Alkyl Monolayers on Silica Surfaces Prepared from Neat, Heated (Tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-dimethylchlorosilane Analyzed by XPS

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Silane monolayers on silica, prepared from mono-, di-, and trichlorosilanes, are widely used in industry for surface functionalization and modification. However, unlike di- and trichlorosilanes, monochlorosilanes are particularly easy to work with because they can dimerize, but not polymerize, upon reaction with water. Typically, an organic solvent is used when depositing a silane monolayer. Here we show XPS spectra of monolayers of (Tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-dimethylchlorosilane on silicon oxide (silicon wafer) prepared using a rapid, solvent-free approach. Reaction conditions are 60 °C for 10 min using the neat (pure) compound, and no inert atmosphere or special treatment of the compound is required. [DOI: 10.1116/11.20020802]

Keywords: *x-ray photoelectron spectroscopy; silane; alkylation; monochlorosilanes*

PACS: *82.80.Pv, 81.05.Lg*

Accession # 00767

Technique: XPS

Host Material: Monolayer (Tridecafluoro-1,1,2,2-tetrahydrooctyl)-1 dimethylchlorosilane/Si

Instrument: Surface Science Laboratories, Inc. SSX-100

Major Elements in Spectrum: C, Si, O, F

Minor Elements in Spectrum: none

Printed Spectra: 5

Spectra in Electronic Record: 5

Spectral Category: technical

INTRODUCTION

Silanes (Ref. 1) attach to silica surfaces by reacting with surface silanols (Si–OH). While monolayers prepared from monochlorosilanes are more subject to hydrolysis than those derived from di- and trichlorosilanes, surface functionalization with the monofunctionalized compounds is generally more straightforward because they cannot polymerize. Numerous preparations of silane monolayers on surfaces have been reported in the literature. For example, Maoz and Sagiv first showed that alkyl monolayers can be prepared on planar silicon using trichlorosilanes (Ref. 2). Recognizing the advantages of mono- over di- and trichlorosilanes, Rabolt and co-workers described a gas phase procedure for depositing perfluorinated alkyldimethylchlorosilanes on SiO_2 (Ref. 3). Both Linton and co-workers (Ref. 4) and Watts and co-workers (Ref. 5) deposited monolayers of alkyldimethlychlorosilanes, including $ClSi(CH_3)_2(CH_2)_{17}CH_3$ 2-tetrahydrooctyl)-1-dimethylchlorosilane, onto silica particles using an organic solvent. Typical surface modifications for know procedures call for exposing a surface to a heated, dilute solution of a silane under inert atmosphere. In contrast, here we take clean, dry, native-oxide-terminated silicon (1.5–2.0 nm), place liquid, neat (Tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-dimethylchlorosilane on its surface, and heat it in an oven at 60 °C for 10 min (relative humidity= 70%). After reacting, the surface is cleaned, dried, loaded into an XPS UHV chamber, and analyzed by XPS, which showed carbon levels consistent with monolayer quantities of surface alkyl chains (ellipsometric thickness is approximately 0.6–0.7 nm, advancing contact angle $\theta_a = 103.2° \pm 0.5°$, receding contact angle (θ_r) $= 86.8° \pm 2.5°$). The results of using this new facil surface silanization technique (for 5 different silanes) is summarized in a note published in Langmuir (Ref. 6).

SPECIMEN DESCRIPTION

Host Material: Monolayer (Tridecafluoro-1,1,2,2-tetrahydrooctyl)-1 dimethylchlorosilane/Si

CAS Registry #: 102448-47-1

Host Material Characteristics: homogeneous; solid; single crystal; semiconductor; ceramic; glass; thin film; coating

Chemical Name: silicon/silicon oxide

Source: Montco Silicon Technologies, Inc.

