After being taken out from the acetonitrile solution containing the pyrrole monomer, the sample was dried naturally. (vi) The oxidative polymerization was carried out for 5 [min] at 30 [°C] by immersing the substrate in the aqueous solution containing ferric chloride or palladium chloride (concentration: 0.85×10^{-3} [mol/L]) [8, 9]. By the above two processes, the polypyrrole thin film connected to PNN-CAM was prepared. (vii) The copper electroless plating was carried out by using the electroless copper plating kit Thru-Cup PEA Ver. 3 (Uyemura & Co., Ltd) on the polypyrrole thin film in order to form an organo-copper complex. (viii) The galvanic electroplating of copper was also carried out in order to increase the thickness of the plated copper layer for evaluating the adhesion force. The positive plate and the negative plate were immersed in a sulfuric acid aqueous solution of 10 [wt%] for 3 [min] at room temperature. Moreover, those plates were immersed in the copper sulfate plating solution TFE 2001 (ADEKA CORPORATION), followed by applying an electricity of 0.02 [A/m²] for 90 [min] at room temperature, and washing by the purified water. (ix) The sample plates were dried by air gun.