XPS characterization of $\text{Al}_2\text{O}_3$/ZnO ultrathin films grown by atomic layer deposition

Cite as: Surf. Sci. Spectra 27, 024012 (2020); https://doi.org/10.1116/6.0000585
Submitted: 26 August 2020. Accepted: 04 November 2020. Published Online: 24 November 2020

Amirhossein Ghods, Chuanle Zhou, and Ian T. Ferguson

COLLECTIONS

This paper was selected as an Editor's Pick

ARTICLES YOU MAY BE INTERESTED IN

Enhancing nanostructured nickel-rich lithium-ion battery cathodes via surface stabilization
Journal of Vacuum Science & Technology A 38, 063210 (2020); https://doi.org/10.1116/6.0000580

Detection of femtosecond spin voltage pulses in a thin iron film
Structural Dynamics 7, 065101 (2020); https://doi.org/10.1063/4.0000037

Sub-kelvin temperature management in ion traps for optical clocks
Review of Scientific Instruments 91, 111301 (2020); https://doi.org/10.1063/5.0024693
XPS characterization of Al$_2$O$_3$/ZnO ultrathin films grown by atomic layer deposition

Amirhossein Ghods, Chuanle Zhou, and Ian T. Ferguson

AFFILIATIONS

1Electrical and Computer Engineering, Missouri University of Science and Technology, Rolla, Missouri 65409
2Southern Polytechnic College of Engineering and Engineering Technology, Kennesaw State University, Marietta, Georgia 30060

ABSTRACT

The near-surface compositional properties of double-layer Al$_2$O$_3$/ZnO ultrathin films, grown on the $n$-type GaAs substrate using the atomic layer deposition (ALD) technique, are analyzed by means of high-resolution x-ray photoelectron spectroscopy (XPS). This structure has been used as the dielectric or the passivation layer in microelectronic devices, such as metal-oxide-semiconductor (MOS) capacitors, field-effect transistors, and Schottky junctions. The XPS spectra of double-layer Al$_2$O$_3$/ZnO thin films were obtained using monochromatic Al $\alpha$ monochromatic radiation at 1486.6 eV and included an overall survey scan, in addition to the high-resolution spectra of Zn 2p, Al 2p, O 1s, Ga 2p, and As 3d.

Key words: Al$_2$O$_3$/ZnO, ultrathin film growth, atomic layer deposition, x-ray photoelectron spectroscopy, near-surface elemental analysis

INTRODUCTION

Surface passivation of semiconductor-based devices has shown to be effective in reducing the nonradiative recombination velocity and improving the overall electrical, optical, and magnetic properties of these devices (Refs. 1 and 2). Deposition of a suitable dielectric material not only passivates the active dangling bonds and defects at the surface of the semiconductor but also introduces attractive or repulsive electric field at the interface of the passivation layer and the semiconductor layer (Refs. 3 and 4). In other words, a reduction in the nonradiative recombination rate is expected by introducing an electric field gradient that repels the charge carriers from coming near to the surface of semiconductor and being trapped there (Refs. 5 and 6). This can be achieved by the injection or formation of a large density of positive or negative fixed charges at the interface between the passivation and semiconductor layers. For example, Al$_2$O$_3$/ZnO has shown to be an effective structure as the passivation layer, mainly due to existence of a negative charge density of more than $\sim 1.0 \times 10^{12}$ cm$^{-2}$ (Refs. 7–9). In this work, a detailed XPS analysis of Al$_2$O$_3$/ZnO ultrathin films, grown using the ALD technique on $n$-type GaAs substrate, is presented. Trimethylaluminum (TMA) and diethylzinc (DEZn) were used as the metalorganic precursors, along with deionized water as the oxidizer, in order to prepare the Al$_2$O$_3$/ZnO sample. ZnO thin films were grown directly on the $n$-type GaAs substrate followed by the deposition of Al$_2$O$_3$ thin films on the ZnO/$n$-GaAs structure (Fig. 1). Transmission electron microscopy (TEM) measurements showed the Al$_2$O$_3$ and ZnO ultrathin films with thicknesses of 3 and 2 nm, respectively. Moreover, a weak polycrystallinelike and an amorphous structure were observed for the as-grown ZnO and Al$_2$O$_3$ thin films (Ref. 7). It should be noted that no high temperature thermal annealing was performed on the sample after the ALD growth process in order to avoid unwanted changes in...
structural and compositional properties of the thin films (Refs. 10 and 11). The sample was then transferred directly from the ALD chamber to the XPS chamber in order to minimize the possibility of cross-contamination. Subsequently, the measurements were carried out using a Kratos Axis 165 XPS system under high-vacuum environment without any sputter etching pretreatment.

