

CHARACTERIZATION OF MANGANESE SULFIDE INCLUSION SURFACES IN 1018 CARBON
STEELS AND INTERFACIAL STUDIES OF GRAPHENE COATED COPPER SURFACES

by

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DEDICATION

This work is dedicated to Janos Fucsko, Eric Rieders, and Frederic Rieders who instilled in me the values of the scientific process, and exposed me to the beauty of the natural world.

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TABLE OF CONTENTS

1. INTRODUCTION	1
1.1 Corrosion and Its Practical Importance	1
1.2 Thermodynamics of Corrosion	1
1.3 Kinetics of Corrosion.....	4
1.4 Pitting Corrosion.....	6
1.5 Graphene as an Anti-Corrosive Coating.....	11
2. EXPERIMENTAL METHODOLOGIES	14
2.1 Surface Electron Microscopy and Microanalysis in Corrosion Science	14
2.2 X-Ray Photoelectron Spectroscopy.....	15
2.3 Spectroscopy and Microscopy with a Focused Electron Beam.....	17
2.4 Measurement of the Work Function Using Onset of Secondary Electron Emission	23
3. CHARACTERIZATION OF MnS INCLUSION SURFACES	43
3.1 Experimental Methods.....	43
3.2 Surface Elemental Composition of MnS Inclusions.....	44
3.3 Chemical Analysis of Inclusion Surfaces	53
3.4 Surface Potential Measurements of MnS Inclusions.....	63
3.5 Crystallographic Study of Inclusion Surfaces	66
3.6 Transmission Electron Microscopy Analysis of the MnS/Ferrite Interface	68
3.7 Conclusion and Future Outlook.....	73
4. STUDY OF GRAPHENE COATED Cu SURFACES	78
4.1 Experimental Methods.....	78
4.2 Characterization of Graphene Coated Cu Surfaces	78
4.3 Oxidation of Graphene Coated Cu Surfaces.....	92
4.4 Inhibition of Oxidation of Graphene Coated Cu Surfaces	103
4.5 The Properties of Intercalated Water.....	111
4.6 Conclusion and Future Outlook.....	119
REFERENCES CITED	125

LIST OF FIGURES

Figure	Page
1.1 Example SEM Image and EDX Map of MnS Inclusion	7
2.1 Schematic of Energy Scale Used in XPS	16
2.2 Schematic of Electron Beam Energy Spectrum	18
2.3 Schematic of Auger Electron Emission Process.....	20
2.4 Schematic of Energy Scale Relevant to Surface Potential Measurements	26
2.5 Example Spectra For Determination of Onset of Secondary Electron Emission	28
2.6 Comparison of Onset Energy and Work Function of Single Crystal Surfaces	29
2.7 Dependence of Precision of Onset Energy Measurement on Probe Current.....	32
2.8 Example of Onset Spectrum Exhibiting Primary and Secondary Onset Energies	33
2.9 Onset Energy Line Profile of Au/Fe Interface.....	36
2.10 The Effect of Surface Topography on Surface Potential Mapping	38
2.11 Example of Dependence of SEM Image Contrast on Beam Voltage.....	40
2.12 Calibration of 200 eV SEM Images for Surface Potential Mapping.....	41
3.1 Representative Auger and EDX Spectra of MnS Inclusion	45
3.2 Auger Elemental Maps and Lines Profiles of MnS Inclusion	46
3.3 Auger Depth Profile of MnS Inclusion.....	47
3.4 Auger Elemental Map of Discrete MnO Phases in MnS Inclusion	49
3.5 Auger Depth Profile of MnS Inclusion Coated with Thin Cu ₂ S Film.....	51
3.6 Auger Elemental Map of Discrete Cu ₂ S and MnO Phases in MnS Inclusion.....	52
3.7 Fe <i>MVV</i> Auger Spectra of Native Oxide on 1018 Carbon Steel	54
3.8 Mn <i>MVV</i> Auger Reference Spectra of MnO, MnO _x S _(1-x) , and MnS.....	55
3.9 Comparison of <i>MVV</i> Auger Spectra between γ -Fe ₂ O ₃ and MnS Inclusion	57
3.10 Mn <i>MVV</i> Auger Depth Profile of MnS Inclusion	58
3.11 Auger Chemical Maps of MnS Inclusion	60
3.12 Fe <i>MVV</i> map of γ -Fe ₂ O ₃ in Vicinity of MnS Inclusion	61
3.13 Surface Potential Line Profile Across MnS Inclusion.....	64
3.14 Surface Potential Measurements Comparing MnS and Cu ₂ S Inclusion Surfaces	65
3.15 EBSD Data from MnS Inclusion	67
3.16 Auger and EDX Spectra from MnS Inclusion after FIB cut	69
3.17 Auger Spectra from FIB Cut MnS Inclusion post Ar ⁺ Sputtering.....	70
3.18 TEM Images of MnS Inclusion and MnS/Ferrite Interface.....	72
4.1 Cu <i>LMM</i> Auger Spectrum from Graphene on Cu	80
4.2 Graphene on Cu Energy Loss Comparison	81
4.3 Evolution of $\sigma+\pi$ Loss and XPS Spectra with Temperature	83
4.4 Suppression of $\sigma+\pi$ Loss and Association with C 1s Binding Energy Shift	84
4.5 C 1s and Cu 2p _{3/2} Photoelectron Spectra of Coupled Graphene on Cu	85
4.6 C <i>KLL</i> Auger Spectrum Graphene on Cu	87
4.7 Map of Graphene distribution using $\sigma+\pi$ Loss	89
4.8 Low Energy Electron Microscopy of Graphene Coated Cu.....	91
4.9 XPS Spectra of Oxidized Graphene on Cu Surface	92

LIST OF FIGURES CONTINUED

Figure	Page
4.10 SEM Images of Oxidized Graphene on Cu	93
4.11 SEM, EDX, AFM, and Auger Spectra of Filamentous Oxide Growth	94
4.12 Growth of Oxide Filament via SiO ₂ Sphere	96
4.13 Surface Potential Map of Graphene on Cu and Oxidation of Substrate	97
4.14 Surface Potential Map and Auger Spectra of Graphene on Cu	100
4.15 XPS, Auger and EDX Spectra of UHV Annealed Graphene on Cu	101
4.16 XPS Spectra of Graphene on Cu Exhibiting Oxidation Resistance	103
4.17 XPS Spectra Exhibiting Defect Introduction into Graphene on Cu	105
4.18 C 1s XPS Spectra Exhibiting Cl Intercalation of Graphene on Cu	107
4.19 Cl <i>LMM</i> Auger Map and Spectra of Oxidation Resistant Graphene on Cu	110
4.20 XPS Spectra of Water Intercalated Graphene on Cu.....	112
4.21 O 1s XPS Spectra of Water Intercalated Graphene on Cu	115
4.22 Auger Map and Spectra of Water Intercalated Graphene on Cu.....	117

ABSTRACT

Manganese sulfide inclusions are known to be sites of localized corrosion in steels, however little is known concerning the physical and chemical properties of inclusion surfaces. Some inclusions have been observed to be more corrosively active than others. In an effort to distinguish between active and inactive inclusions, this work utilizes surface sensitive electron spectroscopies and microscopies to characterize manganese sulfide inclusion interfaces in 1018 carbon steels. A method was developed to measure variations in surface potential with a high degree of spatial resolution using an Auger microscope. It was found that manganese sulfide inclusion surfaces are heterogeneous and possess discrete manganese oxide and copper sulfide phases. Valence band Auger spectroscopy was used to distinguish between various Mn and Fe chemical species. Surface potential measurements indicate that inclusions are more noble than the surrounding steel surface. TEM analysis indicates a high defect content at the inclusion/steel interface. It is hypothesized that active and inactive inclusions can be distinguished via the availability of sulfur. Graphene on copper surfaces were characterized for use as a protective coating against corrosion using surface sensitive spectroscopies. A feature in the copper Auger transition was found to be unique to graphene, and used to identify its presence and degree of substrate coupling. Localized oxidation of the copper substrate was observed to correlate with low surface potential regions, believed to be intercalated oxygen, which enhances the reactivity of the graphene overlayer. Intercalated Cl was observed to inhibit substrate oxidation, and reduce the reactivity of the graphene overlayer. The intercalation of water was observed to occur at room temperature, and molecularly adsorb to the copper surface at temperatures up to 200 C, indicating that graphene inhibits dissociation of water. Distribution of intercalated water was observed using Auger spectroscopy. It is suggested that doping of graphene is an effective strategy for use as an anticorrosive coating on heterogeneous surfaces.