Host Composition: Si/SiO_2

Form: single crystal wafer, *p*-type

Lot #: W9969

Structure: Si (100)

As Received Condition: not specified

Analyzed Region: same as host material

***Ex Situ* Preparation/Mounting:** The silicon surfaces were first cleaned with a solution of NH_4OH (conc.): H_2O_2 (conc.) (50:50) (v/v) for 30 min at room temperature. They were then rinsed with water and finally washed with 5% vol. HCl (conc.) for 1 h. After reaction in the oven (for 10 min at 60 °C), the wafers were rinsed with acetone, cleaned with a soft artists brush using a 2% sodium dodecyl sulfate solution in water, and placed in a Soxhlet apparatus overnight using *m*-xylene (b.p. ~139 °C) as the extraction solvent. The samples were then removed from the Soxhlet, rinsed with water, dried, and mounted into the XPS machine. (Note: source beam size on the instrument was not well characterized and may be up to twice as large as the manufacturer's values given here [See Source Beam Size at Specimen Surface].) Warning: this procedure should not be attempted with volatile silanes. Fumes from a volatile organic compound are potentially explosive. In addition, the NH_4OH/H_2O_2 cleaning solution is extremely caustic and should be used with great care.

***In Situ* Preparation:** none

Charge Control: none

Temp. During Analysis: 298 K

Pressure During Analysis: $<2.053\times10^{-7}$ Pa

INSTRUMENT DESCRIPTION

Manufacturer and Model: Surface Science Laboratories, Inc. SSX-100

Analyzer Type: spherical sector

Detector: resistive anode position detector

Number of Detector Elements: 128

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

■ Spectrometer

Analyzer Mode: constant pass energy

Throughput ($T=E^N$): $N=0$

Excitation Source Window: 10 μm Mylar

Excitation Source: Al K_α monochromatic

Source Energy: 1486.6 eV

Source Strength: 200 W

Source Beam Size: 0.8 mm × 0.8 mm

Signal Mode: multichannel direct

■ Geometry

Incident Angle: 55°

Source to Analyzer Angle: 70.8°

Emission Angle: 55°

Specimen Azimuthal Angle: 0°

Acceptance Angle from Analyzer Axis: 30°

Analyzer Angular Acceptance Width: 30° × 30°

ACKNOWLEDGMENTS

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SPECTRAL FEATURES TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (counts)	Sensitivity Factor	Concen-tration (at. %)	Peak Assignment
00767-02	Si 2*p*	99.4	1.3	13783	0.9	29.9	···
00767-03	C 1*s*	291.9	2.2	12714	1.00	17.4	···
00767-04	O 1*s*	532.2	2.3	30383	2.49	28.1	···
00767-05	F 1*s*	688.9	3.2	49287	3.32	28.9	···

