X-RAY DAMAGE TO CF$_3$CO$_2$-TERMINATED ORGANIC MONOLAYERS ON Si/Au SUPPORTS IS DUE PRIMARILY TO X-RAY INDUCED ELECTRONS

Paul E. Laibinis, Robert L. Graham, Hans A. Biebuyck, and George M. Whitesides
Department of Chemistry
Harvard University
Cambridge MA 02138

Technical Report No. 44 (December 1991)

Interim Technical Report
(Accepted for publication in Science)

PREPARED FOR DEFENSE ADVANCED RESEARCH PROJECTS AGENCY
1400 Wilson Boulevard
Arlington VA 22209

DEPARTMENT OF THE NAVY
Office of Naval Research, Code 1130P
800 North Quincy Street
Arlington VA 22217-5000

Project No.: a400011dd205
Contract No.: N00014-86-K-0756
Effective Date: 86 September 15
Expiration Date: 92 September 14

Principal Investigator: George M. Whitesides
(617) 495-9430

The views and conclusions in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Defense Advanced Research Projects Agency or the U.S. Government.

DISTRIBUTION STATEMENT A
Approved for public release:
Distribution Unlimited
X-rays damage organic materials. The relative importance of the X-rays themselves, and of both X-ray-generated and secondary electrons, in this damage was explored using self-assembled monolayers (SAMs) on multilayer thin film supports. The substrates were prepared by depositing thin films of Si (0, 50, 100 and 200 Å) on thick layers of Au (2000 Å); these systems were supported on chromium-primed silicon wafers. Trifluoroacetyl-terminated SAMs were...
assembled on these substrates and the samples irradiated with monochromatic Al K$_\alpha$ X-rays. The fluxes of X-rays to which the different samples were exposed were the same, but the fluxes and energy distributions of the electrons generated by interactions of the X-rays with the substrates differed. The loss of fluorine from the SAMs was followed by XPS and was slower on substrates emitting a lower flux of electrons. This observation indicated that the electrons, and not the X-rays themselves, were largely responsible for the damage to the organic monolayer films that resulted in loss of fluorine from them.
X-ray Damage to CF₃CO₂-terminated Organic Monolayers on Si/Au Supports is Due Primarily to X-ray Induced Electrons.

Paul E. Laibinis, Robert L. Graham, Hans A. Biebuyck, and George M. Whitesides*

*To whom correspondence should be addressed
Abstract

X-rays damage organic materials. The relative importance of the X-rays themselves, and of both X-ray-generated and secondary electrons, in this damage was explored using self-assembled monolayers (SAMs) on multilayer thin-film supports. The substrates were prepared by depositing thin films of Si (0, 50, 100 and 200 Å) on thick layers of Au (2000 Å); these systems were supported on chromium-primed silicon wafers. Trifluoroacetyl-terminated SAMs were assembled on these substrates and the samples irradiated with monochromatic Al Kα X-rays. The fluxes of X-rays to which the different samples were exposed were the same, but the fluxes and energy distributions of the electrons generated by interactions of the X-rays with the substrates differed. The loss of fluorine from the SAMs was followed by XPS and was slower on substrates emitting a lower flux of electrons. This observation indicated that the electrons, and not the X-rays themselves, were largely responsible for the damage to the organic monolayer films that resulted in loss of fluorine from them.
X-rays damage organic materials (1). This damage can either limit their utility or provide the basis for useful technologies (e.g. X-ray lithography (2,3) or radiation cross-linking of polymers (3)). Understanding the mechanisms of the damage accompanying exposure to X-rays is helpful in designing materials and environments in which this exposure yields the desired results. A basic tenet of areas of technology involving X-ray processing has been that X-rays do not interact strongly with matter (4) and should effect little damage to materials; the photo-generated primary and secondary electrons interact more strongly, and have been postulated to be the damaging species (5).

We and others (6) have recently begun to explore the mechanisms of X-ray-induced damage to organic materials, employing as samples self-assembled monolayers (SAMs) on metal substrates (7-9). SAMs are well suited for this study because they allow a variety of organic functionalities to be incorporated into monomolecular films having well-defined structures. SAMs can be easily generated having dimensions of interest (10-40 Å; the characteristic escape depth (10) for electrons in the energy range encountered -- ≤ 1.5 keV -- is 20-40 Å). A range of substrates can be derivatized using different types of SAMs: two we employ here are alkanethiolates on gold (7), and alkysiloxanes on silica (9,10). We have chosen the trifluoroacetyl group (CF$_3$CO$_2^-$) as a probe for a number of reasons: its surface concentration is easily measured by XPS (11); it decomposes rapidly when irradiated with X-rays (6); it is easily introduced into SAMs (7,8); it is localized at the monolayer-air interface and analysis of the concentration of fluorine in the SAM is not complicated by the presence or generation of other signals.

