The adsorption and decomposition of HS-(CH₂)₂-(CF₂)₇-CF₃ thin films on Au(111)

A.N. Caruso, Ya.B. Losovyj, Jaewu Choi, P.A. Dowben

Abstract

Broad spectrum synchrotron radiation-induced decomposition of HS-(CH₂)₂-(CF₂)₇-CF₃ was studied by ultraviolet photoemission spectroscopy. The photoemission is dominated by the fluorinated alkane molecular backbone and resembles that of polyvinylidene copolymers and polytetrafluoroethylene (PTFE). The film decomposition products appear to be surprisingly homogeneous.

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The X-ray lithography Galvaformung (electroforming) Abformung (molding) LIGA process and other lithography processes, which are the basis of synchrotron based micro-electro-mechanical systems (MEMS) fabrication, utilise ultraviolet and X-ray light induced molecular decomposition. The detailed chemistry of synchrotron radiation-induced decomposition has been of great interest for more than 10 years [1–18]. Highly fluorinated polymers including polytetrafluoroethylene (PTFE) [13], polyvinylidene fluoride (PVDF) [14–17] and the polyvinylidene fluoride–trifluoroethylene P(VDF–TrFE) copolymers [18] have recently been explored as highly stable X-ray resists and show considerable promise. The likely decomposition route is the loss of HF [16–18] but as with all synchrotron induced decomposition, the products are believed, at least initially, to be extremely heterogeneous. Indeed, low energy electron impact (the most likely mechanism for synchrotron induced decomposition) is associated with the dissociation of C–H, C–C, C–S and gold thiolate bonds, as well as loss of orientational order, conformational order and molecular desorption in adsorbed alkane thiols [19]. Regardless of the decomposition process, decomposition and irradiation damage does appear to be facile for the polyvinylidene fluoride copolymers [14–18,20–23].

The possibility of a preferential decomposition pathway or layer-by-layer radiation-induced ablation
of material is evident in our results of synchrotron radiation-induced decomposition of a model short chain fluorinated alkane thiol: HS-(CH$_2$)$_2$-(CF$_2$)$_7$-CF$_3$. Surprisingly, uniform decomposition thin film products are formed, even at high photon energies and large fluxes available from synchrotron radiation light sources.

A clean Au surface, of a gold film deposited on Si(111), was prepared by Ar$^+$ ion sputtering in an ultrahigh vacuum (UHV) system. The alkane thiol, HS-(CH$_2$)$_2$-(CF$_2$)$_7$-CF$_3$ (Synquest Laboratories), was deposited from the vapor on the clean Au surface, pre-cooled to −180 °C. Molecular adsorption, of high coverage (>20 molecular layers, or more than sufficient to obscure photoemission from the Au 5d bands), was established after an exposure of $320 \times 10^{-7}$ mbar s. This corresponds to an exposure of the surface to HS-(CH$_2$)$_2$-(CF$_2$)$_7$-CF$_3$ pressure at $1 \times 10^{-7}$ Torr, uncorrected ionization gauge cross section, for 4 min in a UHV system with a background vacuum of $3 \times 10^{-10}$ Torr.

Light polarization-dependent photoemission spectra were taken using light dispersed by a 3-m toroidal grating monochromator at the Center for Advanced Microstructures and Devices synchrotron radiation source in Baton Rouge, LA (USA). Several photon energies were used, but the spectra shown here were taken at a photon energy of 32 eV. All binding energies are referenced to the Fermi level of the gold substrate, corresponding to the chemical potential.

The photoemission spectra closely resemble the photoemission spectra of PVDF and P(VDF–TrFE) thin films [18,24], as seen in Fig. 1. The prominent photoemission feature at 13-eV binding energy in Fig. 1 is associated with molecular orbitals arising from the carbon chain backbone [16–18,24]. The photoemission spectra of Fig. 1 are indicative of large binding energy for the highest molecular orbital (HOMO) and low density of states at the Fermi level for PVDF [18,24], P(VDF–TrFE) [24] and the alkane thiol, HS-(CH$_2$)$_2$-(CF$_2$)$_7$-CF$_3$. This is characteristic of highly fluorinated and stable organic molecules [16–18,24].