ANALYZER CALIBRATION TABLE

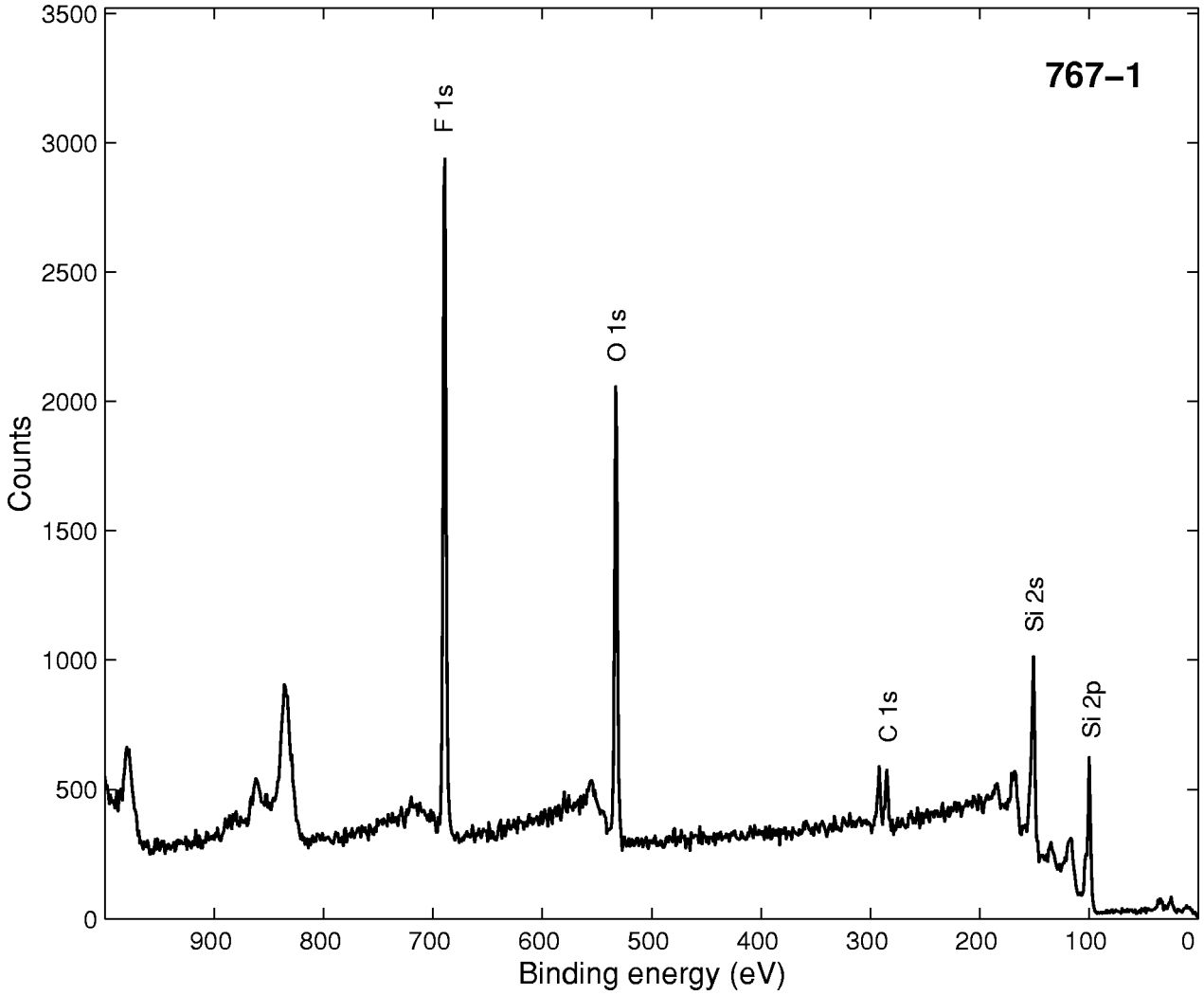
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (counts)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
...[a]	Au $4f_{7/2}$	83.92	0.98	2200	10.67	...	...
...[b]	Au $4f_{7/2}$	83.92	1.6	6000	10.67	...	...
...[c]	Cu $3s$	122.36	3.0	1600	1.05	...	...
...[b]	Cu $2p_{3/2}$	932.45	1.78	4000	9.73	...	...

[a] Spot size 300 μm, pass energy 50 eV, 2 scans
[b] Spot size 800 μm, pass energy 150 eV, 1 scan
[c] Spot size 800 μm, pass energy 150 eV, 3 scans