In this report, we outline a study of the rate of damage to trifluoroacetyl groups attached via an undecyl tether (CF$_3$CO$_2$(CH$_2$)$_{11}$-) to the surface of thin (50-200 Å) silicon films supported on gold. The objective of this study was to examine the
relative rates of damage to the organic components of the system -- the 
CF$_3$CO$_2$-terminated SAM -- as a function of intensities of X-ray photons and of 
electrons. The results provide direct experimental confirmation that, under 
conditions relevant to technologies such as X-ray photolithography, electrons are 
responsible for the majority of damage in one representative organic system. 
The electrons measured in this study include primary (photo- and Auger) and 
secondary electrons; we refer to these collectively as electrons.

To vary the number of electrons generated by interaction of the X-rays with the 
support, we prepared composite substrates (Figure 1) comprising materials -- 
gold and silicon -- characterized by very different electron yields on X-ray 
irradiation; gold produces a higher electron yield than silicon (11). To generate 
intensities of electrons at the CF$_3$CO$_2$ group covering a range of values, we coated 
the gold (-2000 Å) with various thicknesses of evaporated silicon (50, 100 
and 200 Å as determined in situ using a quartz crystal microbalance; each ±10%). 
X-rays are not significantly attenuated by these thicknesses of silicon (4), and the 
number of X-ray photons in the gold films -- and thus the number of X-ray 
induced photoelectrons from the gold -- is similar in all of these samples. The 
electrons generated in the gold are, however, strongly scattered by the silicon.

To confirm the structure of the substrates, we used Rutherford Backscattering 
(RBS) (12) employing 3 MeV He$^+$ for independent characterization of the 
thickness of the silicon overlayer. Figure 2 shows representative spectra; the 
signals associated with silicon (inset) were analyzed (13) and thicknesses of 50, 
105, and 185 Å (values estimated to be ±10 Å) were inferred for the three samples. 
The width of the peak associated with gold suggests the reproducibility of the 
thicknesses of the multilayer substrates we fabricate (~±10%). The spectra 
confirm that neither chromium nor bulk silicon are localized at the 
substrate/vacuum interface; RBS lacked the sensitivity to determine whether gold
Figure 1. Schematic illustration of the structures employed in these studies. The lines denoting interfaces between materials are not meant to indicate that the interfaces are atomically flat; we have not measured their flatness. The lowest layers of Si represent Si(100) wafers (~0.5 mm thick) on which the assemblies were supported; the other layers of Si were prepared by evaporation and are probably amorphous. The evaporated films of Si contain a layer of SiO₂ (not shown) of undetermined thickness (but probably ~15 Å). Chromium was employed as an adhesion layer between the Si wafer and gold.
Figure 2. Rutherford backscattering (RBS) spectra of Si/Cr/Au/Si substrates for different thicknesses of the silicon overlayer. The substrates were prepared by the sequential evaporation onto the surface of a silicon wafer (Si(100) with ~15 Å of native oxide) of 200 Å of Cr, 2000 Å of Au and $n$ Å ($n = 0, 50, 100, 200$) of Si. The thicknesses were determined using a quartz crystal microbalance (QCM) in the evaporator chamber (±10 %). Quantitation of the signals associated with the silicon layer (inset) yielded values of its thickness (error estimated to be ±10 Å): QCM (RBS) 50 Å (50 Å); 100 Å (105 Å); 200 Å (185 Å). The spectrum of silicon is provided for comparison. The markers each illustrate the location of a particular element relative to the vacuum interface; for example, Cr is located ~2000 Å beneath the surface. The assignment of signals is (eV) Au: 2.4-2.8; Cr: 1.9-2.0; Si: 1.7, and the plateaus for $E \leq 1.7$. The spectra are displaced vertically for clarity.
or silicon was present at the surface. By X-ray photoelectron spectroscopy (XPS), the films coated with silicon exhibited no peaks due to gold (only silicon, oxygen and carbon) and were found to be unreactive to alkanethiols (14). These observations suggest that the silicon layers are essentially free of pinholes.

