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HAXPES of Si₃N₄ thin film on Si with Cr K α excitation

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Si₃N₄ thin film grown by low-pressure chemical vapor deposition (LPCVD) was measured by high-energy photoelectron spectroscopy (HAXPES) using monochromatic Cr K α (5414.8 eV) radiation. A survey scan and high-resolution spectra of Si 1s, Si 2s, Si 2p and N 1s are reported.

Keywords: Si₃N₄, HAXPES, Cr K α

Accession#: 01714

Technique: XPS

Host Material: Si₃N₄

Instrument: ULVAC-PHI Quantes

Major Elements in Spectra: Si, N

Minor Elements in Spectra: O, Ar

Published Spectra: 5

Spectra in Electronic Record: 5

Spectral Category: comparison

INTRODUCTION

Silicon nitride (Si₃N₄) is an important material in the field of micro- and nanoelectronics as it can be used as passivation films, etch masks or dielectric layers. Microelectronic devices are made of stacks of different layers. It is thus of primary importance to be able to investigate buried layers and interfaces. To this end, hard x-ray photoelectron spectroscopy (HAXPES) allows to sensibly increase the probing depth compared to XPS. Novel laboratory-based HAXPES systems give researchers the ability to perform such measurements more commonly.

In this work, Si₃N₄ grown by low-pressure chemical vapor deposition (LPCVD) was analyzed by means of high-resolution HAXPES using monochromatic Cr K α radiation.

SPECIMEN DESCRIPTION (ACCESSION # 01714)

Host Material: Si₃N₄

CAS Registry #: 12033-89-5

Host Material Characteristics: Homogeneous; solid; polycrystalline; dielectric; inorganic compound; Thin Film

Chemical Name: Silicon nitride

Source: LPCVD grown-thin film

Host Composition: Si₃N₄

Form: 100 nm thick Si₃N₄ thin film on Si wafer

Structure: Polycrystalline

History & Significance: Si₃N₄ was grown on a Si(100) wafer by low-pressure chemical vapor deposition (LPCVD) at 750°C using SiH₂Cl₂ and NH₃ precursors.

As Received Condition: Piece of a Si wafer

Analyzed Region: Same as host material

Ex Situ Preparation/Mounting: The sample was mounted on the sample holder using double sided conductive tape.

In Situ Preparation: The sample was sputter cleaned by Ar⁺ ions (100 eV) for 1h prior to measurements to remove carbon and oxygen contamination.

Charge Control: Low-energy electrons (1 eV, filament 1.1 A) and low-energy ions (10 eV)

Temp. During Analysis: 300 K

Pressure During Analysis: <2.10⁻⁷ Pa

Pre-analysis Beam Exposure: 0 s

INSTRUMENT DESCRIPTION

Manufacturer and Model: ULVAC-PHI Quantes

Analyzer Type: spherical sector

Detector: multichannel resistive plate

Number of Detector Elements: 32

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

■ Spectrometer

Analyzer Mode: constant pass energy

Throughput (T=E^N): The energy dependence can be modeled using the following equation: $\frac{A}{E_p} = \left(\frac{a^2}{a^2 + R^2}\right)^b$, where a and b are constants, E_p is the pass energy, A is the peak area and R is the retard ratio equal to E/E_p, where E is the kinetic energy. Three spectral regions are recorded on a sputter cleaned sample at different pass energies. The values of a and b are then determined by a linear least square fit of the data applying the equation described above.

Excitation Source Window: Al

Excitation Source: Cr K α monochromatic

Source Energy: 5414.8 eV

Source Strength: 50 W

Source Beam Size: 100 μ m x 100 μ m

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Signal Mode: multichannel direct

■ **Geometry**

Incident Angle: 22 °

Source-to-Analyzer Angle: 46 °

Emission Angle: 45 °

Specimen Azimuthal Angle: 0 °

Acceptance Angle from Analyzer Axis: 0 °

Analyzer Angular Acceptance Width: 20 ° x 20 °

■ **Ion Gun**

Manufacturer and Model: ULVAC-PHI Quantes

Energy: 10 and 100 eV

Current: 1.4×10^{-5} mA

Current Measurement Method: Faraday cup

Sputtering Species: Ar

Spot Size (unrastered): 100 μ m

Raster Size: N/A

Incident Angle: 45 °

Polar Angle: 45 °

Azimuthal Angle: 45 °

Comment: Differentially pumped ion gun used for pre-sputtering of the sample and to prevent reoxidation during the XPS analysis.

DATA ANALYSIS METHOD

Energy Scale Correction: The decrease of photoionization cross-sections in HAXPES (Refs 1 and 2) leads to a very low C 1s intensity. Therefore, the binding energy was referenced to the Si 2p binding energy position measured with Al K α radiation after shifting the C 1s peak to 284.8 eV. Doing so, the Si 2p binding energy was 101.9 eV. The spectra recorded with the Cr K α source were then rescaled by shifting the Si 2p peak to 101.9 eV. It should be mentioned that this rescaling method artificially cancels the recoil experienced by Si core-levels in HAXPES. The recoil effect on Si is of the order of 70 meV (Ref. 3). Hence, nitrogen recoil is diminished by about 70 meV and can be roughly estimated to 100 meV.