PREFACE

Some of the work presented in this dissertation concerning characterization of MnS inclusion surfaces and interfaces (c.f. sections 3.2 and 3.3) has been accepted for publication. The reader is referred to: Rieders *et. al.* New Insights into Sulfide Inclusions in 1018 Carbon Steels. *Metals*. **2021**, 11, 1-17. The use of graphene as an anti-corrosive coating was studied using graphene coated Cu surfaces. The results of this work are believed to be applicable to any substrate of interest, including commercial alloys. A manuscript describing a feature in the Cu *LMM* Auger transition from graphene coated surfaces, which is unique to the presence of graphene (c.f. section 4.2), has been prepared for submission to Physical Review B, the title of this manuscript is: Spectral Signature in the Cu *LMM* Auger Transition from Graphene Coated Cu Surfaces. A manuscript describing the relationship between surface potential variations and localized oxidation of graphene coated Cu surfaces has been prepared for submission to ACS Nano, the title of this manuscript is: Modulation of the Surface Potential by Intercalated Oxygen and its Role in Oxidation of Graphene Coated Polycrystalline Cu Surfaces.

CHAPTER ONE

INTRODUCTION

1.1 Corrosion and Its Practical Importance

The use of metal-based materials in modern society is ubiquitous. It is difficult for one to look at the world around them, and not see numerous examples of materials primarily composed of metals and their alloys. Like most materials, metals degrade over time due to interactions with their surroundings. In aqueous environments, atoms present on a metallic surface can dissolve as ions into solution, eventually compromising the mechanical integrity of the metal. This process is known as corrosion, and is of tremendous technological and economic importance. The United States spends several percent of its GDP combatting corrosion and its deleterious effects [1]. The smelting of iron is responsible for 4-5% of total man-made greenhouse gases [2], underscoring the severe environmental costs. It is the objective of corrosion science to understand the processes that occur at metal surfaces, and lead to corrosion. The practical outcome of such an understanding can lead to the engineering of surfaces, which inhibit or prevent the degradation of materials due to corrosion.

1.2 Thermodynamics of Corrosion

When a metal is immersed in an aqueous environment, an exchange of charges (ions and electrons) takes place between the metal surface and solution, resulting in the formation of a potential difference across the metal/solution interface. The process by which an atom from the

metal surface enters into the solution as an ion, leaving behind one or more electrons, is known as an anodic process, and the metal atom is said to be oxidized. As an example, the anodic dissolution of Fe from a steel surface is written as,



The process by which an ion gains one or more electrons at the metal surface is known as a cathodic process, and the ion is said to be reduced. This is the reverse of the anodic process as written in eq. 1.1. The study of the anodic and cathodic processes, which occur at a metal/solution interface, lies within the realm of electrochemistry [3–5]. Corrosion is the sustained anodic dissolution of a metal, making it an inherently electrochemical phenomenon.

While corrosion is fundamentally a non-equilibrium process, much insight is provided by consideration of the equilibrium of a metal surface in contact with an aqueous solution of its ions. The basic condition of thermodynamic equilibrium between the two phases is given by

$$\tilde{\mu}_{me} = \tilde{\mu}_{aq} \quad 1.2$$

where $\tilde{\mu}_{me}, \tilde{\mu}_{aq}$ are the chemical potentials of an ion on the metal surface and in solution respectively. We may determine the form of $\tilde{\mu}$, by considering the work done at constant temperature and pressure, in removing an ion from the surface of a metal. Recall that $\tilde{\mu} = \left(\frac{\partial G}{\partial N} \right)_{T,p}$, i.e. $\tilde{\mu}$ is the change in the Gibbs free energy, G , at constant temperature and pressure (T, p), with respect to particle number, N . For simplicity, consider the surface of a metal in contact with a vacuum. The removal of an ion from the metal surface may be divided into two steps. First, the bonds of the ion with the surrounding atoms are broken. We write the amount of energy required for this as μ . In the second step, the ion must overcome the surface potential

barrier present on all solid surfaces. For an ion of charge q and surface potential ϕ , the work done in the second step is simply $q\phi$. Therefore we may write the form of $\tilde{\mu}$ as,

$$\tilde{\mu} = \mu + q\phi \quad 1.3$$

$\tilde{\mu}$ is referred to as the *electrochemical potential*. Eq. 1.3 is a modification of the chemical potential, μ , of a particle which possesses a charge q . The first term represents the chemical work required in removing an atom from the surface, while the second term refers to the electrical work. In practice, it is not possible to determine the relative contribution of each in eq. 1.3.

The direct measurement of the potential difference between a metal surface and solution, which results from an exchange of charges between the two phases in an attempt to fulfill eq. 1.1, is not possible. This is because the experimental probe used in performing the measurement introduces an additional interfacial voltage, which is unknown. Instead, an energy scale is created by measuring the potential difference of a metal/solution interface relative to a standard electrochemical reaction. The standard reaction is the evolution of hydrogen gas at the surface of a platinum electrode in thermodynamic contact with a solution of hydrogen ions at unit activity, via the cathodic reduction of the hydrogen ion,



The potential difference, which develops at the interface of a metal in thermodynamic contact with a solution of its own ions at unit activity, is then measured with respect to the reaction given in eq. 1.4, by the creation of a standard electrochemical cell. The reversible work done at constant T and p in transferring n moles of electrons through such a cell is the change in the Gibbs free energy, ΔG^0 , of the system given by,

$$\Delta G^0 = -nFE^0 \quad 1.5$$

where F is Faraday's constant equal to the charge of one mole of electrons, and E^0 is the standard electrochemical potential. A scale of standard electrode potentials is then developed on this basis, and is known as the electrochemical series. The more positive the potential of a metal on this scale, the more resistant to corrosion it will be, and the metal is said to be more noble. The more negative a metal is on this scale, the more susceptible it will be to corrosion. It is worth noting that the standard electrochemical potential of a metal is measured under very specific conditions. The equilibrium potential of a metal immersed in an arbitrary solution, will be different than its standard value. Moreover, the relative nobility of two metals will also depend upon the nature of the solution in which they are immersed. If two dissimilar metals in electrical contact are placed in solution, cathodic processes will occur at the surface of the more noble metal, whilst anodic processes (dissolution) will occur at the surface of the less noble metal. This is known as *galvanic coupling*, and the two metals are said to form a galvanic pair.

1.3 Kinetics of Corrosion

The anodic and cathodic processes described above may occur on the same metal surface. Anodic dissolution at a metal surface may not proceed indefinitely, as the accumulation of charge will decrease the electrochemical potential given by eq. 1.3, to the point where dissolution is no longer thermodynamically favorable. Cathodic processes remove the accumulation of charge, thereby increasing the electrochemical potential of the metal surface atoms, and dissolution may again proceed. Sustained corrosion of a metal surface occurs via the interplay between anodic and cathodic reactions. The respective rates of these reactions are directly relevant to an understanding of corrosion processes.

The equation governing the rate of anodic and cathodic processes at the metal/solution interface is given by the Butler-Volmner equation [5],

$$i = i_0 \left(e^{\frac{-\beta\eta F}{RT}} - e^{\frac{(1-\beta)\eta F}{RT}} \right) \quad 1.6$$

where i , is the total electrode current, i_0 is a constant related to the equilibrium (or steady-state) anodic and cathodic currents, β is the symmetry of the activation energy barrier with β typically equal to 0.5, η is the over-voltage defined as $E - E_0$ where E is the electrode potential, and E_0 is the equilibrium electrode potential, F is the Faraday constant, R is the universal gas constant, and T is the temperature. The first term in eq. 1.6 is the cathodic current, or the rate of reduction at the metal surface. The second term in eq. 1.6 is the anodic current, or rate of oxidation (corrosion) at the metal surface. For a metal surface in thermodynamic contact with an aqueous solution, the cathodic processes are typically the reduction of H^+ or H_2O , whilst the anodic process is the dissolution (corrosion) of the metal. For $\eta=0$, the net current passing across the metal/solution interface is zero. While equilibrium with respect to all ions in the system will result in a net current of zero, it is also possible that the rates of anodic and cathodic processes are equal. For the case of $\eta>0$, the potential of the metal is greater than its equilibrium value. The system responds by releasing metal ions via anodic dissolution, and thereby reducing its potential in an effort to achieve equilibrium. Likewise for $\eta<0$, the potential of the metal is below its equilibrium value, and the system responds by reducing ions from the solution, thereby increasing its potential in an effort to achieve its equilibrium value.