The surfaces were derivatized by the self-assembly technique (7-9). SAMs were formed on the substrates exposing SiO$_2$ by allowing them to react with CH$_2$=CH(CH$_2$)$_9$SiCl$_3$ in hexadecane; the resulting olefin surfaces were transformed into trifluoroacetate surfaces via a two-step procedure using BH$_3$/H$_2$O$_2$ and trifluoroacetic anhydride (TFAA) (8). SAMs were formed on gold by reaction with HS(CH$_2$)$_{11}$OH in deoxygenated absolute ethanol; the alcohol surface was converted to the trifluoroacetate by 30 s exposure to 5% TFAA/hexanes.

Figure 3 displays XPS spectra of representative derivatized substrates. The figure demonstrates that the electron flux through the SAMs decreased as the thickness of the silicon overlayer increased. While peaks directly attributable to gold were not observed when the silicon overlayer was $\geq 50$ Å, we believe that the photoelectrons due to gold were, after inelastic collisions, largely responsible for the increased baseline (relative to pure silicon) for the samples containing an overlayer of silicon. A 200-Å overlayer of silicon virtually masked the presence of the underlying gold: the spectra of this system and that having only silicon as substrate are very similar. Figure 3 further establishes that the intensity of the F(1s) peak from the CF$_3$CO$_2$ groups of the SAMs on the various substrates were approximately equal: the different methods of forming SAMs generated approximately equal numbers of CF$_3$CO$_2$ groups per unit area of surface (15).

The samples were exposed to a constant flux of monochromatized Al K$_\alpha$ X-rays ($E = 1486.6$ eV, anode power = 200 watts) in a Surface Science SSX-100 XPS spectrometer (operating pressure $= 10^{-9}$ torr) using a spot of size $\sim 1$ mm$^2$. 
Figure 3. XPS spectra of trifluoroacetyl-terminated monolayers on Si/Cr/Au/Si substrates. The spectra were obtained on spots that had been previously unexposed to X-rays and required ~15 min of exposure to the beam; the amount of damage to the SAM during this exposure is small (~5%). The spectra have been offset horizontally by -10 eV from the one below it for clarity; the spectra have not been offset vertically. There is no residual gold signal even in the thinnest Si film (50 Å), and thus, we believe, no pinholes. This conclusion is reinforced by other experiments reported in the text. The hydroboration procedure incorporated a contaminant, Ca (KE = 1100 eV), that is present in <1 atomic %. As we compare the rate of damage to electron intensity, presence of an impurity of Ca is not important. Inset: The "universal" curve (10). λ, the inelastic mean free path, is defined as the distance at which the probability an electron tranversing a medium without significant energy loss is 1/e. 1/λ is directly related to the probability of an electron interacting inelastically with a medium.
Photoelectron Intensity (Counts x 10^-4)

Kinetic Energy (eV)

Au(4f)

-750-

-6

-5

-4

-3

-2

-1

0

1

2

3

4

5

6

7

λ (Å)

1

10

100

1000

10000

Au(4s)

Au(4p)

Au(4d)

F(1s)

O(1s)

C(1s)

Si(2p,2s)

O(a)

F(a)

Si/Cr/Au
Si/Cr/Au/Si (50 Å)
Si/Cr/Au/Si (100 Å)
Si/Cr/Au/Si (200 Å)
Si/Si (200 Å)

Kinetic Energy (eV)
Electrons due to F(1s) were detected using a concentric hemispherical analyzer (pass energy = 100 eV).

Figure 4 summarizes the relative intensity of the F(1s) peak upon exposure of the CF₃CO₂-terminated monolayers on the various substrates to Al Kα X-rays. The intensity of the peak was measured during sequential 4 minute intervals. With continued exposure to X-rays, the intensity of the F(1s) peak decreased. The amount of loss of fluorine from the various substrates exposed to common numbers of photons is different (upper panel); the loss of fluorine is faster on the substrates that exhibit greater intensities of electrons upon irradiation with X-rays (Figure 3). The different amounts of damage that occur upon exposing identical monolayers on substrates with different electron yields to a common intensity of X-rays demonstrate that electrons are, at some level, important in causing X-ray-induced damage.

