

Alkyl Monolayers on Silica Surfaces Prepared from Neat, Heated $\text{ClSi}(\text{CH}_3)_2(\text{CH}_2)_{17}\text{CH}_3$ 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 $\text{ClSi}(\text{CH}_3)_2(\text{CH}_2)_{17}\text{CH}_3$ (octadecyldimethylchlorosilane, CAS# 18643-08-8) on silicon oxide (silicon wafer) prepared using a rapid, solvent-free approach. Reaction conditions are 120 °C for 10 min using the neat (pure) compound, and no inert atmosphere or special treatment of the compound is required. © 2003 American Vacuum Society. [DOI: 10.1116/11.20020502]

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

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INTRODUCTION

Silanes (Ref. 1) attach to silica surfaces by reacting with surface silanols ($\text{Si}-\text{OH}$). While monolayers prepared from monochlorosilanes are more subject to hydrolysis than those derived from di- and trichlorosilanes, surface functionalization with the mono-functionalized 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-terminated 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 alkyldimethylchlorosilanes, including $\text{ClSi}(\text{CH}_3)_2(\text{CH}_2)_{17}\text{CH}_3$, onto silica particles using an organic solvent. Typical surface modification conditions 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 $\text{ClSi}(\text{CH}_3)_2(\text{CH}_2)_{17}\text{CH}_3$ on its surface, and heat it in an oven at 120 °C for 10 min (relative humidity = 70%). Above its melting point (28–30 °C) the compound flows over the surface of the silica. 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 = 1.04 ± 0.11 nm, advancing contact angle (θ_a) = $100.1^\circ \pm 2.1^\circ$, receding contact angle (θ_r) = $86.1^\circ \pm 4.2^\circ$].

Three replicate samples were subjected to identical treatment and analysis, to show the reproducibility of our technique. Only one sample, with its spectra, is published here, except that the Table of Spectral Features lists comparable features from all three samples. In addition, complete data and spectra for all three samples are archived in the Surface Science Spectra database.

SPECIMEN DESCRIPTION

Host Material: Alkyl monolayer/on clean, native oxide terminated silicon derived from $\text{ClSi}(\text{CH}_3)_2(\text{CH}_2)_{17}\text{CH}_3$

CAS Registry #: 7440-2-13

Accession # 00734

Technique: XPS

Host Material: Alkyl monolayer/Si – $\text{ClSi}(\text{CH}_3)_2(\text{CH}_2)_{17}\text{CH}_3$

Instrument: Surface Science SSX-100

Major Elements in Spectrum: C, Si, O

Minor Elements in Spectrum: none

Printed Spectra: 7

Spectra in Electronic Record: 21

Spectral Category: technical

Original Submission: 5/23/2002

Accepted for Publication: 9/30/2002

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

Chemical Name: silicon/silicon oxide

Source: Montco Silicon Technologies, Inc.

Host Composition: Si/SiO₂

Form: single crystal wafer, *p*-type

Lot #: W9969 sample 1

Structure: Si(100)

As Received Condition: silicon wafer, 125 mm diameter

Analyzed Region: host material plus prepared monolayer

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 120 °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 entry for 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 $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$ cleaning solution is extremely caustic and should be used with great care.

In Situ Preparation: not specified

Charge Control: not specified

Temp. During Analysis: 298 K

Pressure During Analysis: $<7.87 \times 10^{-7}$ 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 \times 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° \times 30°