1.4 Pitting Corrosion

It may happen that the corrosion of a metal is localized to small regions on the surface. The anodic dissolution which occurs in these regions is rapid, and alters the local electrochemical environment, further catalyzing anodic processes. This results in the initial formation of small ($\sim 1\text{ }\mu\text{m}$ diameter) pits on the metal surface. These small pits may coalesce to form larger pits, and continued dissolution of the pit may eventually perforate the metal, compromising the structural integrity of the material. This phenomenon is known as pitting corrosion [6–8], and is of particular importance due to its destructive capability.

It is currently believed that pitting results from the local destruction of the passive film present on all metal surfaces [6–9]. These passive films are metal-oxides, which may be formed electrochemically in aqueous solutions, or naturally in air. Metal oxide films are highly insoluble in most environments, which limits anodic dissolution, and the metal surface is said to be passivated. Whenever and wherever the passive film is compromised, rapid anodic dissolution of the exposed metal surface occurs. The remainder of the passivated surface may serve as a source of the accompanying cathodic reactions. While the exact mechanisms leading to the breakdown of the passive film are still disputed [10], there is strong empirical evidence that the presence of certain ionic species in the solution, particularly Cl^- , play a fundamental role [6–8,11].

The fact that dissolution is localized to small regions on the metal surface is related to the empirical fact that pits nucleate at some type of heterogeneity or defect. In other words, the efficacy of the passive film is compromised by the inherent presence of defects. Defects may include secondary phases, grain boundaries, dislocations, etc. In the case of commercial steels,

in which the alloy surface is highly heterogeneous, it is found that pits preferentially nucleate and grow at the sites of metal-sulfide inclusions. In particular, MnS inclusions have long been known to be the sites of pit nucleation and growth in ferrous alloys [12–33]. These inclusions are secondary phases, formed during the metallurgical preparation of the steel, whereby Mn is added to remove the undesired presence of S in the ferrite phase. If the steel is rolled into a bar, the inclusion is stretched out along the rolling direction, forming what is known as a “stringer.”

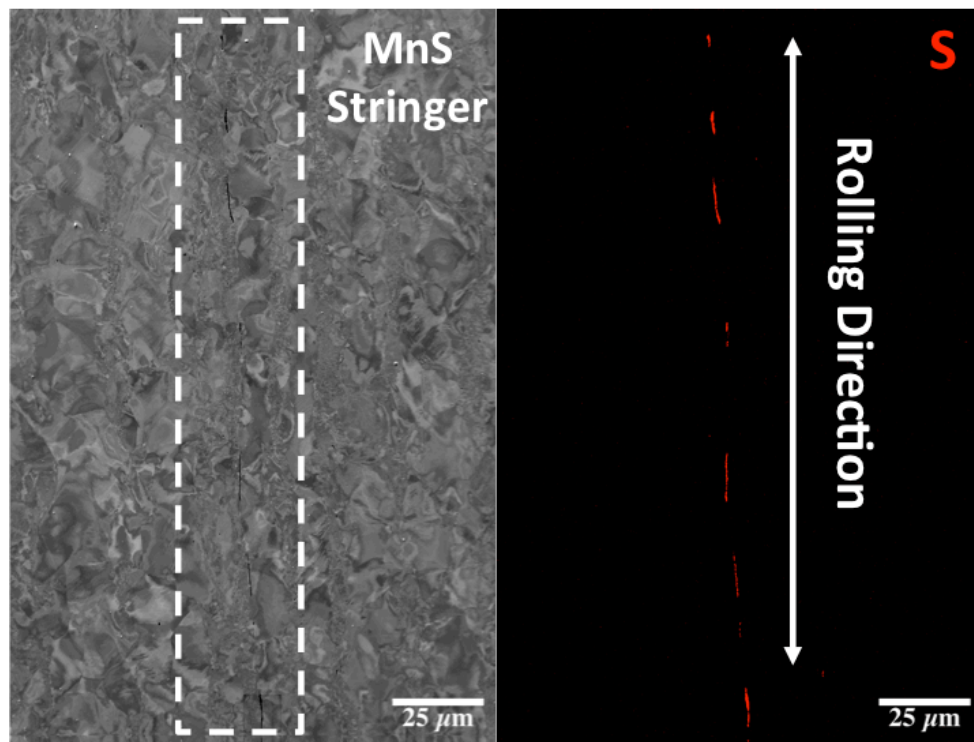


Figure 1.1: Left: SEM image of 1018 carbon steel. Dotted white box indicates the presence of a MnS stringer. Right: S $K\text{-}\alpha$ EDX map showing a MnS stringer, arrows indicate the rolling direction.

Shown in Figure 1.1 is an example of a MnS stringer. The right panel is a S $K\text{-}\alpha$ EDX map showing the extent of the stringer. The corresponding field of view is shown in the SEM image in the left panel, where the MnS stringer is enclosed by the dotted white lines. The arrows in the

right panel indicate the rolling direction of the steel, and one sees that the stringer has been elongated along the rolling direction. Such MnS stringers extend 100s of μm through the bulk steel. The 1018 carbon steel samples used in this work were found to contain 3400 MnS inclusions per mm^2 [34].

Pitting in steels is observed to occur at the *interface* between MnS inclusions and the surrounding Fe matrix. In the case of stainless steels, it has been shown that there exists a depletion in the Cr content at this interface [15]. Because it is the presence of Cr, which is responsible for the passive properties of the oxide film formed on stainless steels, its subsequent depletion at the interface of MnS inclusions, would makes these regions particularly susceptible to dissolution. In the case of carbon steels, chemical heterogeneity at the inclusion interface is also believed to be the cause for localized dissolution, however limited experimental evidence exists to support this hypothesis. As first described by Wranglen [35], some but not all MnS inclusions form the sites for pit initiation and growth. He termed those inclusions which formed the sites for pit growth as active, and those that did not as inactive. Wranglen claimed that MnS inclusions were more noble than the surrounding carbon steel matrix, and that dissolution occurred at the inclusion/steel interface of the active inclusions. He hypothesized that the cause for the high rate of dissolution at these interfaces was the presence of S as FeS. It has been shown that the presence of S at the metal electrolyte interface may enhance dissolution and disrupt the passive film [36]. Others have suggested that dissolution of Fe at the inclusion/steel interface may lower the local pH via metal hydrolysis: $\text{Fe}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_2 + 2\text{H}^+$. At sufficiently low pH (pH<4), the MnS inclusion may begin to dissolve via: $\text{MnS} + 2\text{H}^+ \rightarrow \text{H}_2\text{S} + \text{Mn}$. The H_2S produced in this process may further promote dissolution of Fe [18]. Thus, sulfide

inclusions and their interfaces in steel may serve as a *source* of S, which alters the local electrochemical environment upon dissolution.

While chemical heterogeneity may be one cause for the susceptibility of pitting at inclusion/steel interfaces, the presence of structural defects may also contribute to enhanced dissolution in these regions. During the metallurgical processing of commercial steels, various rolling and other applied mechanical stresses, result in the plastic deformation of the material and the presence of residual strain. The presence of strain has been shown to enhance the chemical reactivity of solid surfaces, a phenomenon known as the mechanochemical effect. Gutman showed that the change in the equilibrium electrode potential, $\Delta\phi$, due to plastic deformation is given by [37],

$$\Delta\phi = -\frac{n\Delta\tau R}{\bar{\alpha}R'zF} \quad 1.7$$

where n is the number of dislocations present, $\Delta\tau$ is the excess stress due to a dislocation, $\bar{\alpha}$ is constant related to the mobile dislocation density dependence on strain, and R' is a modification of the universal gas constant via $R' = k_B N_{max}$ where k_B is Boltzmann's constant and N_{max} is the maximum number of dislocation sites in the solid. Thus the presence of strain decreases the equilibrium potential of a metal, making it less noble. Previous experiments have shown that the electrode potential of a metal can be changed by the application of external stress [38–40]. Eq. 1.7 is a direct relationship between the electrochemical behavior of a metal and its material properties. One might expect the interface at a secondary phase in steel to be highly disordered, and contain a large number of crystalline defects. It has been demonstrated that the interfaces near MnS inclusions in carbon steels are highly strained, and that this strain can be correlated with localized dissolution or pitting corrosion [41,42]. The highly strained interfaces of the MnS

inclusions are significantly more anodic relative to the immediate surroundings, which may act as a source of electrons for the required cathodic processes. In other words strained regions of the metal surface are able to form efficient galvanic couples with relatively less strained regions. The metallurgical history of a steel sample will also inevitably introduce structural changes and additional residual strain, both on macroscopic and microscopic length scales. This has also been shown to effect the local dissolution of steel surfaces [34,41,43–46].