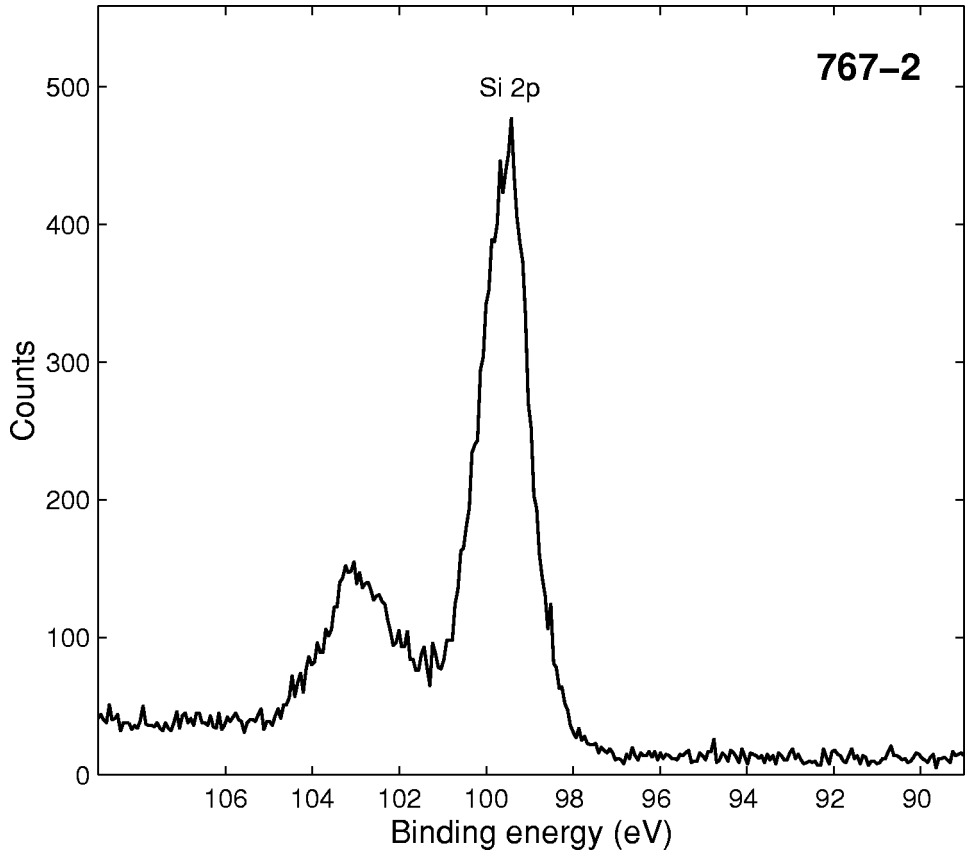
GUIDE TO FIGURES

Spectrum (Accession) #	Spectral Region	Voltage Shift*	Multiplier	Baseline	Comment #
767-1	Survey	0	1	0	
767-2	Si $2p$	0	1	0	
767-3	C $1s$	0	1	0	
767-4	O $1s$	0	1	0	
767-5	F $1s$	0	1	0	

* Voltage shift of the archived (as-measured) spectrum relative to the printed figure. The figure reflects the recommended energy scale correction due to a calibration correction, sample charging, flood gun, or other phenomenon.



Accession #	00767-01
Host Material	Monolayer (Tridecafluoro-1,1,2,2-tetrahydrooctyl)-1 dimethylchlorosilane/Si
Technique	XPS
Spectral Region	survey
Instrument	Surface Science Laboratories, Inc. SSX-100
Excitation Source	Al K_α monochromatic
Source Energy	1486.6 eV
Source Strength	200 W
Source Size	0.8 mm × 0.8 mm
Analyzer Type	spherical sector
Incident Angle	55°
Emission Angle	55°
Analyzer Pass Energy	150 eV
Analyzer Resolution	1.5 eV
Total Signal Accumulation Time	1320 s
Total Elapsed Time	1520 s
Number of Scans	6
Effective Detector Width	15.1 eV
Analyzer Width	1500 μm × 12000 μm
Comment	note C 1*s* split peak and a strong F 1*s* peak



- **Accession #:** 00767-02
- **Host Material:** Monolayer (Tridecafluoro-1,1,2,2-tetrahydrooctyl)-1 dimethylchlorosilane/Si
- **Technique:** XPS
- **Spectral Region:** Si 2*p*