DATA ANALYSIS METHOD

Peak Shape and Background Method: background Shirley function

ACKNOWLEDGMENTS

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REFERENCES

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SPECTRAL FEATURES TABLE

Spectrum ID #	Element/Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (counts)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
00734-02	Si 2p	100.01	1.327	46197	0.9
00734-03	C 1s	285.58	1.919	46891	1.0
00734-04	O 1s	533.02	1.863	82123	2.49
00734-05	Si 2p	100.13	0.84	6067	0.9	36.73	...
00734-06	C 1s	285.63	1.3	6763	1.0	36.189	...
00734-07	O 1s	532.88	1.55	11659	2.49	27.081	...
00734-09	Si 2p	100.20	1.671	47612	0.9
00734-10	C 1s	285.72	1.557	56497	1.0
00734-11	O 1s	532.87	2.211	89425	2.49
00734-12	Si 2p	99.95	1.092	6668	0.9	34.66	...
00734-13	C 1s	285.70	1.33	8389	1.0	40.56	...
00734-14	O 1s	532.87	1.519	12886	2.49	24.79	...
00734-16	Si 2p	101.18	4.33	48513	0.9
00734-17	C 1s	285.74	2.503	46708	1.0
00734-18	O 1s	533.12	1.902	95573	2.49
00734-19	Si 2p	99.88	1.189	7191	0.9	39.83	...
00734-20	C 1s	285.50	1.225	6720	1.0	32.58	...
00734-21	O 1s	533.20	1.421	13644	2.49	27.59	...

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 4 <i>f</i> _{7/2}	83.92	0.98	2200	10.67
... ^b	Au 4 <i>f</i> _{7/2}	83.92	1.6	6000	10.67
... ^c	Cu 3 <i>s</i>	122.36	3.0	1600	1.05
... ^b	Cu 2 <i>p</i> _{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.

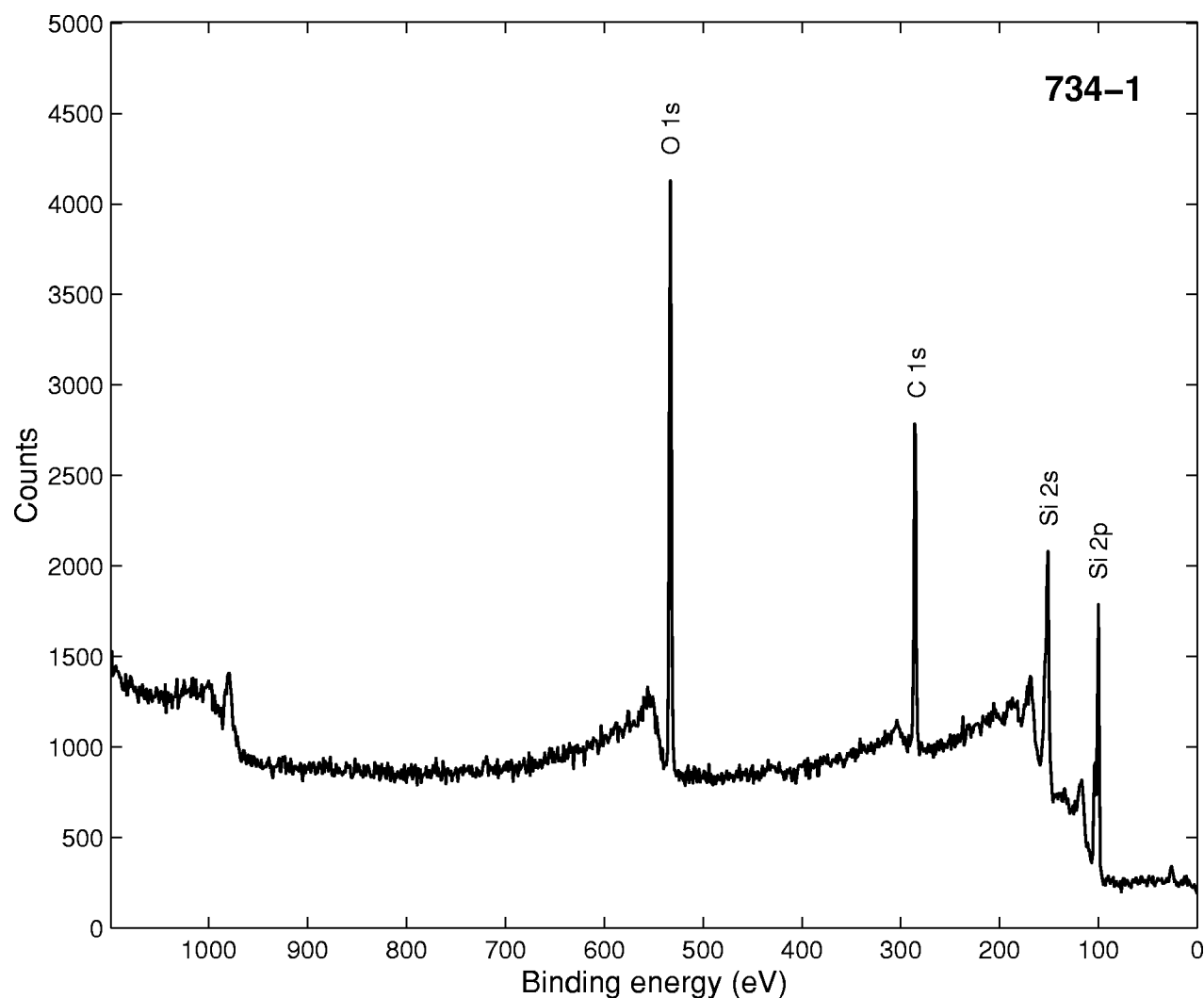
^c Spot size 800 μm, pass energy 150 eV, 3 scans.