Recommended Energy Scale Shift: 1.6 eV for binding energy

Peak Shape and Background Method: Shirley background was employed for peak area determination. No curve fitting was performed on the spectra.

Quantitation Method: PHI Multipak software Version 9.9.0.8 was used to perform quantification. Empirically determined sensitivity factors (RSFs) were provided by the software. The RSFs were derived from the pure-element relative sensitivity factor as defined in ISO 18118:2015 (Ref. 4) which were measured on pure element samples using a Cr K α source. They therefore account for the decrease of cross-section and different escape depth of photoelectrons using higher energy photons. RSFs are reported proportional to the RSF of F 1s equal to 1. The reported concentrations were calculated using these RSFs corrected to include the transmission function and the asymmetry parameter.

ACKNOWLEDGMENTS

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DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available within the article and its supplementary material.

REFERENCES

1. M.B. Trzhaskovskaya and V.G. Yarzhemsky, *At. Data Nucl. Data Tables* **119**, 99 (2018).
2. M.B. Trzhaskovskaya and V.G. Yarzhemsky, *At. Data Nucl. Data Tables* **129-130**, 101280 (2019).
3. L. Köver, *J. Electron Spectrosc. Relat. Phenom.* **178**, 241 (2010).
4. International Organization for Standardization 2015, *Surface chemical analysis - Auger electron spectroscopy and X-ray photoelectron spectroscopy - Guide to the use of experimentally determined relative sensitivity factors for the quantitative analysis of homogeneous materials*, ISO 18118:2015.

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SPECTRAL FEATURES TABLE							
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV x cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
01714-02	Si 1s	1842.0	2.09	14826	4.653	43.2	Si ₃ N ₄
01714-03	Si 2s	153.3	2.42	1123	0.436	...	Si ₃ N ₄
01714-04	Si 2p	101.9	1.97	397	0.110	...	Si ₃ N ₄
01714-05	N 1s	397.6	1.78	1188	0.331	56.8	Si ₃ N ₄

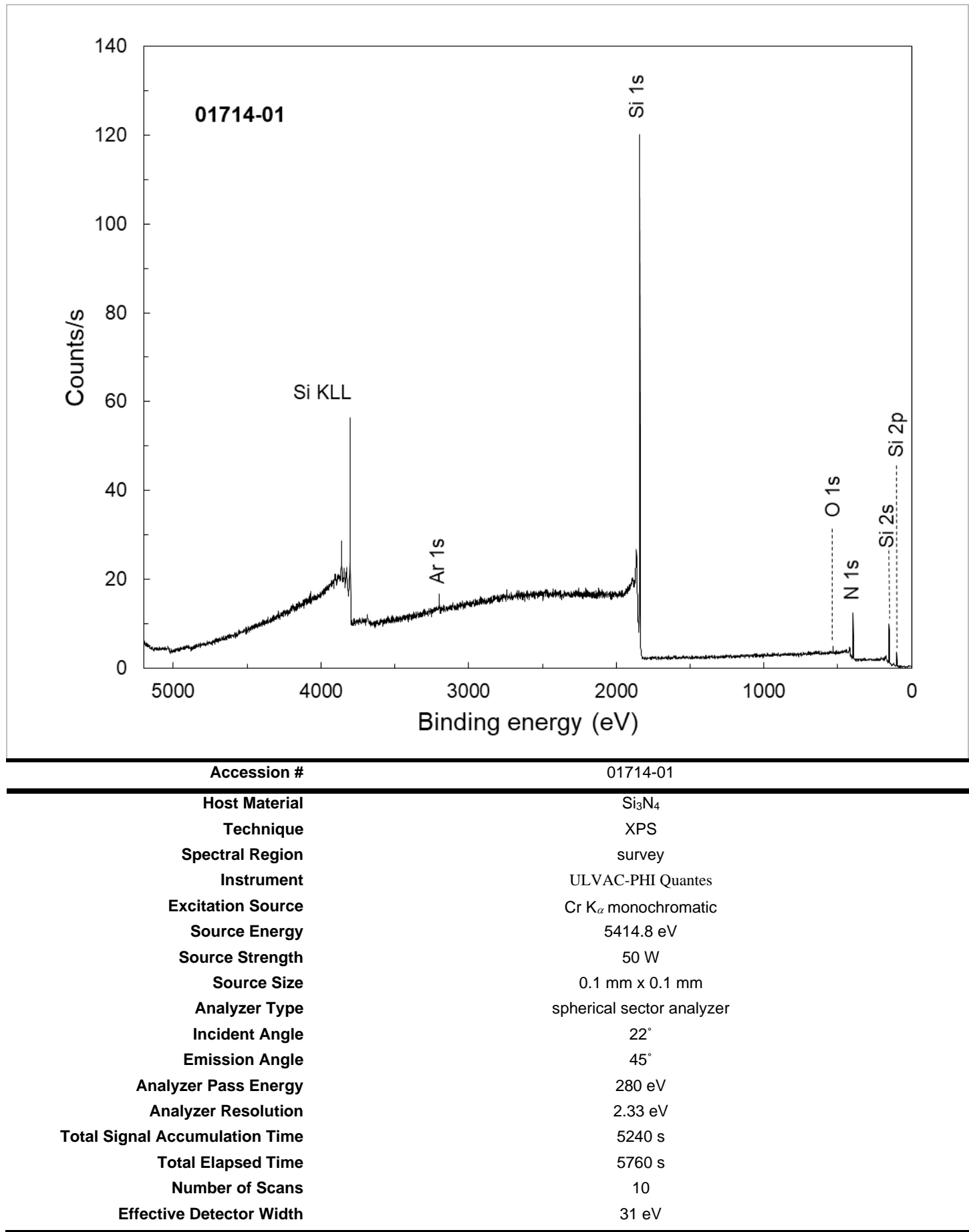
ANALYZER CALIBRATION TABLE							
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV x cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
...	Ag3d _{5/2}	368.12	0.63	114999
...	Cu2p _{3/2}	932.61	0.96	40205
...	Au4f _{7/2}	83.89	0.78	100500

