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Alkyl Monolayers on Silica Surfaces Prepared from Neat, Heated 3-Glycidoxypropyldimethylethoxysilane Analyzed by XPS

Ghaleb A. Husseini, Matthew R. Linford, Matthew C. Asplund, Justin Peacock, and Eric T. Sevy
Dept. of Chemistry and Biochemistry, Brigham Young University, Provo, UT

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 3-glycidoxypropyldimethylethoxysilane (CAS# 17963-04-1) on silicon oxide (silicon wafer) prepared using a rapid, solvent-free approach. Reaction conditions are 100 °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: 10.1116/11.20020504]

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

PACS: *79.60.Fr, 82.80.Pv, 82.65.+r, 81.05.Lg*

Accession # 00740
Technique: XPS
Host Material: Alkyl monolayer/Si–Glycidoxypropyldimethylethoxysilane
Instrument: Surface Science SSX-100
Major Elements in Spectrum: C, Si, O
Minor Elements in Spectrum: none
Printed Spectra: 4
Spectra in Electronic Record: 21
Spectral Category: technical
Original Submission: 5/23/2002
Accepted for Publication: 9/30/2002

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 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, 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 3-glycidoxypropyldimethylethoxysilane on its surface, and heat it in an oven at 100 °C for 10 min (relative humidity = 52%). 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 = 0.70 ± 0.36 nm, advancing contact angle (θ_a) = 63.3° ± 1.0°, receding contact angle (θ_r) = 53.6° ± 0.91].

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 native oxide terminated silicon derived from glycidoxypropyldimethylethoxysilane

CAS Registry #: 7440-2-13

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/SiO_2

Form: single crystal wafer, *p*-type

Lot #: W9969 sample 7

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), 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 NH_4OH/H_2O_2 cleaning solution is extremely caustic and should be used with great care.

***In Situ* Preparation:** not specified

Charge Control: none

Temp. During Analysis: 298 K

Pressure During Analysis: $<1.79\times10^{-7}$ 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

Analyzer Width at 84 eV: 1500 μm × 12000 μm

Signal Mode: multichannel direct

Effective Detector Width: 13.0906 eV

■ 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°

DATA ANALYSIS METHOD

Peak Shape and Background Method: background Shirley function

ACKNOWLEDGMENTS

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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
00740-02	Si 2*p*	99.9	1.674	29792	0.9	39.669	···
00740-03	C 1*s*	285.99	3.805	21639	1.0	26.085	···
00740-04	O 1*s*	532.93	1.851	71096	2.49	34.301	···
00740-05	Si 2*p*	···	···	4911	0.9	···	···
00740-06	C 1*s*	···	···	3937	1.0	···	···
00741-02	Si 2*p*	101.06	4.55	32276	0.9	44.34	···
00741-03	C 1*s*	286.4	3.764	11766	1.0	14.60	···
00741-04	O 1*s*	532.96	2.650	82503	2.49	41.05	···
00741-05	Si 2*p*	100.06	1.218	5172	0.9	···	···
00741-06	C 1*s*	286.43	3.327	1778	1.0	···	···
00741-07	O 1*s*	533.35	1.449	12779	2.49	···	···
00742-02	Si 2*p*	99.73	1.313	48196	0.9	44.75	···
00742-03	C 1*s*	286.06	3.485	18677	1.0	15.67	···
00742-04	O 1*s*	533.10	2.205	117595	2.49	39.58	···
00742-05	Si 2*p*	99.9	1.188	8456	0.9	···	···
00742-06	C 1*s*	286.42	3.983	4014	1.0	···	···
00742-07	O 1*s*	533.01	1.755	21833	2.49	···	···