GUIDE TO FIGURES

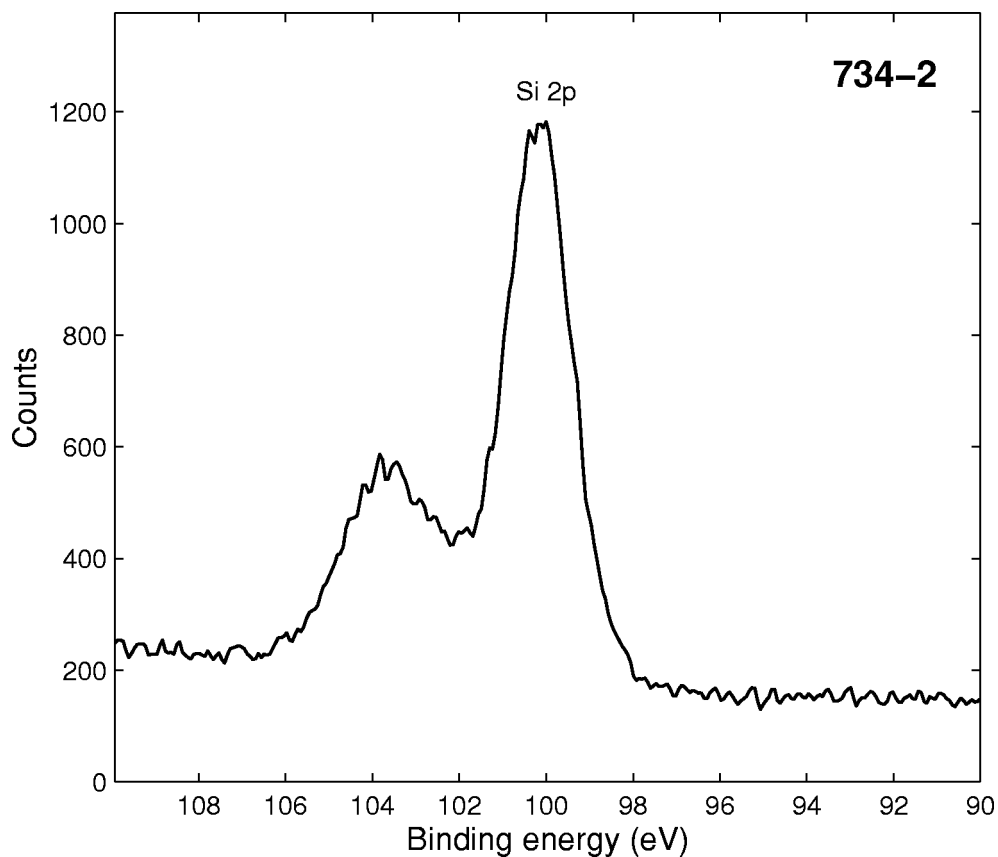
Spectrum (Accession) #	Spectral Region	Voltage Shift*	Multiplier	Baseline	Comment #
734-1	Survey	0	1	0	
734-2	Si 2 <i>p</i>	0	1	0	
734-3	C 1 <i>s</i>	0	1	0	
734-4	O 1 <i>s</i>	0	1	0	
734-5	Si 2 <i>p</i>	0	1	0	
734-6	C 1 <i>s</i>	0	1	0	
734-7	O 1 <i>s</i>	0	1	0	
735-1 [NP]**	Survey	0	1	0	
735-2 [NP]	Si 2 <i>p</i>	0	1	0	
735-3 [NP]	C 1 <i>s</i>	0	1	0	
735-4 [NP]	O 1 <i>s</i>	0	1	0	
735-5 [NP]	Si 2 <i>p</i>	0	1	0	
735-6 [NP]	C 1 <i>s</i>	0	1	0	
735-7 [NP]	O 1 <i>s</i>	0	1	0	
736-1 [NP]	Survey	0	1	0	
736-2 [NP]	Si 2 <i>p</i>	0	1	0	
736-3 [NP]	C 1 <i>s</i>	0	1	0	
736-4 [NP]	O 1 <i>s</i>	0	1	0	
736-5 [NP]	Si 2 <i>p</i>	0	1	0	
736-6 [NP]	C 1 <i>s</i>	0	1	0	
736-7 [NP]	O 1 <i>s</i>	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.