A portion of the work presented in this thesis was devoted to characterizing MnS inclusions and their respective interfaces in 1018 carbon steels. The objective of this work was to provide insight into the empirical fact that these regions of a highly heterogeneous steel surface are particularly susceptible to localized corrosion. It is hypothesized that the pitting behavior of steel is solely determined by the physical and chemical properties of its surface, which in-turn is determined by its metallurgical history, and that regions of the surface where pitting corrosion occurs, are independent of the corrosive environment. As discussed above, there are many properties of the inclusion and its interface, which might explain their susceptibility to localized corrosion. One may ask, if any of these properties are more detrimental with regard to pitting corrosion, than others. In light of the distinction between active and inactive inclusions provided by Wranglen [35], the work presented in this thesis attempts to provide some insight into these questions.

1.5 Graphene as an Anti-Corrosive Coating

A standard way to inhibit or prevent the corrosion of metals is to coat the surface with a film, thereby isolating it from its environment. It has been proposed that graphene films are effective anti-corrosive coatings [47]. Graphene is a monolayer of carbon atoms arranged in a hexagonal lattice, and was originally isolated from bulk graphite [48]. It possesses novel properties, which make it an attractive candidate as an anti-corrosive coating, including: impenetrability to gases and liquids [49] and high mechanical strength [50]. The development of CVD methods to grow graphene films has made it possible to coat a variety of metallic substrates [51,52]. Due to their catalytic activity, graphene is most commonly grown on Cu, Ni, Pt, and Ir substrates. Relatively few attempts have been made to grow these films on more complex steel surfaces.

While some have claimed efficacy in the prevention of corrosion of graphene coated metal surfaces [47,53–65], others' work suggest that no benefit exists in the use of graphene as a protective film [66–68]. CVD methods for graphene growth offer the possibility for large area coverage, however defects such as grain boundaries, vacancies, and wrinkles are still present in these films. It has been suggested that these defects are responsible for the failure of graphene films to protect against corrosion, and that while graphene is in principle highly inert, reactive species may directly interact with the metal substrate via such defects [69]. Due to the high conductivity and relative nobility of the graphene overlayer, efficient galvanic couples may be formed between the graphene film and underlying substrate. Galvanic coupling has been suggested as the mechanism responsible for the increased rate of corrosion of graphene coated metal substrates [66,67]. One method to avoid the deleterious presence of film defects is to

deposit multiple layers of graphene in order to avoid a “continuous path of defects” to the metal surface. There has been mixed success in this regard [56,57,60,65]. In order to improve adhesion to the metal surface, others have used polymer-graphene hybrid films [70,71].

The most commonly proposed mechanism for the failure of graphene coated metal surfaces involves the intercalation of an oxidizing species e.g. H_2O or O_2 . Here, the oxidizing species disrupts the metal-carbon interaction and is adsorbed at the graphene/metal interface, a process known as intercalation. Intercalants may enter the interface via film defects or edges. Many have claimed that in the case of O_2 intercalation, the graphene acts as a freestanding film [72–76], i.e. that it does not interact strongly with the intercalating O_2 atoms. Upon oxygen intercalation, it was suggested that graphene on Ir (111) is etched at high (> 720 K) temperature by the intercalated oxygen atoms [73]. Graphene on Ru (0001) surfaces were found to rupture upon H_2O intercalation, even at low (~ 70 K) temperature [77]. In acidic environments, it has been shown that the rapid evolution of H_2 gas (via eq. 1.4) at a Graphene/Ni interface may cause large bubbles to build in the film [68]. The pressure may become large enough to rupture the graphene, causing catastrophic failure. It has been suggested that consideration of the metal-graphene interaction is more important than the overall quality and coverage of the graphene film, as strong coupling between the graphene and metal substrate was observed to inhibit intercalation [78]. In general, it is not clear what role the intercalation process plays in the failure of graphene films. Are the reaction dynamics in the confined geometry of the interface fundamentally different from similar processes, which might occur at an i.e. metal/vacuum interface? Do the intercalants alter the reactivity of the overlying graphene surface, thus making it susceptible to degradation and failure?

When considering a highly heterogeneous steel surface, an important question is if and how the graphene covers secondary phases (i.e. MnS inclusions) or other types of defects, which will naturally be present. In some sense, this might be the case when considering the efficacy of any coating. However, a related and equally important question is if and how a surface heterogeneity alters the physical and chemical properties of an overlying graphene film. Do such heterogeneities exhibit similar properties to intercalants at the interface between graphene and a pure metal surface? Using surface sensitive electron microscopy and spectroscopy techniques, including a novel method using secondary electron emission to measure surface potential variations; this thesis attempts to address in part, some of these questions.

CHAPTER TWO

EXPERIMENTAL METHODOLOGIES

2.1 Surface Electron Spectroscopy and Microanalysis in Corrosion Science

Because the phenomena which occur during the corrosion process, are confined to a surface or interface, the characterization of metal and metal alloy surfaces has been a major area of research in corrosion science. In this regard, surface sensitivity of the experimental probe is critical in understanding the relationship between a surface's physical and chemical properties, and its corrosion behavior. For this reason, the use of electron based spectroscopy and microscopy have found wide use in the field of corrosion science. The surface sensitivity of these methods is based upon the relatively low kinetic energy of the electrons used to probe surfaces. The inelastic mean free path (IMFP) of electrons in solids are found to obey a universal curve, independent of the type of solid material [79]. The range of electron kinetic energies used to probe solid surfaces is typically 0-1000 eV. This results in a measured signal, which originates within a volume a few nm below the solid surface [80]. Electrons within this energy range may be used to study surface morphology as is done in a scanning electron microscope (SEM), or for compositional and chemical information as is done in Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). Bulk characterization of metal alloys is also of importance in corrosion science, as there is expected to be a correlation between bulk and surface properties. Energy dispersive x-ray spectroscopy (EDX) is a bulk sensitive technique, which measures the photon energies of characteristic x-rays to identify elements present within a volume of $\sim 1 \mu\text{m}$ below the surface [81]. Bulk sensitivity of this technique

results from the relatively low absorbance, in most materials of interest, of x-ray photons with energies in the range of 1-30 keV [81]. Bulk crystallographic structure can be determined using electron backscatter diffraction (EBSD), which probes 10-100 nm below the surface [82,83]. These surface and bulk sensitive techniques were used in the work presented in this thesis. The underlying theory of these methods, and a description of the instrumentation used in this work are presented below.

2.2 X-Ray Photoelectron Spectroscopy

In an XPS experiment, X-rays are irradiated onto a sample surface to produce photoelectrons via the photoelectric effect. The kinetic energy of the photoelectrons (KE) is measured by means of an electrostatic analyzer, and the binding energy, BE, relative to the Fermi level (see Figure 2.1), is determined via,

$$BE = h\nu - KE - \phi \quad 2.1$$

where $h\nu$ is the X-ray photon energy and ϕ is the “work function.” The photon energy and work function are known quantities. An XPS spectrum shows the number of emitted photoelectrons with respect to their binding energy. The core level binding energies of atoms will appear as peaks in the photoelectron spectrum. Each element has a unique set of core level binding energies, which can be used to determine their presence on solid surfaces. Surface composition is the basic piece of information, which can be obtained from an XPS spectrum.