The relative importance of photons and electrons in causing damage to the SAMs can be estimated using the data in Figure 3. The flux of electrons from the various substrates under a common flux of photons is different. We have estimated the relative intensities of electrons from the substrates by integrating (16,17) the XPS spectra in Figure 3 over the energy range kinetic energy (KE) = 387 to 1487 eV. We are limited by the electrostatic analyzer on the XPS to quantitation of electrons of KE ≥ 400 eV and we acknowledge that there may be systematic errors in estimating the relative intensities of electrons in the range of energies that are most damaging (~50 eV) from the observed yield of electrons of energies > 400 eV (17,18). In Figure 4 (lower panel), we plot the intensity of F(1s) from the various substrates vs. the number of electrons to which the SAM has been exposed. To generate similar doses of electrons, the samples containing thicker overlayers of silicon were exposed to the X-ray beam longer than those having thinner overlayers. The profiles in Figure 4 (lower panel) are remarkably
Figure 4. X-ray induced damage to trifluoroacetyl-terminated monolayers on Si/Cr/Au/Si substrates as a function of the number of photons (upper) and electrons (lower) to which the CF$_3$CO$_2$- group were exposed. The intensity of the F(1s) signal was determined from sequential scans (~4 min each). The number of electrons from these samples were estimated by integrating (16,17) the XPS spectra in Figure 3. In the lower panel, the substrates require different lengths of exposure to the X-ray beam to yield similar numbers of electrons. The different rates of loss evidenced in the upper panel and the similarity of the profiles in the lower panel suggest that the damage to the SAMs results primarily from the electrons and not from the photons themselves. A.U. = arbitrary units.
similar (especially given that the substrates had different lengths of exposure to the X-ray beam) and suggest that the primary and secondary electrons are much more important in the damage process than are the X-ray photons. The deviations present are, we believe, primarily due to difficulties in maintaining a constant photon flux.

While the present data do not determine whether electrons are solely responsible for causing damage, they are, however, consistent with primary and secondary electrons being responsible for most (and maybe all) of the damage to a representative organic system upon irradiation with X-rays.
References and Notes


4. For example, the penetration depth of X-rays (KE ~2 kV) into organic materials is of the order of microns; of electrons, it is of the order of ~100 Å [M. P. Seah, in *Practical Surface Analysis*, D. Briggs and M. P. Seah, Eds. (John Wiley & Sons, Chichester, 1983), Chapter 5]. In our experiment, we estimate the flux of X-ray photons experienced by the CF₃CO₂- group to be more than ~100 times greater than the flux of electrons.


10. The so-called "universal" curve (Figure 3, inset) relates the inelastic mean free path of an electron, λ, (the distance required to reduce the probability an electron escaping to 1/e) through a material to the kinetic energy of the electron [M. P. Seah and W. A. Dench, *Surf. Interface Anal.* 1, 2 (1979)].


13. RBS spectra were analyzed using “SA” (Spectrum Analysis), a PC version of the TEK program for RBS analysis developed at Oak Ridge. SA was written by Patrick M. Smith (Harvard University, Division of Applied Sciences).

14. To test for the presence of gold at the surface of the Si/Cr/Au/Si substrates, the Si-coated gold substrates were immersed in an ethanolic solution containing a fluorine-containing alkanethiol (CF$_3$CF$_2$CH$_2$O(CH$_2$)$_{11}$SH) overnight. Thiols react with soft metal/metal oxides -- for example, gold -- but do not react with hard metal/metal oxides -- alumina, silica [P. E. Laibinis, J. J. Hickman, M. S. Wrighton, G. M. Whitesides, *Science* 245, 845 (1989); P. E. Laibinis and G. M. Whitesides, unpublished results]. No fluorine was detected on any substrate exposing Si by XPS suggesting that the Si-coated gold substrates reveal no (or very little) gold at their surface. We estimate that we would have detected 0.1 % of a monolayer of the fluorinated thiolate.

15. We have estimated that the procedure used to derivatize silicon yields ~80% the number of trifluoroacetyl groups as that used to derivatize gold (8).

16. In estimating the relative flux of electrons from the various substrates, the spectra (Figure 3) were corrected for differences in the efficiency of the electrostatic analyzer with the KE of the electron. The effect of this correction on the relative electron flux is small (<2 %).

17. We have also analyzed the XPS spectra incorporating differences in the likelihood of an electron to interact with the SAM (estimated as 1/λ) and find that the correction would be small (<3 %); the direction of this correction is opposite that due to detector inefficiencies (16).