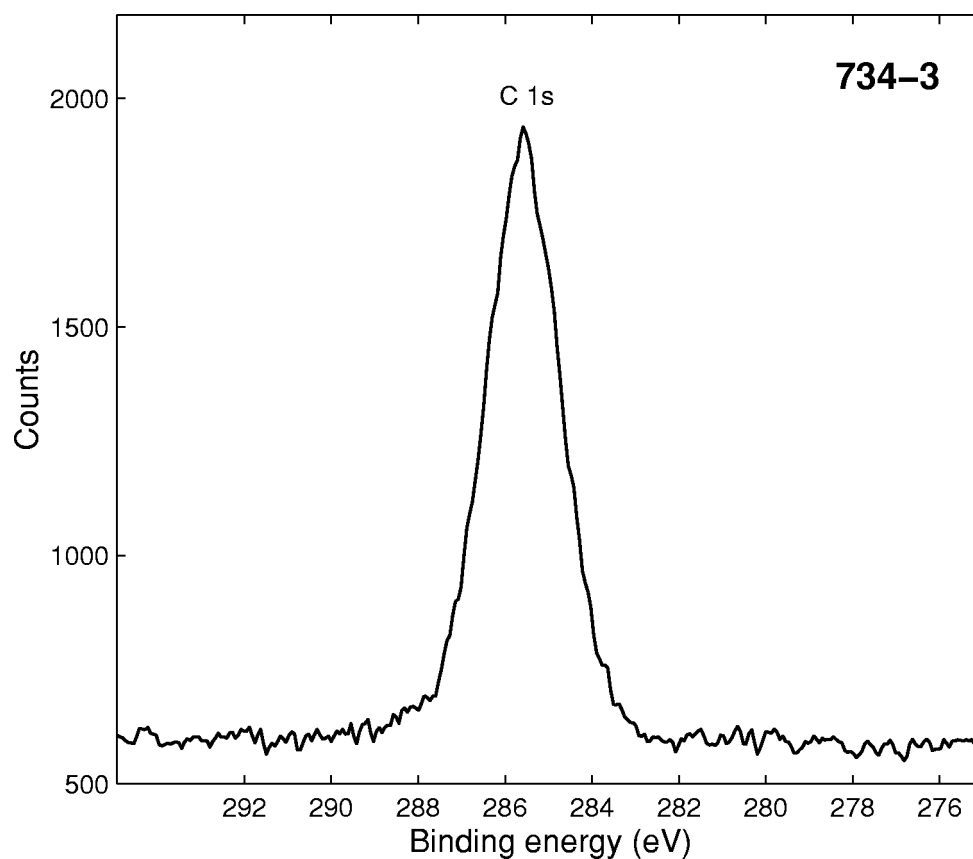
** [NP] signifies not published; digital spectra are archived in SSS database but not reproduced in the printed journal.