Instrument: Surface Science Laboratories, Inc. SSX-100

Excitation Source: Al K_α monochromatic

Source Energy: 1486.6 eV

Source Strength: 200 W

Source Size: 0.8 mm × 0.8 mm

Incident Angle: 55°

Analyzer Type: spherical sector

Analyzer Pass Energy: 50 eV

Analyzer Resolution: 0.5 eV

Emission Angle: 55°

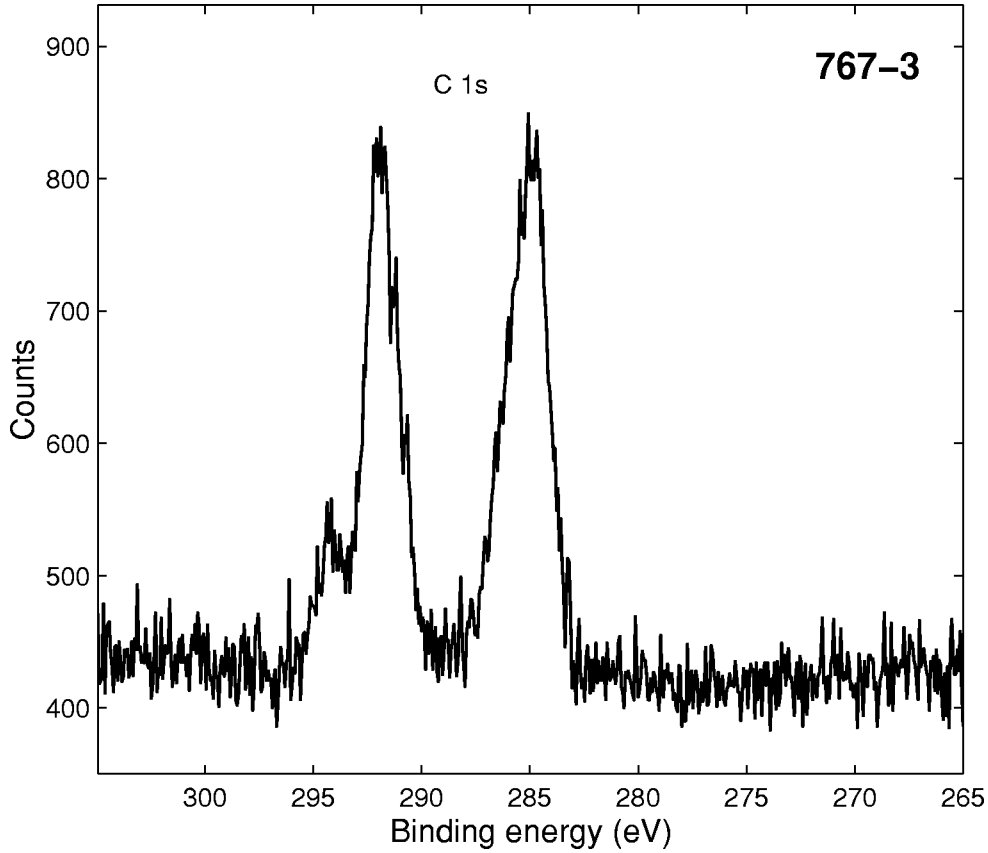
Total Signal Accumulation Time: 368 s

Total Elapsed Time: 537 s

Number of Scans: 6

Effective Detector Width: 6.09 eV

Analyzer Width: 750 μm × 6000 μm



- **Accession #:** 00767-03
- **Host Material:** Monolayer (Tridecafluoro-1,1,2,2-tetrahydrooctyl)-1 dimethylchlorosilane/Si
- **Technique:** XPS
- **Spectral Region:** C 1*s*