In addition to determining the presence of a particular element on a surface, XPS may also be used to determine the local chemical or bonding environment of that element. The bonding environment results in a shift in the core level binding energy, also known as a chemical

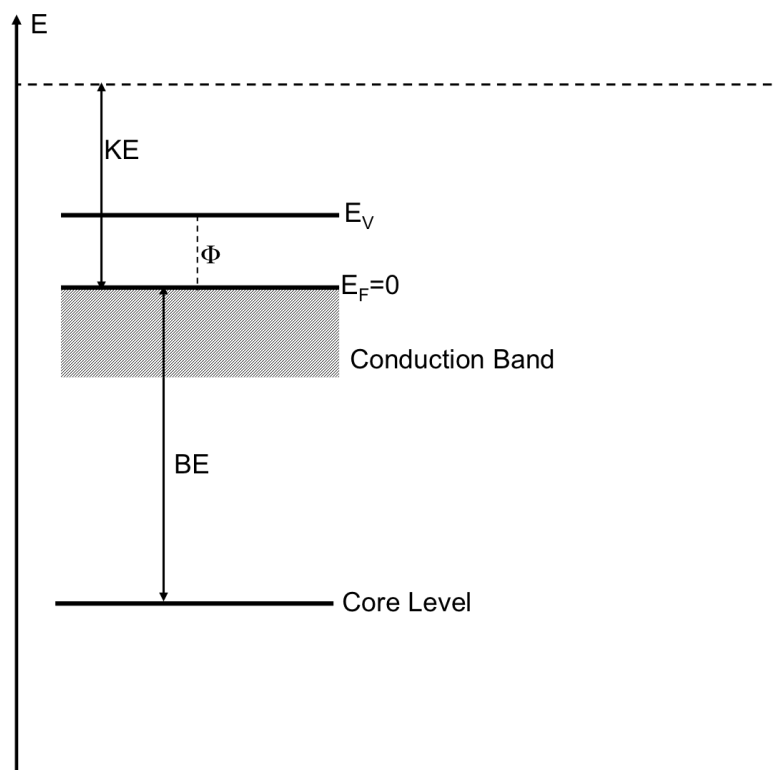


Figure 2.1: A schematic of the defined energy scale in an XPS experiment. A core level electron is liberated from the solid via the photoelectric effect. Its binding energy (BE) is defined with respect to the Fermi level (E_F), and can be calculated via eq. 2.1, by measuring the kinetic energy (KE) of the photoelectron.

shift. At a simple level, binding energy shifts can be explained as changes in electron density near the atom of interest. A chemical bond resulting in an increased electron density near the atom of interest, increases the effective screening of the atomic nucleus, thereby increasing the kinetic energy of the photoelectron, resulting in a downshift in the binding energy. Likewise, a chemical bond which decreases the electron density near the atom of interest, results in an upshift in the binding energy. Chemical shifts in the core level binding energy of elements are tabulated [84], or can be obtained from the literature.

The XPS data presented in this thesis were obtained with a Physical Electronics 5600 spectrometer in the Imaging and Chemical Analysis Laboratory (ICAL) at Montana State

University. This spectrometer is operated under UHV conditions at base pressures of order 10^{-10} Torr. Monochromatic Al K- α X-rays ($h\nu=1486.7$ eV) were used as the photoelectron excitation source. The source power was typically set to 250 W, resulting in typical photoemission currents in the range of $\sim 0.1 - 1$ nA. The kinetic energy of the photoelectrons were measured with a hemispherical analyzer with a spectral resolution $\Delta E/E \sim 0.5\%$. The spectrometer was operated in the constant pass energy mode, with typical pass energies in the range of 23.50-46.95 eV. Photoelectrons were detected with a multichannel detector. The X-ray source and analyzer are oriented at 45 degrees with respect to the sample horizontal. The instrument is equipped with an Ar^+ ion sputtering gun, typically operated at an accelerating voltage of 2 kV, and sputter currents ~ 1 μA . UHV annealing was accomplished by radiatively heating the sample with a tantalum filament. The temperature of the sample was monitored with a K-type thermocouple placed in between the heating filament and sample. The data was collected with the RBD software *AugerScan*.

2.3 Spectroscopy and Microscopy with a Focused Electron Beam

When a beam of energetic electrons impinges upon a solid surface, various measurable signals are generated, which can provide information pertaining to the physical and chemical properties of the sample. By use of electromagnetic lenses, electron beams can be focused to very small ($\sim$ nm) sized probes. Thus, it is possible to measure the signals generated by electron beam-sample interactions, with a high degree of spatial resolution. This principle forms the basis of electron beam microscopy and spectroscopy.

Shown in Figure 2.2 is a characteristic spectrum of energies of electrons emitted from a solid surface irradiated with a beam of electrons with energy, E_p . Here, the number of emitted electrons, $N(E)$, is plotted with respect to their kinetic energy, KE. Several features can be seen in this spectrum, the first is an intense peak at the primary beam energy. This peak represents primary beam electrons with kinetic energy E_p , which have been elastically backscattered. Inelastically backscattered primary beam electrons form the background present throughout the entire spectrum. A second rather intense peak, can be seen on the low energy side of the spectrum from 0 to ~ 50 eV. This peak represents secondary electrons, which are emitted from the solid due to interactions with the primary beam. Because of their surface sensitivity, secondary electrons are used to image surfaces in a SEM.

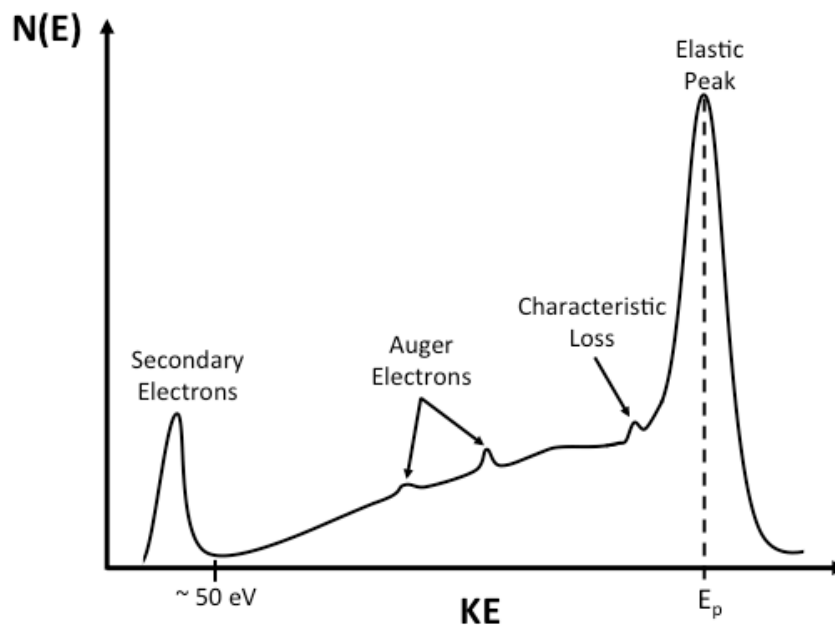


Figure 2.2: Schematic of the energy spectrum of emitted electrons from a solid surface irradiated by a high-energy electron beam.

Superimposed on the inelastic background, relatively less intense peaks can be observed. These are known as Auger electrons, which result from the relaxation of a core-level ionized atom. The Auger process is schematically shown in Figure 2.3. Here, a core-hole is generated in the atomic state with binding energy E_a , and is filled by an electron from the state with binding energy E_b . The excess energy is transferred to an electron with binding energy E_c , and the electron is emitted from the atom with kinetic energy, E_k , approximately given by,

$$E_k = E_a - E_b - E_c \quad 2.2$$

The emitted electron is known as an Auger electron. The kinetic energy of the Auger electron is independent of the primary beam energy, and depends solely on the atom from which it came. Each element has a unique spectrum of Auger electron kinetic energies, which can be used to determine its presence on the surface of a solid. The measurement of kinetic energies of Auger electrons forms the basis for Auger electron spectroscopy.

The expression given in Eq. 2.2 suggests that as in the case of XPS, AES can also be used to determine the chemical state of elements present on the surface. While in principle this is true, we note that the measured kinetic energy does not depend in a simple way on a single binding energy state, but rather three. Moreover, two of those binding energies are with respect to a singularly ionized atom. Auger transitions involving valence band electrons can, and are used to identify the chemical state of elements on the surface [85]. This is done by considering the peak shape of the valence band Auger transition, rather than the peak position. The determination of the chemical state from such Auger transitions can be accomplished by acquiring spectra from well-defined standards, or by comparison with the literature.