ANALYZER CALIBRATION TABLE

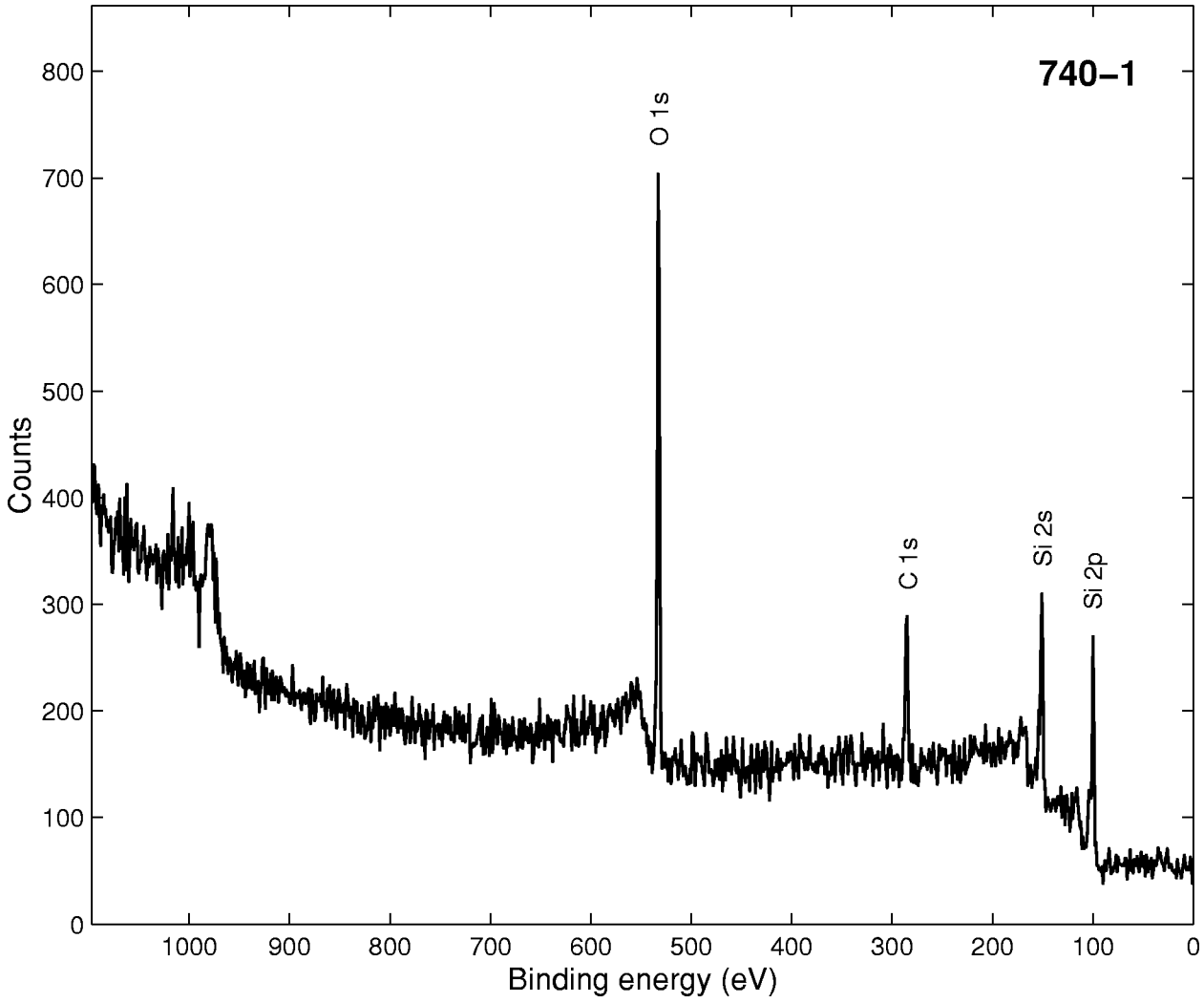
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (counts)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
...[a]	Au $4f_{7/2}$	83.92	0.98	2200	10.67	...	...
...[b]	Au $4f_{7/2}$	83.92	1.6	6000	10.67	...	...
...[c]	Cu $3s$	122.36	3.0	1600	1.05	...	...
...[b]	Cu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