Instrument: Surface Science Laboratories, Inc. SSX-100

Excitation Source: Al K_α monochromatic

Source Energy: 1486.6 eV

Source Strength: 200 W

Source Size: 0.8 mm × 0.8 mm

Incident Angle: 55°

Analyzer Type: spherical sector

Analyzer Pass Energy: 50 eV

Analyzer Resolution: 0.5 eV

Emission Angle: 55°

Total Signal Accumulation Time: 1227 s

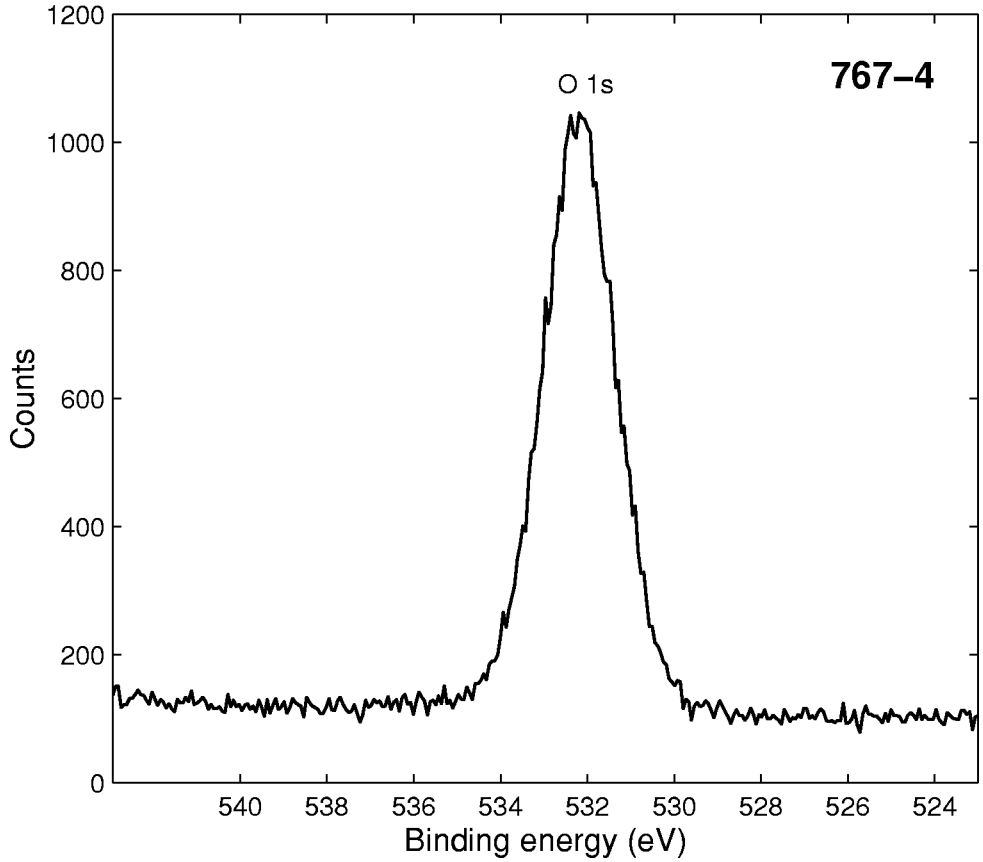
Total Elapsed Time: 1396 s

Number of Scans: 20

Effective Detector Width: 6.09 eV

Analyzer Width: 750 μm × 6000 μm

Comment: Three carbon species are visible: $-CH_2$, $-CF_2$, $-CF_3$



- **Accession #:** 00767-04
- **Host Material:** Monolayer (Tridecafluoro-1,1,2,2-tetrahydrooctyl)-1 dimethylchlorosilane/Si
- **Technique:** XPS
- **Spectral Region:** O 1*s*