**SPECIMEN DESCRIPTION (ACCESSION # 01672)**

**Host Material:** Al₂O₃/ZnO thin film

**CAS Registry #:** 1344-28-1 (Al₂O₃) and 1314-13-2 (ZnO)

**Host Material Characteristics:** Homogeneous; solid; weak polycrystalline-like (ZnO); amorphous (Al₂O₃); unknown conductivity; semiconductor; and thin film

**Chemical Name:** Aluminum oxide and zinc oxide

**Source:** Strem Chemicals (see below)

**As Received Condition:** In the form of metalorganic sources: trimethylaluminum (TMA-liquid) for aluminum and diethylzinc (DEZn-liquid) for zinc. The sources react with the oxidizing agent in the ALD chamber to form the double-layer thin film.

**Analyzed Region:** The top surface of the sample

**Ex Situ Preparation/Mounting:** Cleaned with acetone and methanol, rinsed in DI H₂O, and blow-dried using clear air.

**In Situ Preparation:** None

**Charge Control:** Low energy electron via tungsten filament

**Temp. During Analysis:** 300 K (room temperature)

**Pressure During Analysis:** 1 × 10⁻⁵ Pa

**Preanalysis Beam Exposure:** 1200 s warm up

**INSTRUMENT DESCRIPTION**

**Manufacturer and Model:** Kratos Axis 165

**Analyzer Type:** Spherical sector

**Detector:** Channeltron

**Number of Detector Elements:** 8

**INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA**

**Spectrometer**

**Analyzer Mode:** Constant pass energy

**Throughput (T = E⁰):** N = 0

**Excitation Source Window:** X-ray characteristics line equals to 1.0 eV

**Excitation Source:** Al Kα monochromatic, no flood source gun

**Source Energy:** 1486.6 eV

**Source Strength:** 180 W

**Source Beam Size:** 0.7 × 0.3 mm²

**Signal Mode:** Multichannel direct

**Geometry**

**Incident Angle:** 68°

**Source-to-Analyzer Angle:** 68°

**Emission Angle:** 78°
Specimen Azimuthal Angle: 0°

Ion Gun

Comment: No ion sputtering was used

DATA ANALYSIS METHOD

Energy Scale Correction: The C 1s spectrum at 284.80 eV was used as the reference to remove the effect of sample charging (Ref. 12).

Recommended Energy Scale Shift: −0.8 eV

Peak Shape and Background Method: The position, width, and area of peak spectra were found using a Gaussian–Lorentzian fitting function and the Shirley background (Refs. 13 and 14).

Quantitation Method: Quantification was done using CASAXPS version 2.3.23.

ACKNOWLEDGMENTS

This research was carried out by financial support from Columbus Photovoltaics, LLC. The authors would also like to acknowledge the technical support received throughout this work from Materials Research Center (MRC) at Missouri S&T regarding XPS characterization of the thin films.