An alternative relaxation process to Auger electron emission, is the emission of an x-ray photon. Here, a core level hole is filled by an electron from a higher atomic orbital, followed by emission of an x-ray photon with energy,

$$h\nu = E_a - E_b \quad 2.3$$

The energy of the emitted photon is unique to the element from which it came, and can be used to identify elements present within the sample bulk. The measurement of the energies of emitted X-ray photons, forms the basis for energy dispersive spectroscopy (EDS). Auger electron and x-ray photon emission are two competing relaxation mechanisms for core level ionization of atoms. Their relative probability is dependent on the element, as well as the orbitals involved in the transition [86].

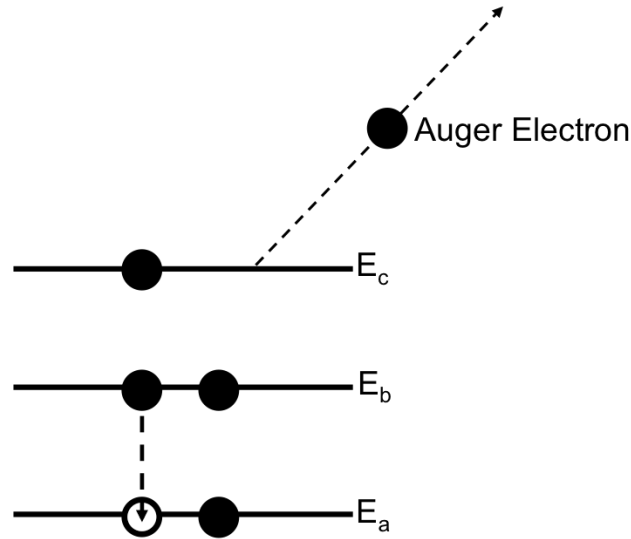


Figure 2.3: Schematic of the Auger emission process. An electron with binding energy E_B fills a hole in the state with binding energy E_A . An electron with binding energy E_C is emitted with kinetic energy approximately given by Eq. 2.2.

The secondary electrons shown in Figure 2.2 may be used to form an image of solid surfaces. This is accomplished by measuring the secondary electron emission intensity at

discrete points in a regular raster pattern across the sample surface. The intensity of secondary electron emission at any given point is related to the composition and surface topography. This forms the principle of image formation in a scanning electron microscope. We note that in practice, the backscattered electrons which form the background shown in Figure 2.2, also contribute to the image intensity in an electron microscope. The relative contribution of secondary and backscattered electrons to the image intensity depends upon the accelerating voltage of the electron beam [86].

The backscattered electrons with energies near that of the primary beam may be used to probe the bulk crystallographic structure of solids. This technique is known as EBSD. Here, a high energy, typically 20 keV electron beam, is incident at grazing angle, typically 20 degrees with respect to the sample horizontal. Coherent scattering will occur for those backscattered electrons which satisfy the Laue condition,

$$\vec{k} - \vec{k}' = \vec{G} \quad 2.4$$

where $\vec{k}$ is the incident wave vector of the backscattered electron, $\vec{k}'$ is the wave vector of the scattered electron, and $\vec{G}$ is a reciprocal lattice vector of the crystallographic plane. Because the backscattered electrons are scattered equally in all directions, a cone of coherent scattering satisfying 2.3 is formed for each crystallographic plane. The intersection of these cones with a planar detector produces a pattern of bands, known as a Kikuchi pattern. Each band is associated with a crystallographic plane. The widths of these bands are inversely proportional to the lattice spacing. The relative orientation of the bands may be used to determine the orientation of the crystal. Kikuchi patterns may also be used to determine the crystalline phases present in a sample by comparing the pattern to reference data. In order to form high quality Kikuchi

patterns, the sample surface is typically highly polished. EBSD patterns can be collected from discrete points across a sample surface, thereby generating a map of the spatial distribution of crystallographic phases, as well as their orientations.

Primary beam electrons may lose discrete amounts of energy when interacting with a solid surface via collective excitations i.e. phonons and plasmons, electronic interband transitions, or core level ionization. These characteristic losses are indicated schematically in Figure 2.2. The measurement and determination of these characteristic losses forms the basis for electron energy loss spectroscopy (EELS). These losses may be used to study the presence and vibrational properties of adsorbents, electronic structure of solids, and core level chemical shifts.

The techniques described above were employed to study MnS inclusions in carbon steels and Graphene coated Cu surfaces using an integrated Auger Nanoprobe in the Imaging and Chemical Analysis Laboratory at Montana State University. The Auger Nanoprobe is built around the Physical Electronics Auger Microscope 710. This microscope is operated under UHV conditions at pressures of order 10^{-10} Torr. It is equipped with a field emission electron source, which may produce electron beams with probe diameters down to 5 nm. The energy spectrum of emitted electrons is measured with a cylindrical mirror analyzer (CMA), which is positioned coaxial to the electron beam. The CMA is operated in the variable pass energy mode, with a resolution $\Delta E/E \sim 0.5\%$. SEM images were generated by collecting secondary and backscattered electrons with a scintillator biased to 10kV. The working distance of the microscope was fixed at the focal point of the CMA at 8.5 mm. The focal point was determined by use of a 1 keV elastic peak. An Ar^+ ion gun was used to clean sample surfaces, as well as perform depth profile experiments. Typical ion beam energies ranged from 500 eV to 2 keV,

with probe currents in the $0.5 - 2 \mu\text{A}$ range. In the case of low energy (500 eV) sputtering, the ion gun is floated to achieve sufficient beam current. A 100 nm SiO_2 on Si film was used to calibrate the sputter rate of the Ar^+ ion gun at various beam energies. Auger spectra and control of the microscope was performed using the SmartSoft software. EDX spectra were acquired with a Bruker XFlash silicon drift detector using the Espirit software (Bruker Billerica, MA). EBSD patterns were imaged with a phosphorus screen placed in front of a CCD camera (ThorLabs 1500M-GE-EX1), and acquired using the TEAM software (EDAX Inc. Mahwah, NJ). Analysis of the data was performed using the OIM software package (EDAX Inc. Mahwah, NJ).

2.4 Measurement of the Work Function Using Onset of Secondary Electron Emission

As described in sections 1.2 and 1.3, electrochemical reactions occurring at an actively corroding metal surface involves the transfer of charges across the metal solution interface. It has been suggested, that the potential difference which develops at a metal/solution interface, directly depends on the work function of the metal [87]. As shown in Figure 2.1, the work function is the difference between the vacuum level, E_v , and Fermi level, E_F . It is the minimum work required to remove an electron from a solid. A linear correlation has been shown to exist between the work function of a metal surface and its open circuit potential [88–90]. It was found that the larger the work function of a metal surface, the more positive its open circuit potential. In other words, the relative nobility of a metal increases with its work function. Recalling that the second term of the electrochemical potential in eq. 1.3, $q\phi$, is the work required in removing a particle of charge q from the phase of interest, that a relationship between the work function

and the electrochemical behavior of a surface is not surprising. Thus, observed variations in the work function can be correlated to variations in the electrochemical potential on a given surface.

With regard to pitting corrosion, it is expected that the regions of active dissolution, are those which exhibit relatively large electrochemical potentials. Thus by measuring variations in the work function across a surface, it should be possible to predict locations which are susceptible to dissolution. Moreover, the ability to identify active regions on a surface, allows one to probe the underlying physical and chemical properties of these regions. Such information is useful in developing an understanding of surface processes, such as pitting corrosion. Using kelvin probe force microscopy (KPFM) [91], one may image variations in the contact potential difference (work function) across a sample surface. This widely applied technique has been used to identify regions on alloy surfaces, which are susceptible to corrosion [88,89,92–97].