Instrument: Surface Science Laboratories, Inc. SSX-100

Excitation Source: Al K_α monochromatic

Source Energy: 1486.6 eV

Source Strength: 200 W

Source Size: 0.8 mm × 0.8 mm

Incident Angle: 55°

Analyzer Type: spherical sector

Analyzer Pass Energy: 50 eV

Analyzer Resolution: 0.5 eV

Emission Angle: 55°

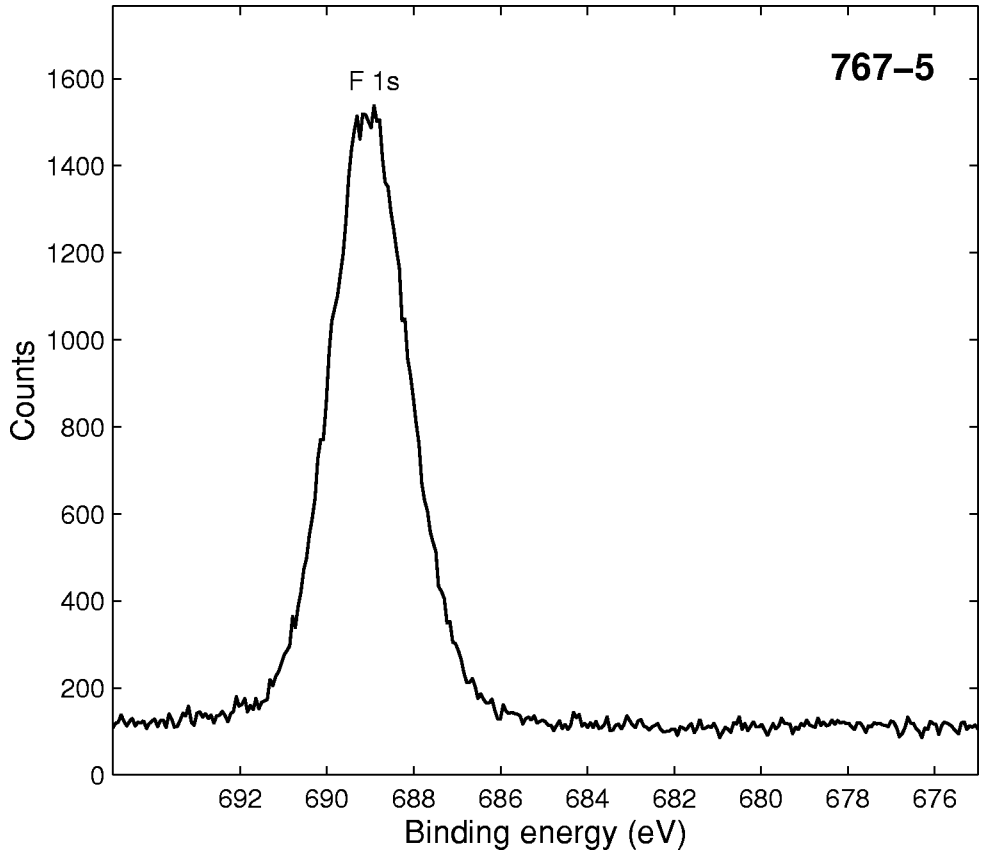
Total Signal Accumulation Time: 368 s

Total Elapsed Time: 537 s

Number of Scans: 6

Effective Detector Width: 6.09 eV

Analyzer Width: 750 μm × 6000 μm



- **Accession #:** 00767-05
- **Host Material:** Monolayer (Tridecafluoro-1,1,2,2-tetrahydrooctyl)-1 dimethylchlorosilane/Si
- **Technique:** XPS
- **Spectral Region:** F 1*s*

Instrument: Surface Science Laboratories, Inc. SSX-100

Excitation Source: Al K_α monochromatic

Source Energy: 1486.6 eV

Source Strength: 200 W

Source Size: 0.8 mm × 0.8 mm

Incident Angle: 55°

Analyzer Type: spherical sector

Analyzer Pass Energy: 50 eV

Analyzer Resolution: 0.5 eV

Emission Angle: 55°

Total Signal Accumulation Time: 368 s

Total Elapsed Time: 537 s

Number of Scans: 6

Effective Detector Width: 6.09 eV

Analyzer Width: 750 μm × 6000 μm