University of Technology, Sydney

Doctoral Thesis

Development and Implementation of Environmental Photoelectron Yield Spectroscopy

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Declaration of Authorship

I, Toby William Shanley, declare that this thesis titled, Development and Implementation of Environmental Photoelectron Yield Spectroscopy, and the work presented in it is my own.

- I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.
- I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signed: _____

Date: _____

"Productive stupidity means being ignorant by choice."

Martin Schwartz

UNIVERSITY OF TECHNOLOGY, SYDNEY

Abstract

Faculty of Science
School of Physics and Advanced Materials

Doctor of Philosophy

Development and Implementation of Environmental Photoelectron Yield Spectroscopy

by Toby William Shanley

Environmental photoelectron yield spectroscopy (EPYS) is a novel, low vacuum, surface analysis technique that probes the electronic structure of solid-gas interfaces. Unlike its conventional, ultra high vacuum counterparts that interrogate ideal surfaces in non-realistic conditions, EPYS enables real-time characterisation of dynamic surface processes in semi-realistic, reactive gaseous environments. This capability is a requirement for the technological progress and fundamental understanding of processes in nanotechnology, materials physics, chemistry and bio-sciences.

The system has been built and implemented from the outset of its existence at UTS. This project has contributed to the development of EPYS, and further developed a number of novel applications. Specifically, its application in elucidating the nature of four, fundamentally different physical phenomena is demonstrated. The thesis describes the origins of EPYS in ultra high vacuum photoelectron emission spectroscopy and the theoretical groundwork on which it is based. It also details the EPYS development, and demonstrates applications of the EPYS in the analysis of gas ionisation cascades, subsurface defects, surface termination, and adsorbate coverage.

The value of this study is partly in the instrumentation development itself, but also in the demonstration of its application in studies of material systems responding to their environments.

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Abbreviations

AES	**A**uger **E**lectron **S**pectroscopy
APD	**A**valanche **P**hoto**d**iode
ARPES	**A**ngle **R**esolved **P**hotoelectron **E**emission **S**pectroscopy
BSE	**B**acks**s**cattered **E**lectron
CBM	**C**onduction **B**and **M**inimum
CCD	**C**harge **C**oupled **D**etector
CL	**C**athodo**l**uminescence
DAP	**D**onor **A**cceptor **P**air
DAQ	**D**ata **Acq**uisition
DOS	**D**ensity **O**f **S**tates
$\mathbf{E_{CB}}$	**E**nergy of **C**onduction **B**and minimum
$\mathbf{E_F}$	**E**nergy of **F**ermi level
$\mathbf{E_V}$	**E**nergy of a free electron in **V**acuum
$\mathbf{E_{VB}}$	**E**nergy of **V**alence **B**and maximum
EPYS	**E**nvironmental **P**hotoelectron (emission) **Y**ield **S**pectroscopy
ESEM	**E**nvironmental **S**canning **E**lectron **M**icroscope
FWHM	**F**ull **W**idth **H**alf **M**aximum
GED	**G**aseous **E**lectron **D**etector
GL	**G**reen **L**uminescence
LEED	**L**ow **E**energy **E**lectron **D**iffraction
MFC	**M**ass **F**low **C**ontroller
NBE	**N**ear **B**and **E**dge
NEA	**N**egative **E**lectron **A**ffinity
NV	**N**itrogen **V**acancy
$\mathbf{O_i}$	**I**nterstitial **O**xygen

PE	**P**rimary **E**lectron
PEA	**P**ositive **E**lectron **A**ffinity
PES	**P**hotoelectron **E**mission **S**pectroscopy
PI	**P**ositive **I**on
PID	**P**roportional-**I**ntegral-**D**erivative
PL	**P**hoto**l**uminescence
PMT	**P**hoto**m**ultiplier **T**ube
PYS	**P**hotoelectron (emission) **Y**ield **S**pectroscopy
RGA	**R**esidual **G**as **A**nalyser
RL	**R**ed **L**uminescence
SE	**S**econdary **E**lectron
SEM	**S**canning **E**lectron **M**icroscope
SFG	**S**um **F**requency **G**eneration
SHE	**S**tandard **H**ydrogen **E**lectrode
TDS	**T**hermal **D**esorption **S**pectroscopy
TMP	**T**urbo **M**olecular **P**ump
UHV	**U**ltra **H**igh **V**acuum
UPS	**U**ltraviolet **P**hotoelectron (emission) **S**pectroscopy
UV	**U**ltra**v**iolet
$\mathbf{V_O}$	**O**xygen **V**acancy
$\mathbf{V_{Zn}}$	**Z**inc **V**acancy
VBM	**V**alence **B**and **M**aximum
WRG	**W**ide **R**ange **G**auge
XANES	**X**-ray **A**bsorption **N**ear **E**dge **S**tructure
XPS	**X**-ray **P**hotoelectron (emission) **S**pectroscopy
XRD	**X**-**r**ay **D**iffraction
YL	**Y**ellow **L**uminescence
$\mathbf{Zn_i}$	**I**nterstitial **Z**inc
ZPL	**Z**ero **P**honon **L**ine

Contributing Publications

- Localized Chemical Switching of the Charge State of Nitrogen-Vacancy Luminescent Centers in Diamond, **Toby Shanley**, Aiden Martin, Igor Aharonovich, Milos Toth, *Applied Physics Letters 105*, 063103, Published 11 August 2014

- Role of Gas Molecule Complexity in Environmental Electron Microscopy and Environmental Photoelectron Yield Spectroscopy, **Toby Shanley**, Fadi Bonnie, John Scott, Milos Toth, *in submission*

- Band Structure of Stoichiometrically dissimilar ZnO surfaces, **Toby Shanley**, Suranan Anantachaisilpm Matthew Phillips, Milos Toth, *in submission*

Non-Contributing Publications

- Silicon Oxide Nanowire Growth Mechanisms Revealed by Real-Time Electron Microscopy, Miroslav Kolibal, Libor Novak, **Toby Shanley**, Milos Toth, Tomas Sikola, *Nanoscale 8* 266-275, Published 26 November 2015

- Synthesis of Liminescent Europium Defects in Diamond, Andrew Magyar, Wenhao Hu, **Toby Shanley**, Michael Flatte, Evelyn Hu, Igor Aharonovich, *Nature Communications 5* 3523, Published 24 March 2014