In order to accurately measure the absolute value of the work function from a region of the sample surface with KPFM, the work function of the probe must be determined. This can be done by use of well defined reference standards, which possess a known or measured work function [98]. A bigger issue, is that most KPFM experiments are conducted under ambient conditions, and thus on ill-defined surfaces. Here, we describe a method to measure and image variations in the work function across a given surface. This method utilizes the onset of secondary electron emission [99,100] to determine the absolute value of the surface potential. It was developed as part of this thesis using the Integrated Auger Nanoprobe in ICAL at Montana State University. There are several advantages of this method over traditional KPFM measurements: First, the measurements are conducted in UHV, and thus can be performed on well-defined surfaces. As will be shown below, the presence of environmental contamination on

the sample surface alters the measured value of the work function. Second, with a calibrated spectrometer, this method is able to determine the absolute value of the work function from a surface. Finally, the availability of other surface and bulk characterization techniques on this microscope (AES, EDX, EBSD), allows for direct correlation between variations in surface potential and compositional and structural properties. The principle of this technique and its validation is described in the following.

The energy distribution of secondary electron generation in metals ranges from 0 to ~50 eV (see Figure 2.2). However, those secondary electrons which escape the solid surface, must overcome the work function. The energy of the *onset* of secondary electron emission can be used to determine the work function of a sample surface. Consider the diagram shown in Figure 2.4, which schematically depicts the energy levels relevant in the measurement of the energy of an electron excited above the Fermi level. The kinetic energy of the electron, KE , as measured by the analyzer, KE' , is given by,

$$KE' = KE + (\Phi_S - \Phi_A) - eV_B \quad 2.5$$

where Φ_S and Φ_A are the work functions of the sample and analyzer respectively, and V_B , is an applied DC bias. We see that when $KE = 0$, $KE' = (\Phi_S - \Phi_A) - eV_B$. A value of $KE = 0$ corresponds to the minimum energy an electron must possess in order to overcome the work function of the sample, Φ_S . Since the value Φ_A is a known constant of the spectrometer, and V_B is a known constant of the measurement, the work function of the sample, Φ_S can be determined via eq. 2.5. The measured kinetic energy under this condition, $KE' = (\Phi_S - \Phi_A) - eV_B$, corresponds to the *measured* onset of secondary electron emission.

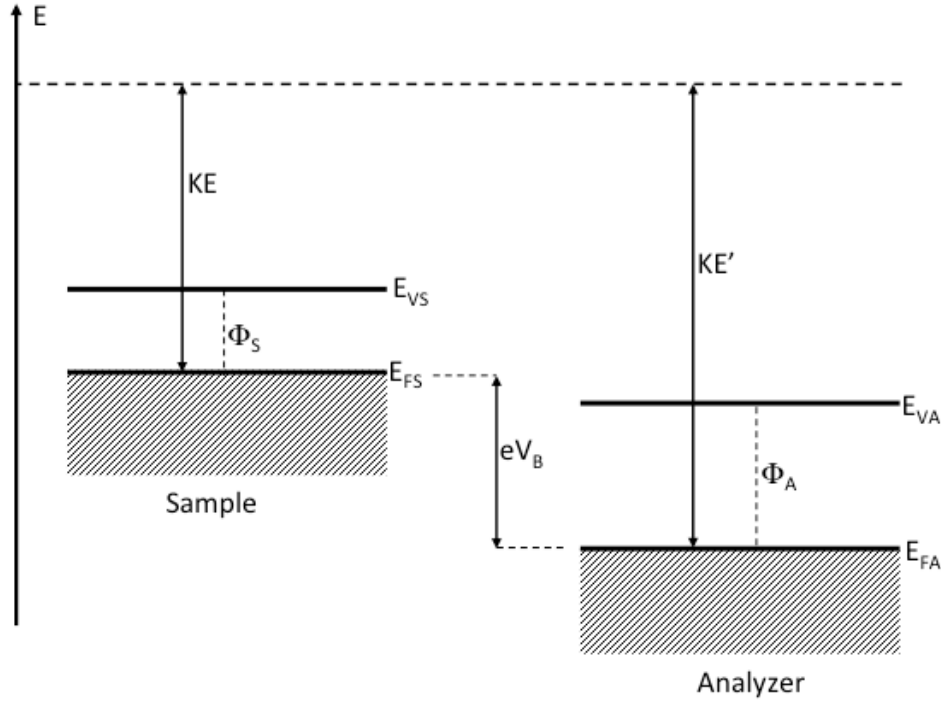


Figure 2.4: Schematic depiction of the measurement of the kinetic energy of a secondary electron emitted from a sample surface.

In the absence of a DC bias, the onset energy of secondary electron emission, $(\Phi_S - \Phi_A)$, is quite small: a few 100 meV. Thus a negative DC bias of 20 – 50 V is typically applied to the sample in order to accelerate these low energy electrons to the detector. The bias rigidly shifts the entire electronic spectrum allowing for observation of the onset of secondary electron emission. Samples are mounted on a stage electrically isolated from the rest of the microscope. A grounded Mo mask with a ~ 1 mm hole is placed very near (< 1 mm) to the surface of the sample. The mask and the sample are electrically isolated. The importance and purpose of this mask is described below.

Figure 2.5 shows an example of two onset spectra (red and blue lines). The two arrows in Figure 2.5 indicate the kinetic energies corresponding to the onset of secondary electron

emission in the two spectra. We note that the value of the work function of the analyzer is incorporated into the energy scale. One needs to only account for the value of the sample bias, in this case -20 V, to determine the absolute value of the work function. The energy of onset of secondary electron emission of the red spectrum is lower than in the case of the blue spectrum. The difference in their respective onset energies is equal to the work function difference, $\Delta\Phi$, between the two spectra. In this case $\Delta\Phi \sim 0.4$ eV. This means that the work function from the region of the sample surface represented by the red spectrum is lower than the region corresponding to the blue spectrum. A quantitative map of the variation in the surface potential can be obtained by acquiring an onset spectrum at discrete points (pixels) across a region of a surface, and determining the energy of onset at every pixel. This however is time consuming, which as will be detailed below, may introduce error into the measurement. An alternative method is to collect a qualitative map of the surface potential variation. This can be done by fixing the pass energy of the analyzer, and measuring variations in the secondary electron signal intensity at this energy. The value of the pass energy used to acquire surface potential maps is schematically shown as E_{pass} in Figure 2.5. A region of bright contrast (high signal intensity) in such an image, would correspond to a lower surface potential region relative to a region of dark contrast (small signal intensity). This has the advantage of being a rapid method to image surface potential distributions.

Ideally, the accuracy of this method could be verified by measurement of high purity and single crystal standards. Unfortunately, there exists a fair amount of disagreement in the literature with respect to work function values acquired from such standards [101,102]. This is primarily due to the sensitivity of the work function to the experimental conditions, both intrinsic

to the sample as well as the measurement apparatus. For example, differences in the work function acquired from single crystal Ag samples are found to differ by ~ 400 meV [103,104]. In the context of the motivation for this work, namely identification of electrochemically active regions on a give surface, it is not the absolute accuracy of the work function measurement which is of importance. Rather, it is the *difference* or variation in a surface potential map, which is meaningful in identifying heterogeneous regions on a given surface. So long as any experimental bias is systematic throughout the measurement, this bias is not believed to be significant with regard to interpretation of the data.

