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TITLE: **Low Energy Ion Scattering Studies of Metal, Metal Oxide and Alloy Surfaces**

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Low Energy Ion Scattering Studies of Metal, Metal Oxide and Alloy Surfaces

by

Marc Walker

Thesis

Submitted to the University of Warwick in partial fulfilment of the requirements for admission to the degree of

Doctor of Philosophy

Department of Physics

March 2006

THE UNIVERSITY OF WARWICK

Contents

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Next, we come to the students and Post-Docs who have graced CAICISS since the summer of 2002. Thanks to Charlie Parkinson who showed me the ropes and helped to record and decipher much of the data contained in this thesis, before he went to play with toothpaste at Glaxo's! Also thanks to Markus Draxler for his help in the final 18 months of my time, and for being defeated on the golf course.... TWICE! I shouldn't forget our new ~~victim~~ recruit, Matt Brown. Good luck!

No experimental PhD in the group would be possible without the expertise of our technician, Rob Johnston. He is thanked for his humour and fixing many, many things over the last three and a half years. Most importantly, he is also thanked for the funny video clips, discovering Google Earth and a never-ending supply of tea.

When times are bad, always remember that there is someone worse off than you....... which brings me on to *"the other half"* of room 422, Stu and Gavin, who can always be relied on for some good banter, sarcasm and interesting stories. The members of the *"HMA"* group (Tim, Imran, Louis and Paul), are acknowledged for the exercise gained in constantly having to retrieve tools from room 421a, as well as showing us why we shouldn't vent the chamber through a diffusion pump (if only we'd have listened....). Thanks also go to Miguel (yes, American cars really are THAT big), Gaz, Paul and Agenor for allowing me to air my opinions on the MEIS facility and helping with the analysis from our runs at Daresbury. And finally, the other people who have been fortunate enough to work in the group over the last three and a half years are thanked for the help, support and humourous interludes that they have provided.

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Declarations

This thesis contains an account of my research, undertaken at the Department of Physics at the University of Warwick between October 2002 and March 2006, under the supervision of Professor C.F. McConville. The work reported here has not been submitted, either wholly or in part, at this or any other academic institution for admission to a higher degree.

The CAICISS, AFM and SEM data recorded from the InN(0001) surfaces presented in chapter 8 were analysed in collaboration with Dr. M. Draxler and Mr. L.F.J. Piper, whilst the interpretation of the CAICISS and XPS data recorded from the Pt(111) surface following the adsorption of 1.3 ML of oxygen, as presented in chapter 5, was carried out in conjunction with Dr. C.R. Parkinson. The remaining data and interpretation presented in this thesis was carried out by the author and has been published in peer-reviewed scientific literature and presented at international conferences.

. . . .

Marc Walker

March 2006.

All of the work presented in this thesis has been published or is in the process of being published at the time of thesis submission (March 2006):

- C.R. Parkinson, M. Walker and C.F. McConville
  "Reaction of atomic oxygen with a Pt(111) surface: chemical and structural determination using XPS, CAICISS and LEED"
  Surf. Sci. **545** (2003) 19-33.

- M. Walker, C.R. Parkinson, M. Draxler and C.F. McConville
  "Growth of thin platinum films on Cu(100): CAICISS, XPS and LEED studies"
  Surf. Sci. **584** (2005) 153-160.

- L.F.J. Piper, T.D. Veal, M. Walker, I. Mahboob, C.F. McConville, H. Lu and W.J. Schaff
  "Clean wurtzite InN surfaces prepared with atomic hydrogen"
  J. Vac. Sci. Technol. A **23** (2005) 617-620.

- M. Walker, T.D. Veal, H. Lu, W.J. Schaff and C.F. McConville
  "InN(0001) polarity by ion scattering spectroscopy"
  Phys. Stat. Sol. C **2** (2005) 2301-2304.

- M. Walker, M. Draxler, C.R. Parkinson and C.F.McConville
  "Characterisation of Pt Deposition on Clean and Oxidised Ni(110) Surfaces"
  Nucl. Instr. and Meth. B (in press).

- M. Draxler, M. Walker and C.F. McConville
  "Determination of a correction factor for the interaction potential of He^{+} ions backscattered from a Cu(100) surface"
  Nucl. Instr. and Meth. B (in press).

- M. Draxler, M. Walker and C.F. McConville
  "Formation of metallic indium during atomic hydrogen cleaning of InN(0001) surfaces"
  Nucl. Instr. and Meth. B (in press).

- M. Walker, C.R. Parkinson, M. Draxler, M.G. Brown and C.F. McConville
  "Initial Growth of Platinum on Oxygen-Covered Ni(110) Surfaces"
  Surf. Sci. (submitted).

Much of this work has also been presented at major international conferences (presenting author in bold):

- **M. Walker**, C.R. Parkinson and C.F. McConville
  "Growth of Thin Pt Films on Ni(100) and Ni(110): A CAICISS, LEED and XPS Study"
  The IoP Condensed Matter and Materials Physics Conference (CMMP04), University of Warwick, UK (April, 2004) - Poster presentation.

- **M. Walker**, C.R. Parkinson, M. Draxler and C.F. McConville
  "Growth of Thin Platinum Films on Cu(100): A CAICISS, LEED and XPS Study"
  The 51st Annual Conference of the American Vacuum Society (AVS-51), Anaheim, CA, USA (November, 2004) - Poster presentation.

- **M. Walker**, C.R. Parkinson, M. Draxler and C.F. McConville
  "Initial growth of platinum on clean and oxidised Ni(110) surfaces"
  The 17th International Conference on Ion Beam Analysis, Sevilla, Spain (June, 2005) - Oral presentation.