The spectra in the analyzer calibration table were recorded using Al K α photons.

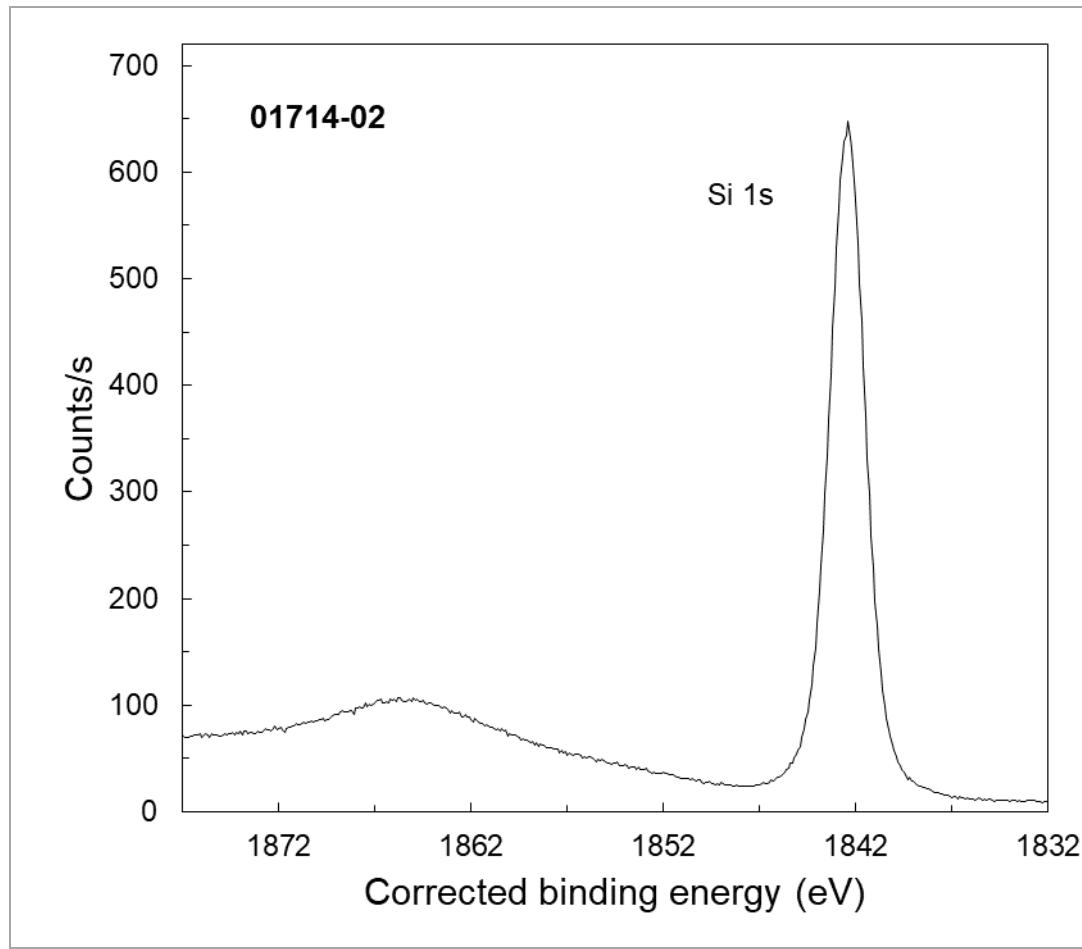
GUIDE TO FIGURES					
Spectrum (Accession) #	Spectral Region	Voltage Shift*	Multiplier	Baseline	Comment #
01714-01	Survey	0	1	0	...
01714-02	Si 1s	-1.6	1	0	...
01714-03	Si 2s	-1.6	1	0	...
01714-04	Si 2p	-1.6	1	0	...
01714-05	N 1s	-1.6	1	0	...

*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.