The photoelectrons were collected along surface normal to preserve the highest possible symmetry in light polarization dependence studies, possibly because of the highly plane polarized light from the synchrotron. The changes in the relative photoemission intensities with changes in the incident angle light polarization dependence from p to s+p polarized light (70° compared to 45° incidence angle with

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**Fig. 1.** Comparison of photoemission spectra from a thin HS-(CH$_2$)$_2$-(CF$_2$)$_7$-CF$_3$ film (left), and polyvinilidene– trifluoroethylene copolymer films (right). Photoemission spectra from a thin HS-(CH$_2$)$_2$-(CF$_2$)$_7$-CF$_3$ film formed by vapor deposition and P(VDF–TrFE) were taken as a function of exposure time and synchrotron beam current (proportional to the broad band synchrotron light fluence). The shift in the bands is an indication of the effects of decomposition on the molecular orbital binding energies.
respect to the surface normal) indicate that the HS-(CH$_2$)$_2$-(CF$_2$)$_7$-CF$_3$ has a preferential adsorbate bonding orientation. Like the partly fluorinated alkane thiols [25,26], HS-(CH$_2$)$_2$-(CF$_2$)$_7$-CF$_3$ is also likely to be canted, placing the molecular chain axis at some finite angle with respect to the surface normal. Because of the canted configuration and the fact that in the C$_{1h}$ point group symmetry of the adsorbed molecule, we are not able to resolve the molecular orbitals of $a$ and $a'$ symmetries, we cannot reliably identify the preferential orientation from this limited data.

Synchrotron light contains a broad spectrum of photon energies, with extinction (for this monochromator) in the region $E_{hv}=202$ eV or $\lambda=61$ Å. White or zero-order synchrotron light exposure to the adsorbed molecular film was undertaken to induce molecular decomposition. The prominent backbone chain molecular orbital bands at 13-eV binding energy shift toward smaller binding energies, towards $E_F$, with increased exposure to the broad band synchrotron white light (a shift to 11–12-eV binding energy after 0.25-μA-min exposure), as do indeed all the observed photoemission bands of HS-(CH$_2$)$_2$-(CF$_2$)$_7$-CF$_3$ (Fig. 1). The decrease in observed molecular orbital binding energies is common with UV-induced photodecomposition [9–13,16–18], and is typically a result of the smaller HOMO-LUMO gap from the remaining molecular fragments. With molecular overlayers that are also good dielectrics, UV-induced ablation (photoinduced desorption) can result in a decrease in binding energies due to better screening of the photoemission final state [27].

The decrease in binding energies, observed for HS-(CH$_2$)$_2$-(CF$_2$)$_7$-CF$_3$ (Fig. 1), is qualitatively very similar to that observed for PVDF and P(VDF–TrFE) [18], as summarized in Fig. 2. For PVDF and P(VDF–TrFE) [17,18], the decomposition route has been identified and is associated with HF elimination from the film.

The band shifts associated with broad band synchrotron light exposure to the alkane thiol, HS-(CH$_2$)$_2$-(CF$_2$)$_7$-CF$_3$, towards smaller binding energies, are accompanied by a decrease in the photoemission peak widths, as summarized in Fig. 2. This surprising result indicates that there is a sequential fragmentation process from this molecule, as a consequence of the synchrotron UV photolysis where multiple decomposition products [28] are suppressed. In most examples of UV photolysis of molecular adsorbates, the photoemission binding energy shifts are generally accompanied by an increase in the photoemission peak widths due to spectroscopic sampling of a number of parent molecule and fragment species [9–12,28].

Alternatively, the synchrotron-induced stimulated molecular desorption of the film (irradiation induced ablation) proceeds layer by layer, with the films of uniform thickness and subject to uniform photovoltaic charging. The decrease in binding energy is thus a systematic and uniform decrease in an unscreened photoemission final state caused by a systematic decrease in film thickness. It is very unlikely that

![Fig. 2](image_url)
the film is consistently of uniform thickness, but since there is no evidence of coexistence of multiple final states, and hence coexistence of different thicknesses in the film, final state effects (or photovoltaic charging changes) are unlikely to be the major factor leading to the observed binding energy shifts. Layer-by-layer ablation is unlikely to lead to changes in the photoemission final state screening, consistent with the observed data. The molecules are not seen to have a high degree of preferential order within the film and layer-by-layer growth was not observed. Such UV photoinduced changes to the molecular thin films, in particular the decrease in photoemission feature widths, have been associated with photoisomerization [29] and selective UV-induced polymerization [30], not decomposition [1–23]. Bonding of this fluorinated alkane thiol molecule to the Au surface is very strong and the adsorbed film is stable. After vapor deposition at \(-180^\circ C\), the sample temperature was raised to 20 \(^\circ C\) and above where no thermal desorption or pyrolytic decomposition of the molecular thin film was observed. This stability, and the fact that the alkane thiol is highly fluorinated, suggests that UV photoinduced desorption and polymerization are far less likely, compared to photo-decomposition. A preferential and sequential decomposition process, as is indicated for this fluorinated alkane thiol, would provide considerable added functionality to an X-ray molecular photoresist.

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