- **M. Walker**, C.R. Parkinson, M. Draxler and C.F. McConville
  "Growth of thin Pt films on the Cu(100) surface"
  The 17th International Conference on Ion Beam Analysis, Sevilla, Spain (June, 2005) - Poster presentation.

- **M. Draxler**, M. Walker, N.R. Wilson, L.F.J. Piper, T.D. Veal and C.F. McConville
  "Metallic indium formation during atomic hydrogen cleaning of InN(0001) surfaces"
  The 17th International Conference on Ion Beam Analysis, Sevilla, Spain (June, 2005) - Poster presentation.

- **M. Draxler**, M. Walker and C.F. McConville
  "How accurate are interaction potentials at low energies?"
  The 17th International Conference on Ion Beam Analysis, Sevilla, Spain (June, 2005) - Poster presentation.

- M. Walker, C.R. Parkinson, **M.Draxler** and C.F. McConville
  "Growth of thin Platinum films on Clean and Oxidised Ni(110) Surfaces"
  The 55th Meeting of the Austrian Physical Society (ÖPG-55), Vienna, Austria (September, 2005) - Oral presentation.

- M. Walker, T.D. Veal, H. Lu, W.J. Schaff and **C.F. McConville**
  "Polarity of InN determined by ion scattering spectroscopy"
  The International Workshop on Nitride Semiconductors (IWN 2004), Pittsburgh, PA, USA (July, 2004) - Oral presentation.

Abstract

Coaxial impact collision ion scattering spectroscopy (CAICISS), low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) have been used to study the oxidation of the Pt(111) and Ni(110) surfaces, as well as to investigate the deposition of Pt on the Cu(100), Ni(110)-(3×1)-O and NiO(110) surfaces at room temperature. CAICISS has also been used to study the relaxations in the near-surface region of the clean Pt(111) and Cu(100) surfaces.

The structure of the clean Pt(111) surface has been studied using CAICISS, with a small outward expansion of the two outermost atomic layers being observed. The adsorption of molecular oxygen on the Pt(111) surface had previously been shown to saturate at a coverage of 0.25 ML. It has been demonstrated that the use of atomic oxygen leads to an oxygen saturation coverage of $\sim$ 1.3 ML, with some of the oxygen atoms in sub-surface substitutional sites, producing a Pt-oxide layer. Annealing of this structure to 500°C yielded a sharp p(2×2) diffraction pattern and the elimination of the sub-surface oxide.

The clean Cu(100) surface has also been investigated using CAICISS, with relaxations observed in the near-surface region in line with previously reported values. There have been conflicting reports on the growth mode of Pt on the Cu(100) surface, however, in this work CAICISS has been used to demonstrate the existence of sub-surface Pt atoms at coverages below 0.55 ML, and hence the formation of a Cu-Pt alloy. With increasing Pt coverage, the outermost layers became Pt-rich, in addition to a small Pt overlayer on top of the alloyed surface, suggesting the onset of the growth of a disordered Pt film. Annealing of the structure at a Pt coverage of 2.75 ML to 300°C led to the migration of Pt atoms into the bulk Cu(100) structure.

The Ni(110) surface was exposed to a series of molecular oxygen doses in order to observe the (3×1) added row, (2×1) and (3×1) missing row structures with LEED. Further exposure to atomic oxygen saw the LEED background intensity increase, with a disordered NiO(110) surface observed. CAICISS has been used to investigate the structure of the Ni(110)-(3×1)-O (added row) surface, finding expansions in the structure in the near-surface region as a result of the adsorption of 0.33 ML of oxygen. The deposition of Pt on to this surface at room temperature yielded a Ni-Pt alloy structure up to total Pt coverages approaching 2 ML. Pt deposition on the NiO(110) surface yielded XPS and CAICISS spectra suggesting that a thin Pt film formed on top of the surface, with a sub-surface Ni-Pt alloy formed following annealing to 400°C.

CAICISS has also been used to determine the polarity of InN(0001) films following cleaning with atomic hydrogen, clearly distinguishing between In-polarity and N-polarity material. This was in spite of the formation of metallic In droplets during the cleaning process, which have been observed with AFM and SEM and have led to the revision of the cleaning method in order to produce flat, stoichiometric InN(0001) surfaces. CAICISS has also been used to study the ion-atom interaction potential at low energies, posing some interesting questions which must be addressed.

Common abbreviations

AES ... Auger electron spectroscopy
AFM ... Atomic force microscopy
AHC ... Atomic hydrogen cleaning
CAICISS ... Coaxial impact collision ion scattering spectroscopy
DFT ... Density functional theory
ESD ... Electron-stimulated desorption
FAT ... Fixed analyser transmission
FWHM ... Full width half maximum
H* ... Atomic hydrogen
HREELS ... High resolution electron energy loss spectroscopy
IBA ... Ion bombardment and annealing
ISD ... Ion stimulated desorption
LEED ... Low energy electron diffraction
LEIS ... Low energy ion scattering
MBE ... Molecular beam epitaxy
MEIS ... Medium energy ion scattering
O* ... Atomic oxygen
RBS ... Rutherford backscattering
RHEED ... Reflection high energy electron diffraction
SEM ... Scanning electron microscopy
TFM ... Thomas-Fermi model
TOA ... Take-off angle
ToF ... Time-of-flight
UHV ... Ultra-high vacuum
UPS ... Ultra-violet photoelectron spectroscopy
XPS ... X-ray photoelectron spectroscopy
ZBL ... Ziegler-Biersack-Littmark