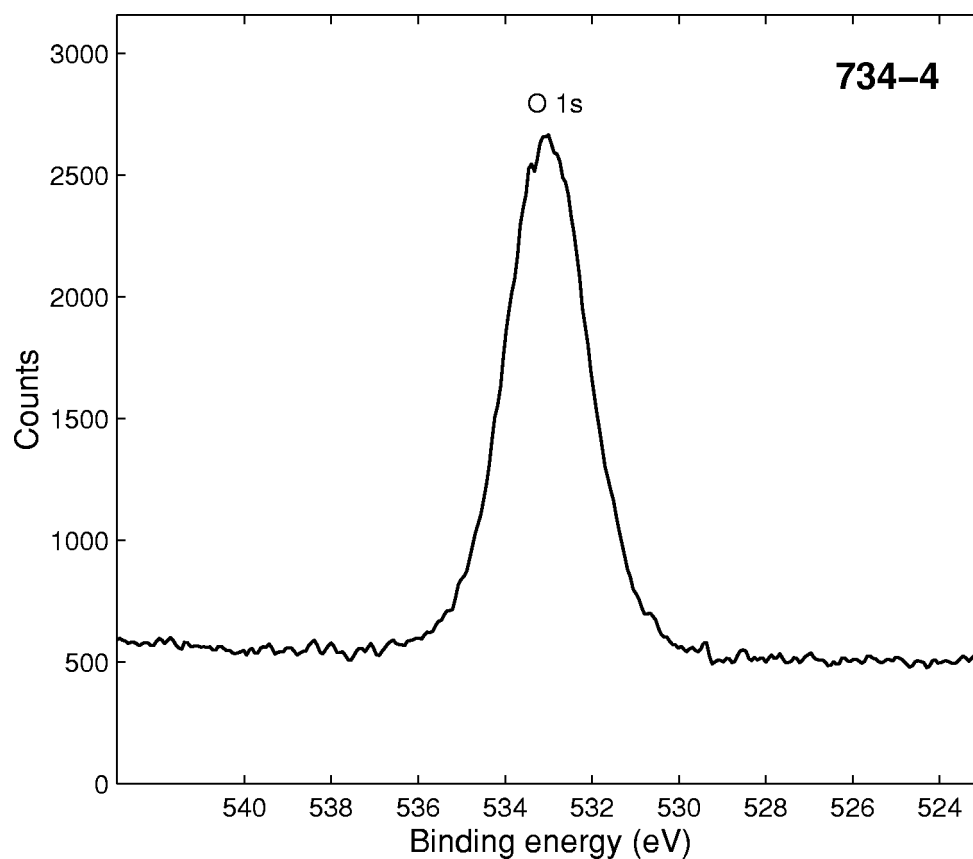
Accession #	00734-01
Host Material	Alkyl monolayer/Si – ClSi(CH ₃) ₂ (CH ₂) ₁₇ CH ₃
Technique	XPS
Spectral Region	survey
Instrument	Surface Science SSX-100
Excitation Source	Al K _α monochromatic
Source Energy	1486.6 eV
Source Strength	200 W
Source Size	0.8 mm × 0.8 mm
Analyzer Type	spherical sector
Incident Angle	55°
Emission Angle	55°
Analyzer Pass Energy	150 eV
Analyzer Resolution	1.5 eV
Total Signal Accumulation Time	220 s
Total Elapsed Time	420 s
Number of Scans	1
Effective Detector Width	13.0906494 eV
Analyzer Width	1500 μm × 12000 μm