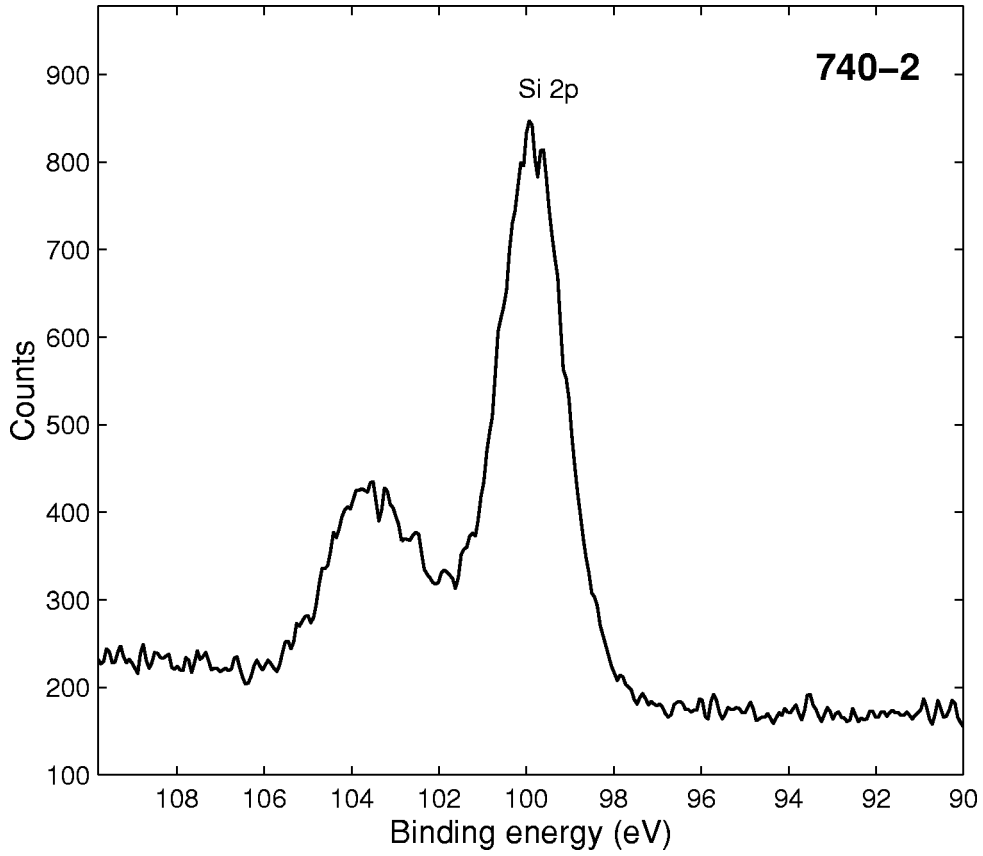
GUIDE TO FIGURES

Spectrum (Accession) #	Spectral Region	Voltage Shift*	Multiplier	Baseline	Comment #
740-1	Survey	0	1	0	
740-2	Si $2p$	0	1	0	
740-3	C $1s$	0	1	0	
740-4	O $1s$	0	1	0	
740-5 [NP]**	Si $2p$	0	1	0	
740-6 [NP]	C $1s$	0	1	0	
740-7 [NP]	O $1s$	0	1	0	
741-1 [NP]	Survey	0	1	0	
741-2 [NP]	Si $2p$	0	1	0	
741-3 [NP]	C $1s$	0	1	0	
741-4 [NP]	O $1s$	0	1	0	
741-5 [NP]	Si $2p$	0	1	0	
741-6 [NP]	C $1s$	0	1	0	
741-7 [NP]	O $1s$	0	1	0	
742-1 [NP]	Survey	0	1	0	
742-2 [NP]	Si $2p$	0	1	0	
742-3 [NP]	C $1s$	0	1	0	
742-4 [NP]	O $1s$	0	1	0	
742-5 [NP]	Si $2p$	0	1	0	
742-6 [NP]	C $1s$	0	1	0	
742-7 [NP]	O $1s$	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.
**[NP] signifies not published; digital spectra are archived in *SSS* database but not reproduced in the printed journal.



Accession #	00740-01
Host Material	Alkyl monolayer/Si–Glycidoxypropyldimethylethoxysilane
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	13.0906 eV



- **Accession #:** 00740-02
- **Host Material:** Alkyl monolayer/Si– Glycidoxypropyldimethylethoxysilane
- **Technique:** XPS
- **Spectral Region:** Si 2*p*