19. This research was supported in part by the Office of Naval Research, the Defense Advanced Research Projects Agency, and the National Science Foundation (Grant CHE-88-12709). XPS and RBS spectra were obtained using instrumental facilities purchased under the DARPA/URI program and maintained by the Harvard University Materials Research Laboratory. We thank John F. Chervinsky and Patrick M. Smith (Harvard University, Division of Applied Sciences) for help in characterizing the substrates by RBS, John P. Folkers for supplying the \( \text{H}_2\text{C=CH(CH}_2\text{)}_9\text{SiCl}_3 \), Dr. Colin D. Bain (Cambridge University) for invaluable discussions and suggestions, and our colleagues Steven M. Bonser, John P. Folkers, and John P. Mathias for critical readings of this manuscript.
TECHNICAL REPORT DISTRIBUTION LIST (June 1991)

Office of Naval Research
Chemistry Division, Code 1113
800 North Quincy Street
Arlington VA  22217-5000

Dr. James S. Murday
Chemistry Division, Code 6100
Naval Research Laboratory
Washington DC  20375-5000

Dr. Robert Green, Director
Chemistry Division, Code 385
Naval Weapons Center
China Lake CA  93555-6001

Dr. Eugene C. Fischer
Code 2840
David Taylor Research Center
Annapolis MD  21402-5067

Dr. Elek Lindner
Naval Ocean Systems Center
Code 52
San Diego CA  92152-5000

Commanding Officer
Naval Weapons Support Center
Attn: Dr. Bernard E. Douda
Crane IN  47522-5050

Dr. Richard W. Drisko
Naval Civil Engineering Laboratory
Code L52
Fort Hueneme CA  93043

Dr. Harold H. Singerman
David Taylor Research Center
Annapolis MD  21402-5067
ATTN: Code 283

Chief of Naval Research
Special Assistant for Marine Corps Matters, Code OOMC
800 North Quincy Street
Arlington VA  22217-5000

Defense Technical Information Center
Building 5, Cameron Station
Alexandria VA  22314
ABSTRACT DISTRIBUTION LIST (June 1991)

Prof. Robert W. Armstrong  
Department of Chemistry  
University of California  
405 Hilgard Avenue  
Los Angeles CA  90024

Prof. Peter Dervan  
Department of Chemistry  
Calif Institute of Technology  
Pasadena CA  91125

Prof. Arthur E. Martell  
Department of Chemistry  
Texas A&M University  
College Station TX  77843-3255

Dr. Joseph Boyer  
Department of Chemistry  
University of New Orleans  
New Orleans LA  70148

Prof. Francois N. Diederich  
Department of Chemistry  
University of California  
405 Hilgard Avenue  
Los Angeles CA  90024

Prof. William L. Mock  
Department of Chemistry  
University of Illinois at Chicago  
Chicago IL  60680

Professor Jerald S. Bradshaw  
Department of Chemistry  
Brigham Young University  
Provo UT  84602

Prof. Dennis A. Dougherty  
Department of Chemistry  
Calif Institute of Technology  
Pasadena CA  91125

Prof. Martin E. Newcomb  
Department of Chemistry  
Texas A&M University  
Box 3578  
College Station TX  77843-3255

Prof. Ronald Breslow  
Department of Chemistry  
Columbia University  
New York NY  10027

Prof. Kenneth M. Doxsee  
Department of Chemistry  
University of Oregon  
Eugene OR  97403

Prof. Peter Schultz  
Department of Chemistry  
University of California  
Berkeley CA  94720

Dr. Duncan W. Brown  
Advanced Technology Materials  
520-B Danbury Road  
New Milford CT  06776

Prof. Margaret C. Etter  
Department of Chemistry  
University of Minnesota  
207 Pleasant Street SE  
Minneapolis MN  55455

Prof. Carol Venanzi  
Department of Chemistry  
New Jersey Inst of Technology  
323 King Blvd.  
Newark NJ  07102

Prof. Cynthia J. Burrows  
Department of Chemistry  
State University of New York  
Stony Brook NY  11794-3400

Prof. Wilmer K. Fife  
Department of Chemistry  
Indiana Univ/Purdue Univ  
1125 East 38th Street  
Indianapolis IN  46223

Prof. Howard W. Whitlock  
Department of Chemistry  
University of Wisconsin  
Madison WI  53706

Professor Peter Chen  
Department of Chemistry  
Harvard University  
Cambridge MA  02138

Prof. Samuel H. Gellman  
Department of Chemistry  
University of Wisconsin  
Madison WI  53706

Prof. Jeffrey D. Winkler  
Department of Chemistry  
The University of Chicago  
5735 S. Ellis Avenue  
Chicago IL  60637

Prof. Anthony W. Czarnik  
Department of Chemistry  
Ohio State University  
120 West 18th Avenue  
Columbus OH  43210-1173

Prof. Thomas J. McCarthy  
Department of Polymer Science  
University of Massachusetts  
701 Graduate Research Center  
Amherst MA  01003