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■ **Accession #:** 01714-02

■ **Host Material:** Si₃N₄

■ **Technique:** XPS

■ **Spectral Region:** Si 1s

Instrument: ULVAC-PHI
Quantes

Excitation Source:

Cr K_α monochromatic

Source Energy: 5414.8 eV

Source Strength: 50 W

Source Size: 0.1 mm x 0.1 mm

Analyzer Type: spherical sector

Incident Angle: 22 °

Emission Angle: 45 °

Analyzer Pass Energy 112 eV

Analyzer Resolution: 1.17 eV

Total Signal Accumulation

Time: 3670 s

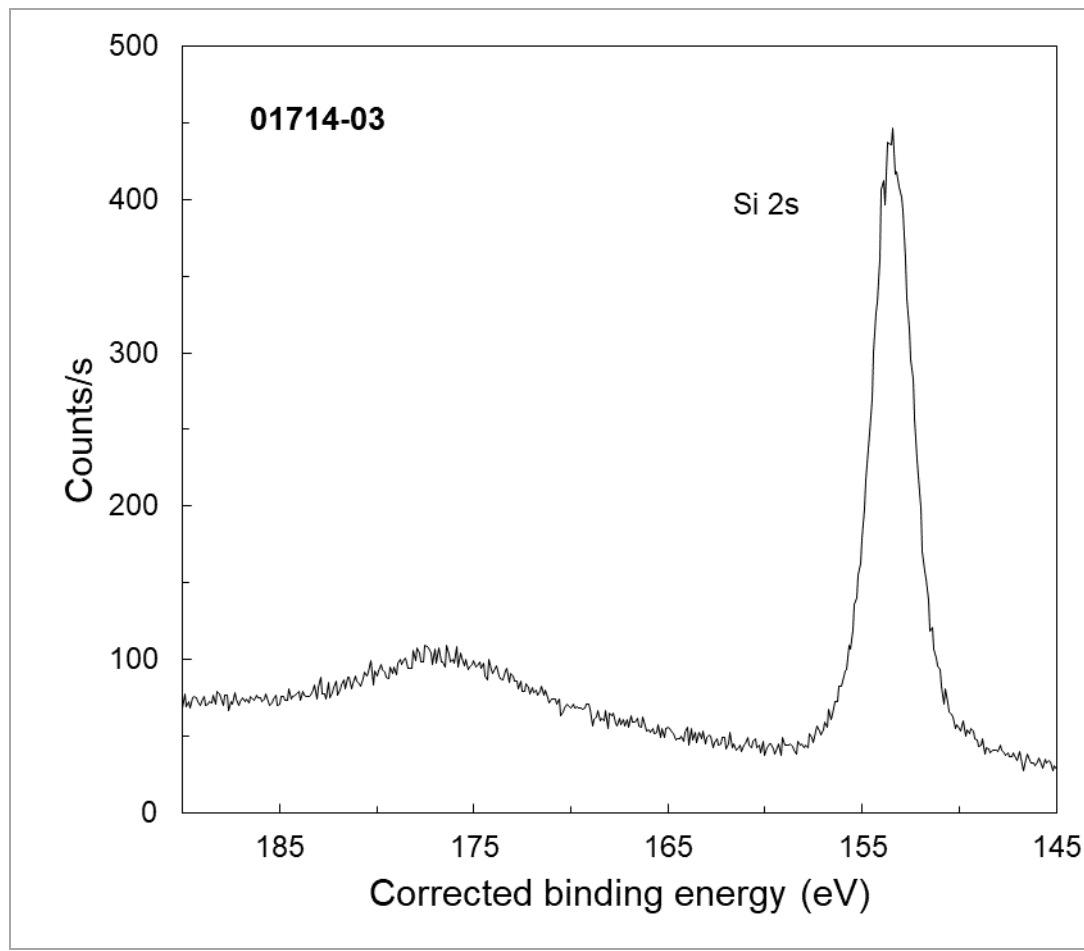
Total Elapsed Time: 4040 s

Number of Scans: 16

Effective Detector Width: 12.4
eV

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■ **Accession #:** 01714-03

■ **Host Material:** Si₃N₄

■ **Technique:** XPS

■ **Spectral Region:** Si 2s

Instrument: ULVAC-PHI

Quantes

Excitation Source:

Cr K_α monochromatic

Source Energy: 5414.8 eV

Source Strength: 50 W

Source Size: 0.1 mm x 0.1 mm

Analyzer Type: spherical sector

Incident Angle: 22 °

Emission Angle: 45 °

Analyzer Pass Energy 112 eV

Analyzer Resolution: 1.17 eV

Total Signal Accumulation

Time: 3670 s

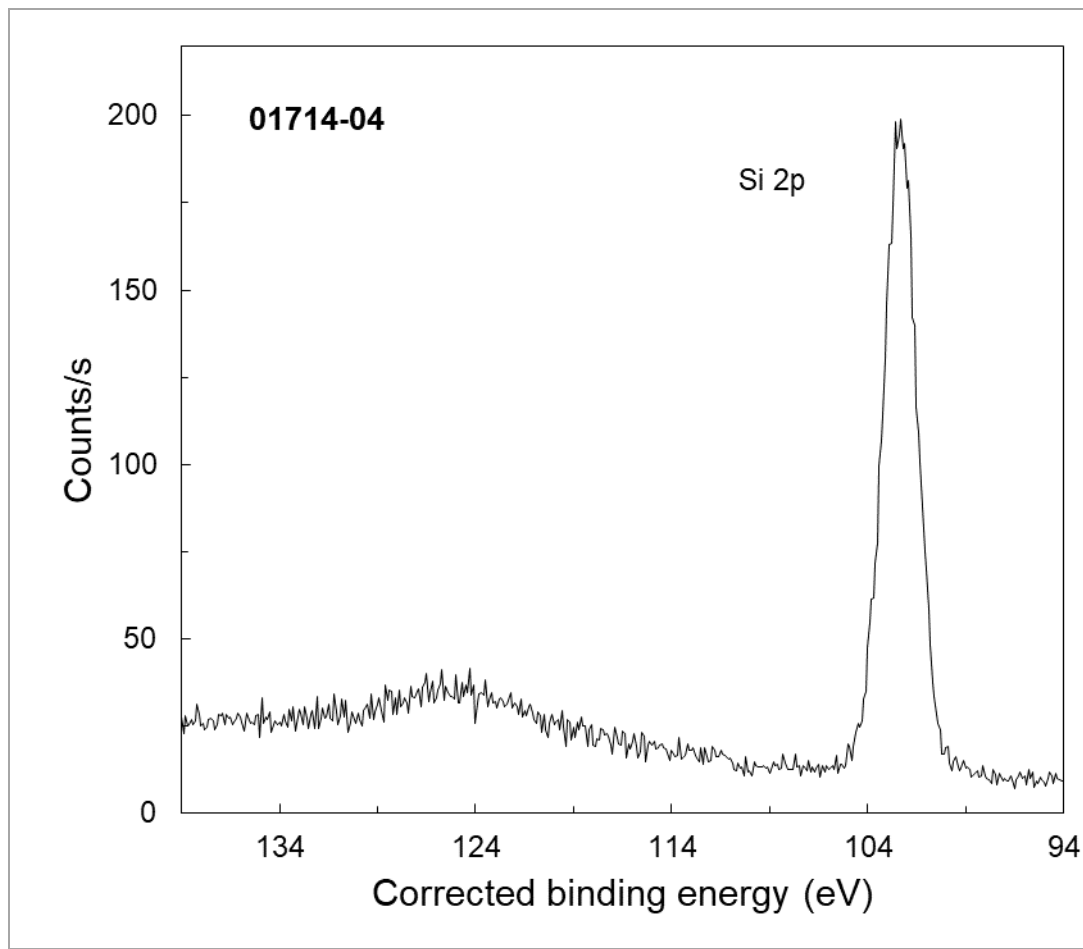
Total Elapsed Time: 4040 s

Number of Scans: 16

Effective Detector Width: 12.4 eV

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■ **Accession #:** 01714-04

■ **Host Material:** Si₃N₄

■ **Technique:** XPS

■ **Spectral Region:** Si 2p

Instrument: ULVAC-PHI

Quantes

Excitation Source:

Cr K_α monochromatic

Source Energy: 5414.8 eV

Source Strength: 50 W

Source Size: 0.1 mm x 0.1 mm

Analyzer Type: spherical sector

Incident Angle: 22 °

Emission Angle: 45 °

Analyzer Pass Energy 112 eV

Analyzer Resolution: 1.17 eV

Total Signal Accumulation

Time: 3670 s

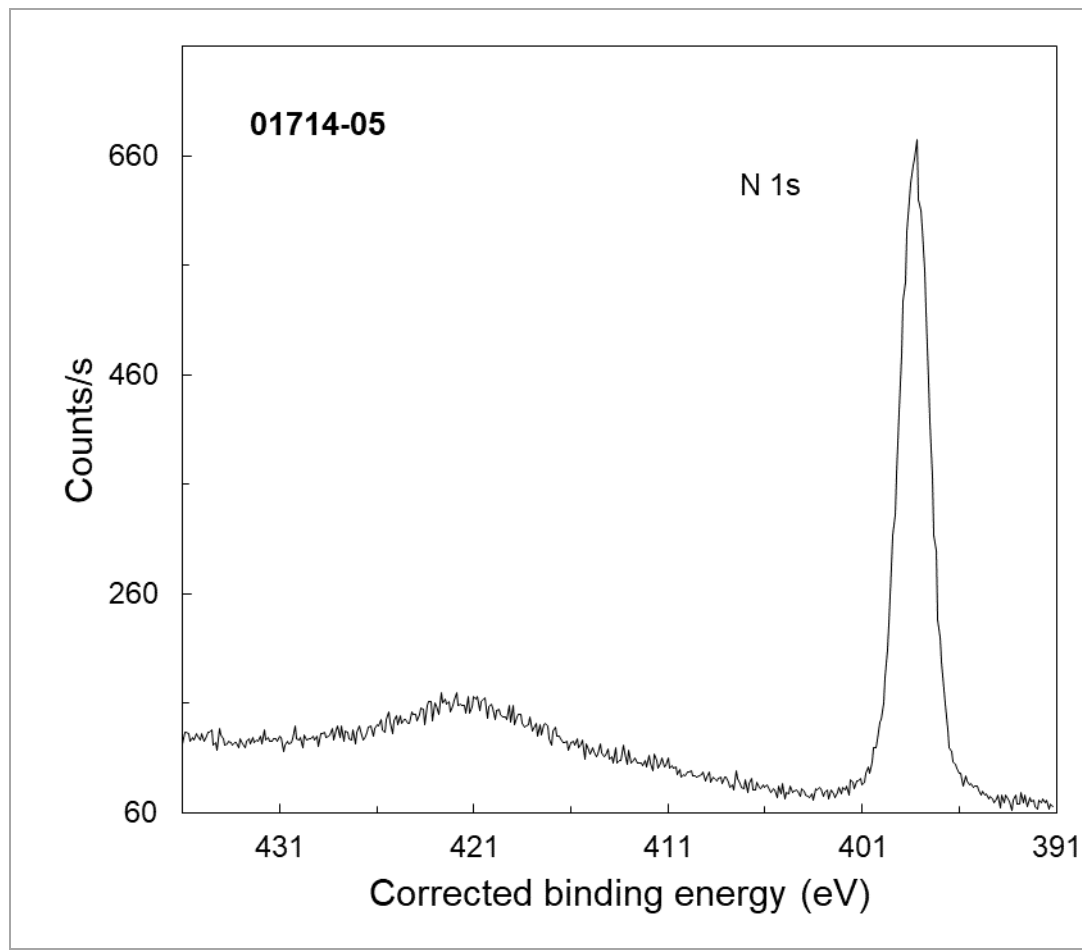
Total Elapsed Time: 4040 s

Number of Scans: 16

Effective Detector Width: 12.4 eV

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■ **Accession #:** 01714-05

■ **Host Material:** Si₃N₄

■ **Technique:** XPS

■ **Spectral Region:** N 1s

Instrument: ULVAC-PHI

Quantes

Excitation Source:

Cr K α monochromatic

Source Energy: 5414.8 eV

Source Strength: 50 W

Source Size: 0.1 mm x 0.1 mm

Analyzer Type: spherical sector

Incident Angle: 22 °

Emission Angle: 45 °

Analyzer Pass Energy 112 eV

Analyzer Resolution: 1.17 eV

Total Signal Accumulation

Time: 3670 s

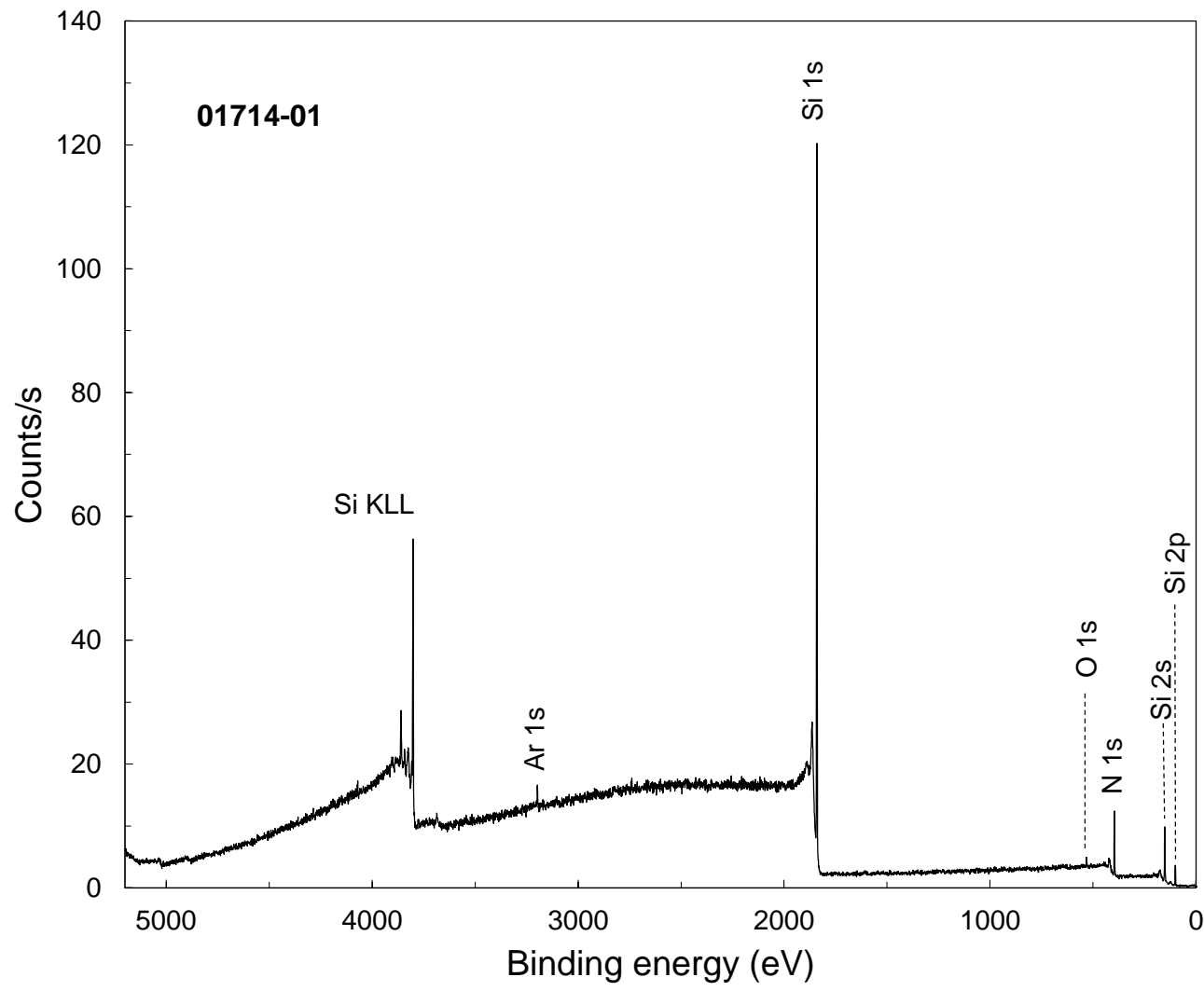
Total Elapsed Time: 4040 s