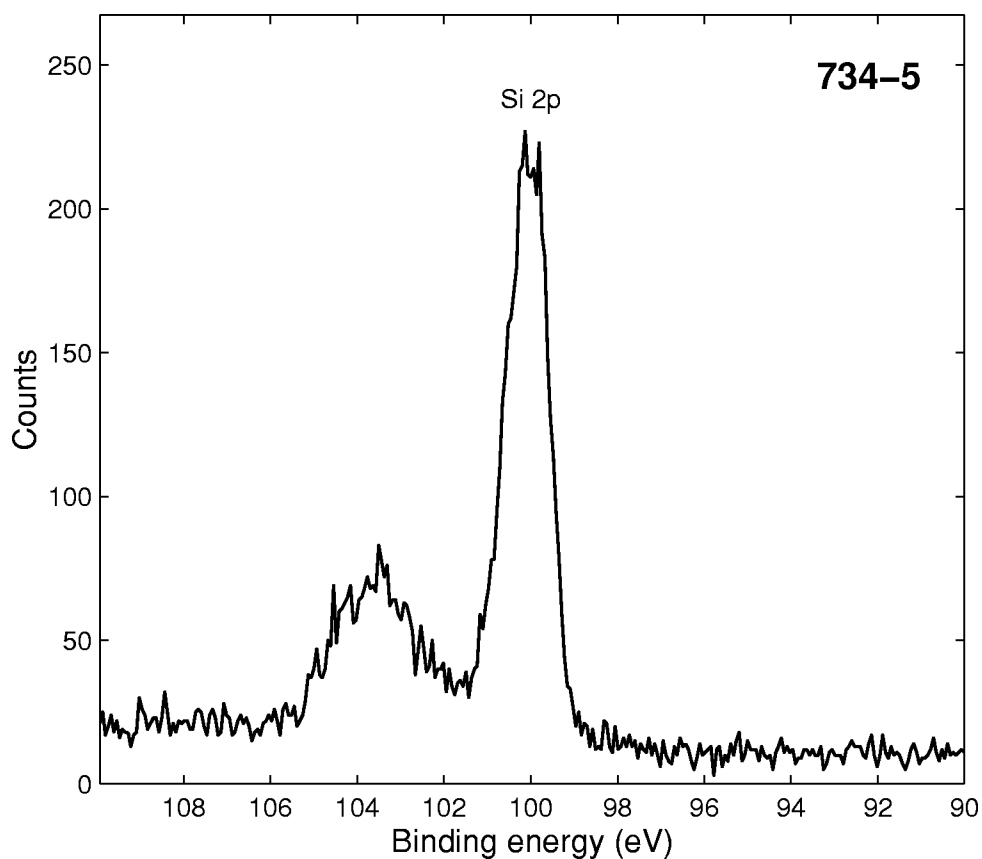
Accession #	00734-02
Host Material	Alkyl monolayer/Si – ClSi(CH ₃) ₂ (CH ₂) ₁₇ CH ₃
Technique	XPS
Spectral Region	Si 2 <i>p</i>
Instrument	Surface Science SSX-100
Excitation Source	Al <i>K</i> _α monochromatic
Source Energy	1486.6 eV
Source Strength	200 W
Source Size	0.8 mm × 0.8 mm
Incident Angle	55°
Analyzer Type	spherical sector
Analyzer Pass Energy	150 eV
Analyzer Resolution	1.5 eV
Emission Angle	55°
Total Signal Accumulation Time	184 s
Total Elapsed Time	353 s
Number of Scans	3
Effective Detector Width	13.0906494 eV
Analyzer Width	1500 μm × 12000 μm