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

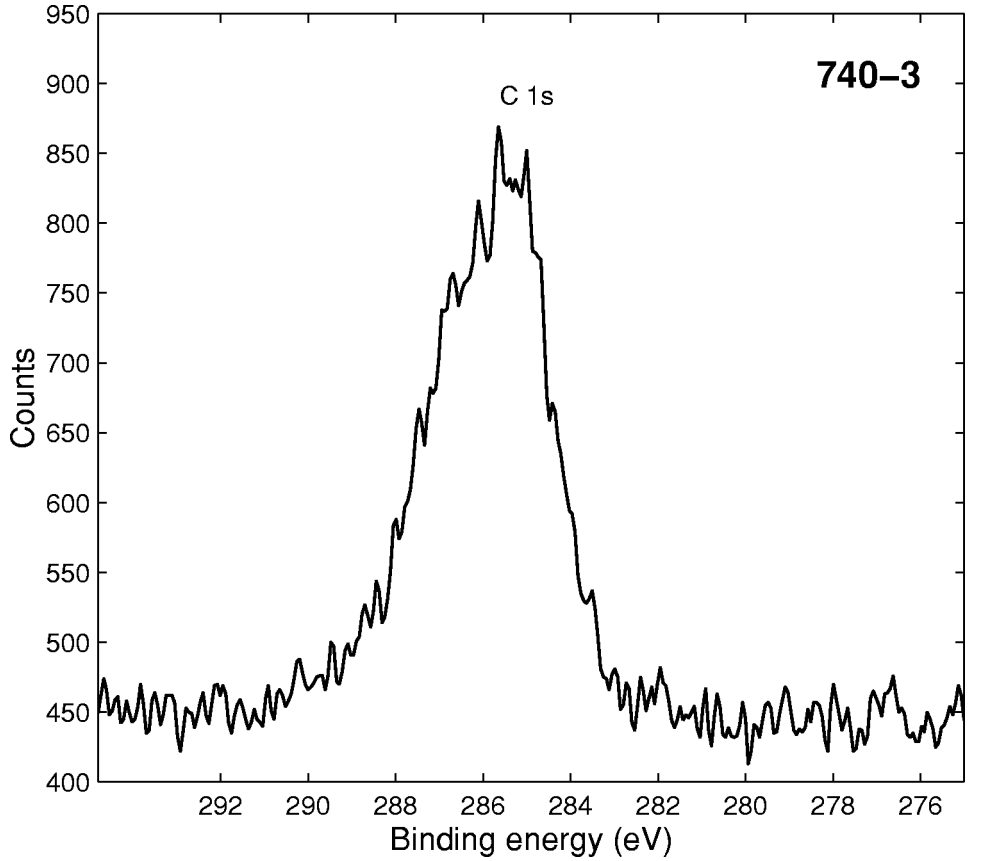
Emission Angle: 55°

Total Signal Accumulation Time: 184 s

Total Elapsed Time: 353 s

Number of Scans: 3

Effective Detector Width: 13.0906 eV



- **Accession #:** 00740-03
- **Host Material:** Alkyl monolayer/Si–Glycidoxypropyldimethylethoxysilane
- **Technique:** XPS
- **Spectral Region:** C 1*s*

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

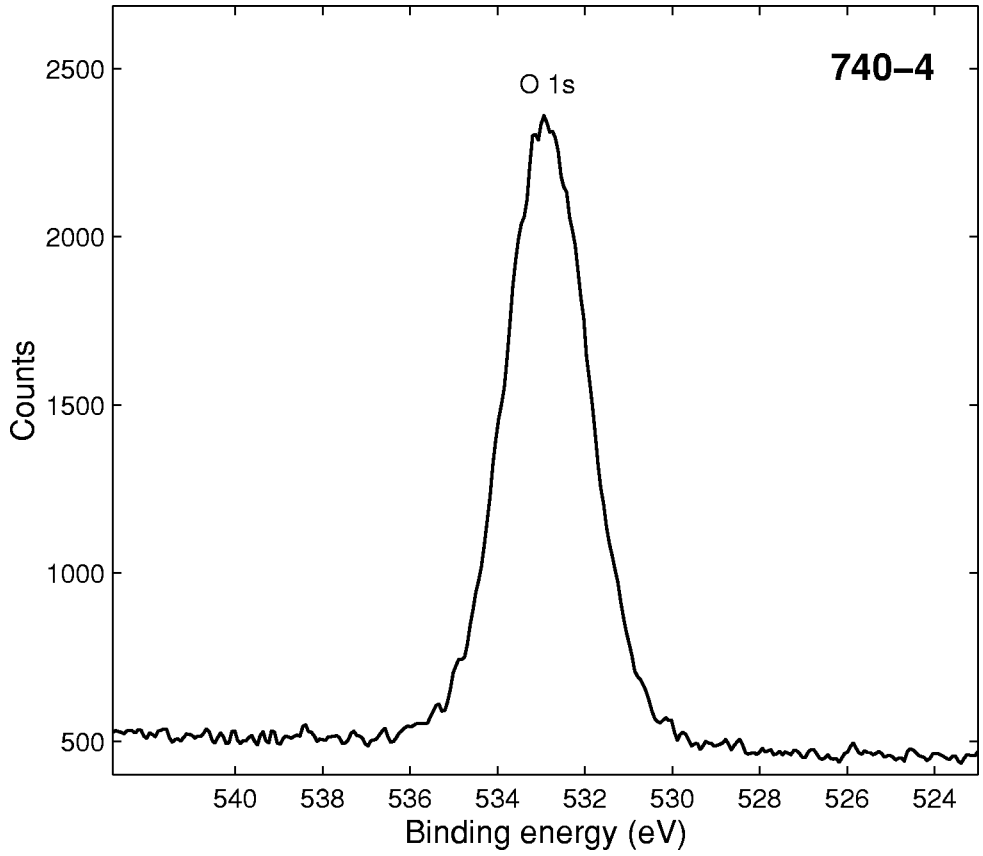
Emission Angle: 55°

Total Signal Accumulation Time: 184 s

Total Elapsed Time: 353 s

Number of Scans: 3

Effective Detector Width: 13.0906 eV



- **Accession #:** 00740-04
- **Host Material:** Alkyl monolayer/Si–Glycidoxypropyldimethylethoxysilane
- **Technique:** XPS
- **Spectral Region:** O 1*s*

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: 13.0906 eV