Number of Scans: 16

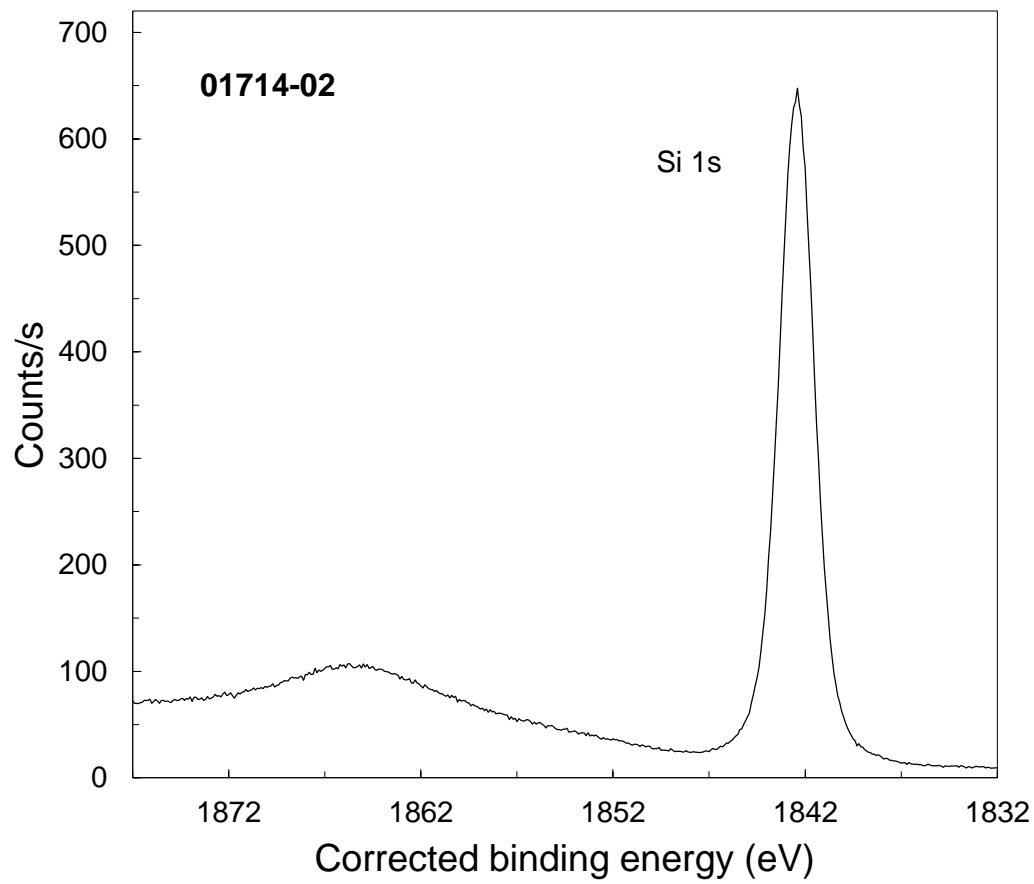
Effective Detector Width: 12.4 eV

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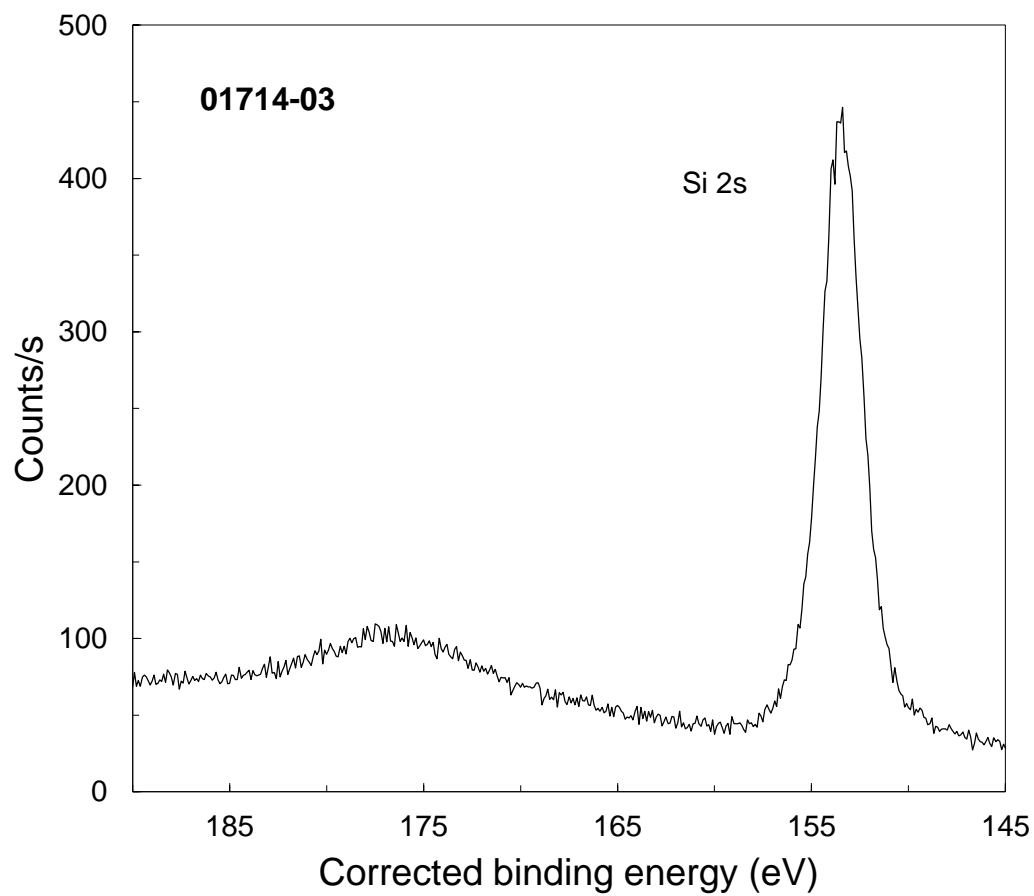


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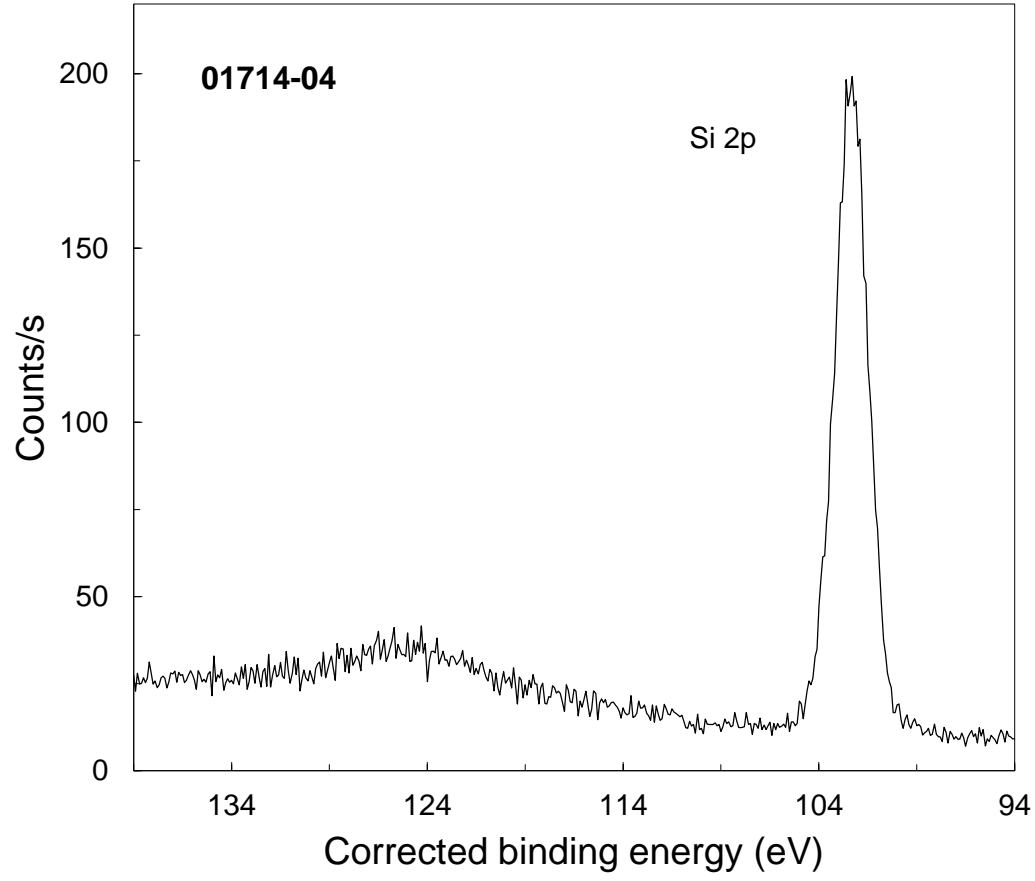
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