REFERENCES

### Spectral Features Table

<table>
<thead>
<tr>
<th>Spectrum ID #</th>
<th>Element/Transition</th>
<th>Peak Energy (eV)</th>
<th>Peak Width FWHM (eV)</th>
<th>Peak Area (eV x counts/s)</th>
<th>Sensitivity Factor</th>
<th>Concentration (at. %)</th>
<th>Peak Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>01672-01</td>
<td>Ga LMM</td>
<td>1067.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GaAs</td>
</tr>
<tr>
<td>01672-01</td>
<td>As LMM</td>
<td>1225.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GaAs</td>
</tr>
<tr>
<td>01672-02</td>
<td>C 1s</td>
<td>284.8</td>
<td>1.839</td>
<td>2531.6</td>
<td>0.278</td>
<td>6.78</td>
<td></td>
</tr>
<tr>
<td>01672-03</td>
<td>O 1s</td>
<td>530.7</td>
<td>2.386</td>
<td>64438.9</td>
<td>0.780</td>
<td>56.45</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>01672-04</td>
<td>Al 2p</td>
<td>74.1</td>
<td>1.886</td>
<td>6794.4</td>
<td>0.193</td>
<td>26.26</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>01672-05</td>
<td>Zn 2p</td>
<td>...</td>
<td>...</td>
<td></td>
<td></td>
<td></td>
<td>ZnO</td>
</tr>
<tr>
<td>01672-05</td>
<td>Zn 2p½</td>
<td>1021.0</td>
<td>1.833</td>
<td>2458.5</td>
<td>...</td>
<td>...</td>
<td>ZnO</td>
</tr>
<tr>
<td>01672-05</td>
<td>Zn 2p½</td>
<td>1044.1</td>
<td>1.934</td>
<td>1213.6</td>
<td>...</td>
<td>...</td>
<td>ZnO</td>
</tr>
<tr>
<td>01672-06</td>
<td>Ga 2p</td>
<td>...</td>
<td>...</td>
<td></td>
<td></td>
<td></td>
<td>...</td>
</tr>
<tr>
<td>01672-06</td>
<td>Ga 2p½</td>
<td>1116.4</td>
<td>1.626</td>
<td>8867.0</td>
<td>...</td>
<td>...</td>
<td>GaAs</td>
</tr>
<tr>
<td>01672-06</td>
<td>Ga 2p½</td>
<td>1117.8</td>
<td>1.573</td>
<td>1348.2</td>
<td>...</td>
<td>...</td>
<td>Ga₂O₃</td>
</tr>
<tr>
<td>01672-07</td>
<td>As 3d</td>
<td>...</td>
<td>...</td>
<td></td>
<td></td>
<td></td>
<td>...</td>
</tr>
<tr>
<td>01672-07</td>
<td>As 3d</td>
<td>41.0</td>
<td>1.558</td>
<td>7699.3</td>
<td>...</td>
<td>...</td>
<td>GaAs</td>
</tr>
<tr>
<td>01672-07</td>
<td>As 3d</td>
<td>43.8</td>
<td>2.095</td>
<td>510.1</td>
<td>...</td>
<td>...</td>
<td>As₂O₃</td>
</tr>
</tbody>
</table>

*Auger kinetic energy

### Analyzer Calibration Table

<table>
<thead>
<tr>
<th>Spectrum ID #</th>
<th>Element/Transition</th>
<th>Peak Energy (eV)</th>
<th>Peak Width FWHM (eV)</th>
<th>Peak Area (eV x counts/s)</th>
<th>Sensitivity Factor</th>
<th>Concentration (at. %)</th>
<th>Peak Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>...</td>
<td>Ag 3d½</td>
<td>368.6</td>
<td>0.672</td>
<td>173 363.1</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

### Guide to Figures

<table>
<thead>
<tr>
<th>Spectrum (Accession) #</th>
<th>Spectral Region</th>
<th>Voltage Shifta</th>
<th>Multiplier</th>
<th>Baseline</th>
<th>Comment #</th>
</tr>
</thead>
<tbody>
<tr>
<td>01672-01</td>
<td>Survey</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>...</td>
</tr>
<tr>
<td>01672-02</td>
<td>C 1s</td>
<td>0.8</td>
<td>1</td>
<td>0</td>
<td>...</td>
</tr>
<tr>
<td>01672-03</td>
<td>O 1s</td>
<td>0.8</td>
<td>1</td>
<td>0</td>
<td>...</td>
</tr>
<tr>
<td>01672-04</td>
<td>Al 2p</td>
<td>0.8</td>
<td>1</td>
<td>0</td>
<td>...</td>
</tr>
<tr>
<td>01672-05</td>
<td>Zn 2p</td>
<td>0.8</td>
<td>1</td>
<td>0</td>
<td>...</td>
</tr>
<tr>
<td>01672-06</td>
<td>Ga 2p</td>
<td>0.8</td>
<td>1</td>
<td>0</td>
<td>...</td>
</tr>
<tr>
<td>01672-07</td>
<td>As 3d</td>
<td>0.8</td>
<td>1</td>
<td>0</td>
<td>...</td>
</tr>
</tbody>
</table>

*aVoltage shift calculated based on the difference between the as-measured spectrum relative to the printed figure. This voltage shift is calculated to offset the effect of sample charging during the XPS measurement.*
Accession #