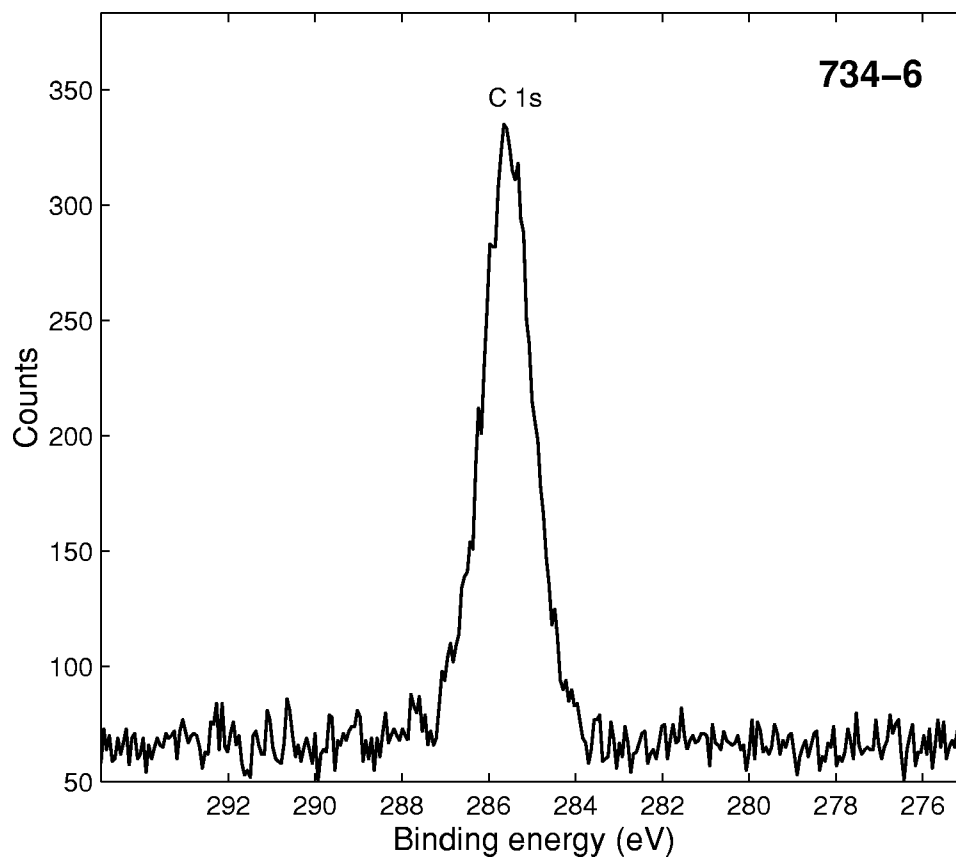
Accession #	00734-03
Host Material	Alkyl monolayer/Si – ClSi(CH ₃) ₂ (CH ₂) ₁₇ CH ₃
Technique	X<PS
Spectral Region	C 1s
Instrument	Surface Science SSX-100
Excitation Source	Al K _α monochromatic
Source Energy	1486.6 eV
Source Strength	200 W
Source Size	0.8 mm × 0.8 mm
Incident Angle	55°
Analyzer Type	spherical sector
Analyzer Pass Energy	150 eV
Analyzer Resolution	1.5 eV
Emission Angle	55°
Total Signal Accumulation Time	184 s
Total Elapsed Time	353 s
Number of Scans	3
Effective Detector Width	13.0906494 eV
Analyzer Width	1500 μm × 12000 μm



