ACKNOWLEDGEMENTS

I thank my advisor, David F. Cox, for giving me the opportunity to work in a very interesting area, and for his support and guidance throughout my graduate studies at Virginia Tech.

I thank the members of my committee for their time and effort as well as the D.O.E. for the financial support of my work.

I thank my parents for their love and support while I decided to be a “professional” student for awhile.

I thank Steve York, Mark Abee, and Todd St. Clair for making the lab a tolerable and even at times an enjoyable place to come to each day.

I thank Kevin Rosso and the other “rock-boys” in Geology for their invaluable help during the STM portion of this study.

Finally, I thank all the friends I’ve met over my many years at Virginia Tech especially Joe Edwards, Jeremy Koren, Wes Lang, and Justin Nave. I learned a great deal from each of you, none of which I can remember now.
# TABLE OF CONTENTS

**Introduction** 1

**Chapter 1: STM Imaging of the SnO₂ Surface**

1.1 Introduction 3
1.2 Experimental 5
1.3 Results and Discussion 9
   1.3.1 Synthetic SnO₂ Sample 9
   1.3.2 Natural SnO₂ Sample 14
   1.3.3 Single Crystal Cu₂O (111) Sample 19
1.4 Conclusions 21
1.5 References 22

**Chapter 2: Water Adsorption on the stoichiometric Cr₂O₃ (1012) Single Crystal Surface**

2.1 Introduction 23
2.2 Experimental 26
2.3 Results 28
   2.3.1 Thermal Desorption Spectroscopy 28
   2.3.2 Ultraviolet Photoelectron Spectroscopy 31
2.4 Discussion 33
2.5 Conclusions 35
2.6 References 36

**Chapter 3: Halogen-Oxygen Exchange on Cr₂O₃ (1012) Single Crystal Surfaces**

3.1 Introduction 38
3.2 Experimental 42
3.3 Results 45
   3.3.1 Oxygen-Halogen Exchange on a Chlorinated Surface 45
   3.3.2 Halogen-Oxygen Exchange on an Oxygenated Surface 46
   3.3.3 Thermally Activated Diffusion of Oxygen 48
3.4 Discussion 50
   3.4.1 Oxygen-Halogen Exchange 50
   3.4.2 Halogen-Oxygen Exchange 52
   3.4.3 Comparison to Powder Studies 53
3.5 Conclusions 54
3.6 References 55
LIST OF FIGURES

1.1 (a) 600 nm x 600 nm and (b) 250 nm x 250 nm STM images of the synthetic SnO₂ sample obtained at a sample bias of +2.0 V and a 0.14 nA tunneling current. Both images were collected in constant current mode.

1.2 (a) 432 nm x 432 nm STM image of the synthetic SnO₂ sample obtained at a sample bias of +2.0 V and a 0.18 nA tunneling current. The image was collected in constant current mode. (b) 432 nm x 432 nm AFM image of the synthetic SnO₂ sample obtained following a series of high temperature treatments.

1.3 Ball model illustration of the ideal stoichiometric SnO₂ (110) surface. The unit cell is 6.70 Å (A) by 3.19 Å (B). Small circles represent Sn cations, larger circles represent O anions.

1.4 (a) 6.0 nm x 6.0 nm STM image of the natural SnO₂ sample obtained at a sample bias of +2.0 V and a 0.4 nA tunneling. Image was collected in constant height mode. (b) 1.6 nm x 1.6 nm enlargement of an area from Figure 1.3 (a).

1.5 20 nm x 20 nm STM image of the single crystal Cu₂O (111) sample obtained at a sample bias of –3.0 V and a 0.6 nA tunneling current. The image was collected in constant current mode.

2.1 Ball model illustration of the ideal, stoichiometric Cr₂O₃ (1012) surface.

2.2 Thermal desorption traces for water following adsorption at 163 K on the nearly stoichiometric Cr₂O₃ (1012) surface.

2.3 H₂O desorption peak areas following adsorption at 163 K on the nearly stoichiometric Cr₂O₃ (1012) surface.

2.4 Thermal desorption traces for a 1/4 L exposure of D₂O and H₂O following adsorption at 163 K on the nearly stoichiometric Cr₂O₃ (1012) surface.

3.1 Ball model illustration of the ideal, stoichiometric Cr₂O₃ (1012) surface.

3.2 AES spectra for the three types of surface preparations (clean, oxygenated, and chlorinated) studied.

3.3 AES O:Cr and Cl:Cr ratios following consecutive 1/8 L oxygen exposures at 173 K on a chlorinated surface.

3.4 AES O:Cr and Cl:Cr ratios following consecutive 1/8 L CFCl₂CH₂Cl exposures at 173 K on an oxygenated surface.

3.5 AES Cl:Cr ratio following consecutive 1/8 L CFCl₂CH₂Cl exposures at 173 K on clean and oxygenated surfaces.