<table>
<thead>
<tr>
<th>Field</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Host Material:</td>
<td>Al₂O₃/ZnO thin film</td>
</tr>
<tr>
<td>Technique:</td>
<td>XPS</td>
</tr>
<tr>
<td>Spectral Region:</td>
<td>Survey</td>
</tr>
<tr>
<td>Instrument:</td>
<td>Kratos Axis 165</td>
</tr>
<tr>
<td>Excitation Source:</td>
<td>Al Kα monochromatic</td>
</tr>
<tr>
<td>Source Energy:</td>
<td>1486.6 eV</td>
</tr>
<tr>
<td>Source Strength:</td>
<td>180 W</td>
</tr>
<tr>
<td>Source Size:</td>
<td>0.7 × 0.3 mm²</td>
</tr>
<tr>
<td>Analyzer Type:</td>
<td>Spherical sector analyzer</td>
</tr>
<tr>
<td>Incident Angle:</td>
<td>68°</td>
</tr>
<tr>
<td>Emission Angle:</td>
<td>78°</td>
</tr>
<tr>
<td>Analyzer Pass Energy:</td>
<td>160 eV</td>
</tr>
<tr>
<td>Analyzer Resolution:</td>
<td>0.5 eV</td>
</tr>
<tr>
<td>Total Signal Accumulation Time:</td>
<td>575 s</td>
</tr>
<tr>
<td>Total Elapsed Time:</td>
<td>1150 s</td>
</tr>
<tr>
<td>Number of Scans:</td>
<td>1</td>
</tr>
</tbody>
</table>
**Accession #:** 01672-02  
**Host Material:** Al₂O₃/ZnO thin film  
**Technique:** XPS  
**Spectral Region:** C 1s

Instrument: Kratos Axis 165  
Excitation Source: Al Kα, monochromatic  
Source Energy: 1486.6 eV  
Source Strength: 180 W  
Source Size: 0.7 × 0.3 mm²  
Analyzer Type: Spherical sector  
Incident Angle: 68°  
Emission Angle: 78°  
Analyzer Pass Energy: 40 eV  
Analyzer Resolution: 0.1 eV  
Total Signal Accumulation Time: 303 s  
Total Elapsed Time: 606 s  
Number of Scans: 6

---

**Accession #:** 01672-03  
**Host Material:** Al₂O₃/ZnO thin film  
**Technique:** XPS  
**Spectral Region:** O 1s

Instrument: Kratos Axis 165  
Excitation Source: Al Kα, monochromatic  
Source Energy: 1486.6 eV  
Source Strength: 180 W  
Source Size: 0.7 × 0.3 mm²  
Analyzer Type: Spherical sector  
Incident Angle: 68°  
Emission Angle: 78°  
Analyzer Pass Energy: 40 eV  
Analyzer Resolution: 0.1 eV  
Total Signal Accumulation Time: 40.5 s  
Total Elapsed Time: 81 s  
Number of Scans: 1
Accession #: 01672-04
Host Material: Al₂O₃/ZnO thin film
Technique: XPS
Spectral Region: Al 2p

Instrument: Kratos Axis 165
Excitation Source: Al Kα, monochromatic
Source Energy: 1486.6 eV
Source Strength: 180 W
Source Size: 0.7 × 0.3 mm²
Analyzer Type: Spherical sector
Incident Angle: 68°
Emission Angle: 78°
Analyzer Pass Energy: 40 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 101 s
Total Elapsed Time: 202 s
Number of Scans: 2

Accession #: 01672-05
Host Material: Al₂O₃/ZnO thin film
Technique: XPS
Spectral Region: Zn 2p

Instrument: Kratos Axis 165
Excitation Source: Al Kα, monochromatic
Source Energy: 1486.6 eV
Source Strength: 180 W
Source Size: 0.7 × 0.3 mm²
Analyzer Type: Spherical sector
Incident Angle: 68°
Emission Angle: 78°
Analyzer Pass Energy: 40 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 573 s
Total Elapsed Time: 1146 s
Number of Scans: 6
Accession #: 01672-06
Host Material: Al₂O₃/ZnO thin film
Technique: XPS
Spectral Region: Ga 2p

Instrument: Kratos Axis 165
Excitation Source: Al K\(_\alpha\) monochromatic
Source Energy: 1486.6 eV
Source Strength: 180 W
Source Size: 0.7 × 0.3 mm\(^2\)
Analyzer Type: Spherical sector
Incident Angle: 68°
Emission Angle: 78°
Analyzer Pass Energy: 40 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 162 s
Total Elapsed Time: 324 s
Number of Scans: 4

Accession #: 01672-07
Host Material: Al₂O₃/ZnO thin film
Technique: XPS
Spectral Region: As 3d

Instrument: Kratos Axis 165
Excitation Source: Al K\(_\alpha\) monochromatic
Source Energy: 1486.6 eV
Source Strength: 180 W
Source Size: 0.7 × 0.3 mm\(^2\)
Analyzer Type: Spherical sector
Incident Angle: 68°
Emission Angle: 78°
Analyzer Pass Energy: 40 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 66 s
Total Elapsed Time: 132 s
Number of Scans: 2