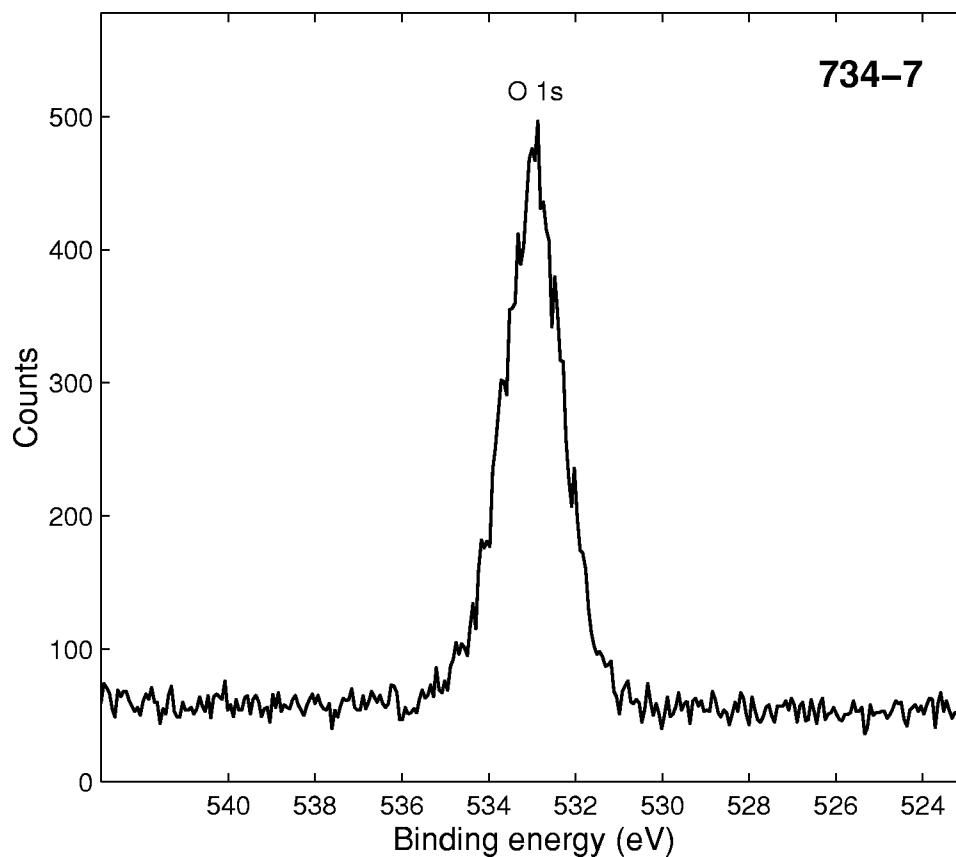
Accession #	00734-04
Host Material	Alkyl monolayer/Si – ClSi(CH ₃) ₂ (CH ₂) ₁₇ CH ₃
Technique	XPS
Spectral Region	O 1s
Instrument	Surface Science SSX-100
Excitation Source	Al K _α monochromatic
Source Energy	1486.6 eV
Source Strength	200 W
Source Size	0.8 mm × 0.8 mm
Incident Angle	55°
Analyzer Type	spherical sector
Analyzer Pass Energy	150 eV
Analyzer Resolution	1.5 eV
Emission Angle	55°
Total Signal Accumulation Time	184 s
Total Elapsed Time	353 s
Number of Scans	3
Effective Detector Width	13.0906494 eV
Analyzer Width	1500 μm × 12000 μm



Accession #	00734-05
Host Material	Alkyl monolayer/Si – $\text{ClSi}(\text{CH}_3)_2(\text{CH}_2)_{17}\text{CH}_3$
Technique	XPS
Spectral Region	Si 2p
Instrument	Surface Science SSX-100
Excitation Source	Al K_α monochromatic
Source Energy	1486.6 eV
Source Strength	200 W
Source Size	0.8 mm \times 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	184 s
Total Elapsed Time	353 s
Number of Scans	3
Effective Detector Width	5.441887 eV
Analyzer Width	750 μm \times 6000 μm



Accession #	00734-06
Host Material	Alkyl monolayer/Si – ClSi(CH ₃) ₂ (CH ₂) ₁₇ CH ₃
Technique	XPS
Spectral Region	C 1s
Instrument	Surface Science 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	184 s
Total Elapsed Time	353 s
Number of Scans	3
Effective Detector Width	5.441887 eV
Analyzer Width	750 μm × 6000 μm



Accession #	00734-07
Host Material	Alkyl monolayer/Si – ClSi(CH ₃) ₂ (CH ₂) ₁₇ CH ₃
Technique	XPS
Spectral Region	O 1s
Instrument	Surface Science 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	184 s
Total Elapsed Time	353 s
Number of Scans	3
Effective Detector Width	5.441887 eV
Analyzer Width	750 μm × 6000 μm