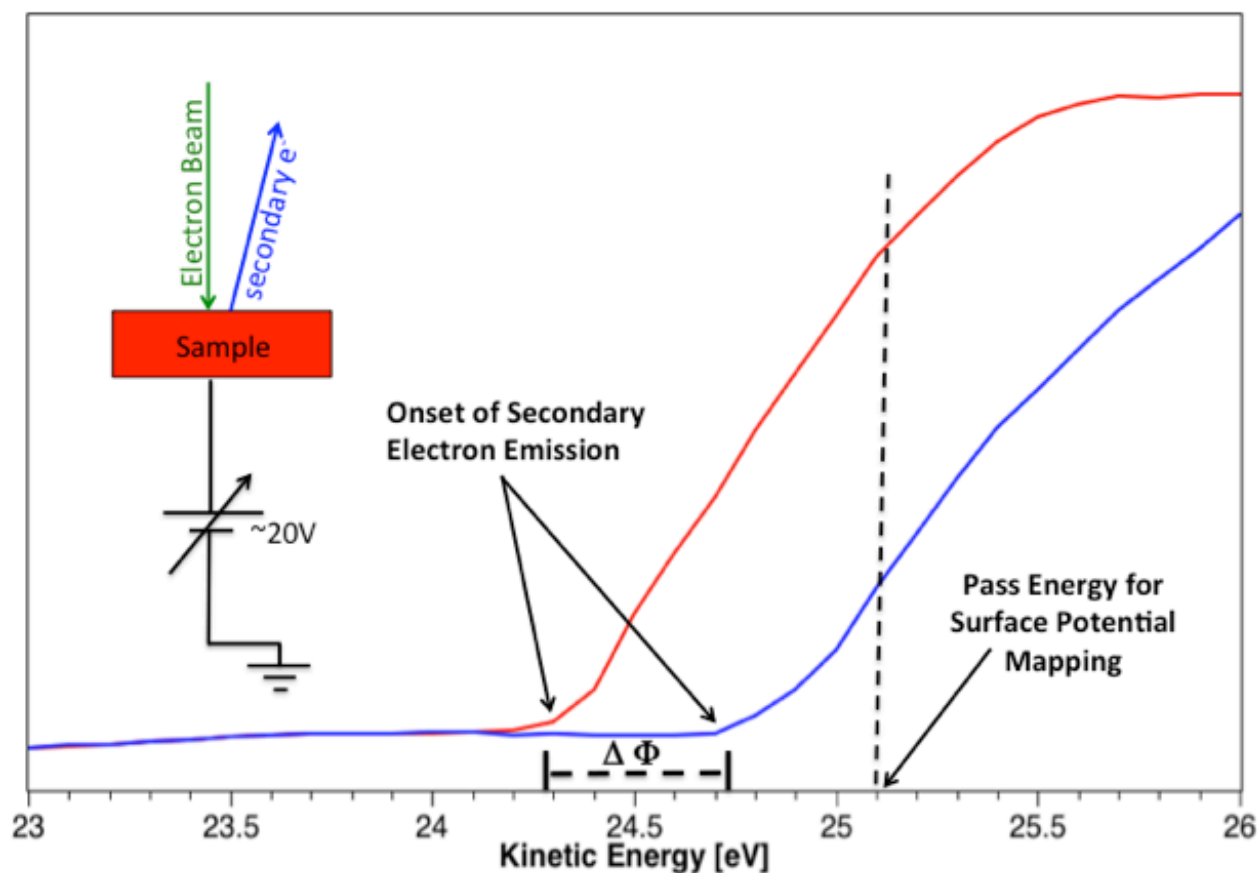


Figure 2.5: Example onset spectra exhibiting the principle of determining differences in work function, $\Delta\Phi$, between two regions. The dashed vertical line indicates the fixed pass energy used when imaging the variation in the work functions across a sample surface.

Nonetheless, work function values reported in the literature were compared with the measured onset energy of secondary electron emission from 5 single crystal standards: Au (100), Ag (111), Ta (110), Rh (100), Ru (0001). The samples were sputter cleaned with Ar^+ ions, and their respective cleanliness and purity were checked by collecting Auger spectra from the sputtered region. A DC bias was applied to the samples via a 9 V battery, which was checked with a digital multimeter after the collection of each onset spectrum.

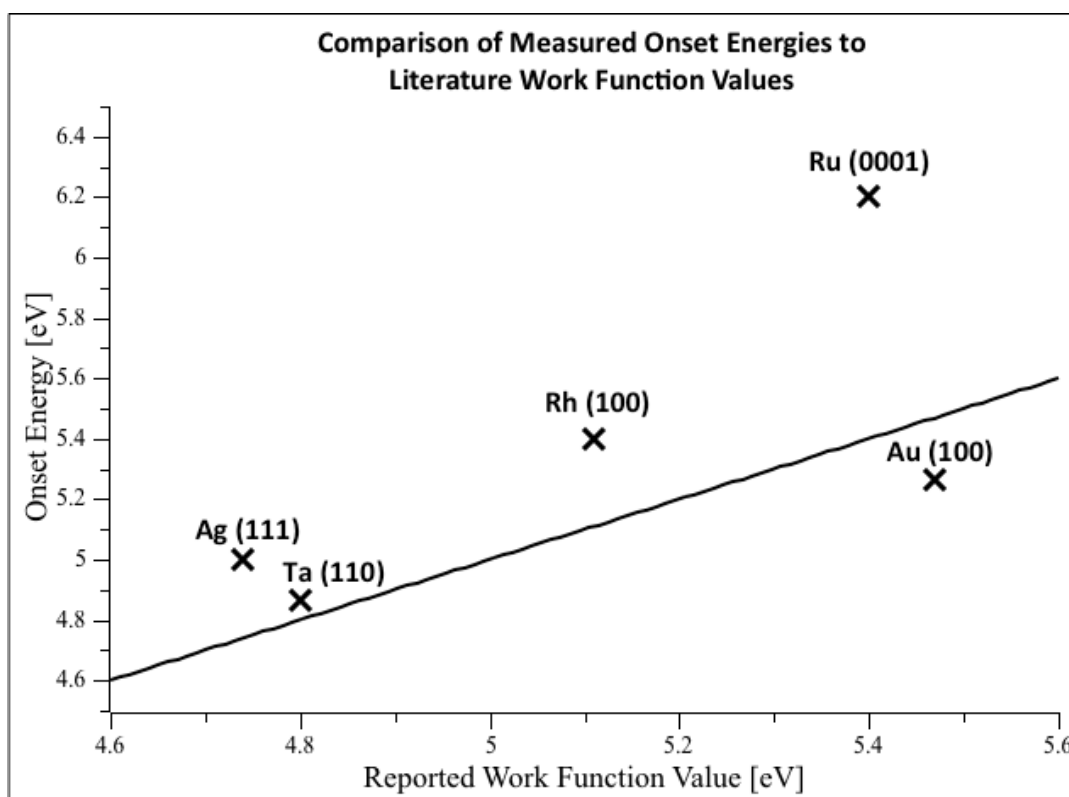


Figure 2.6: Comparison between measured onset energy and reported work function values from single crystal surfaces. The literature values are as follows: Ag (111) 4.74 eV [101], Ta (110) 4.80 eV [101], Rh (100) 5.11 eV [105], Ru (0001) 5.4 eV [106], Au (100) 5.47 eV [101]. $E_p=10\text{keV}$, $V_B=-9\text{V}$.

3 replicate spectra were collected from 3 different regions (within the sputtered area) for each single crystal surface. The onset energy was determined by the maximum in the second

derivative of the onset spectrum. Figure 2.6 compares the average of the three replicate measurements of the onset energy with work function values reported in the literature. Agreement between the measured and reported values varies significantly between the metal surfaces. The best agreement is found with the Ta (110) surface. This is encouraging, as the work function of single crystal Ta surfaces have been extensively studied for the purposes of characterizing electron emitters, and there exists a high degree of confidence in their reported values [101]. The largest discrepancy is found in the case of the Ru (0001) surface. The reported work function value was obtained from a surface, which was sputtered cleaned with reactive O and H ion beams. It is possible that these contributed to the differences observed in our measurements. Overall, there appears to be a slight positive bias in the onset energy relative to the literature values. It is possible that this is due to the fact that the method relies on determining the *onset* of a signal above the background. The detection limits of the CMA, as well as the use of the 2nd derivative to determine the onset energy may all contribute to the observed bias. It is also possible that the crystallographic structure of the single crystal surfaces was altered during sputter cleaning with Ar⁺ ions. The surface must be cleaned in order for these measurements to be meaningful, and so this procedure is unavoidable in this microscope. Having the ability to remove surface contaminants via low temperature UHV annealing, would avoid use of the ion beam.

Given the importance of the surface condition in conducting repeatable measurements, various experimental parameters must be optimized. Environmental surface contamination is unavoidable, and has a significant impact on work function measurements. Under the action of the electron beam, organic contaminants present on the surface (i.e. hydrocarbons) may

polymerize, thus changing the surface properties in the irradiated area [107]. This phenomenon is colloquially known as “raster burning.” The thickness of the carbonaceous film, d_c , scales with the beam parameters via,

$$d_c \propto \frac{I_p t}{a} E^{-0.8} \quad 2.6$$

where I_p is the probe current, t is the irradiation time, a is the irradiation area, and E is the primary beam energy [86]. Thus to minimize the degree to which the surface is compromised by virtue of the measurement process, the probe current and measurement time should be minimized. This has the obvious detrimental effect of reducing the signal intensity of secondary electron emission, and increasing the noise level. Maximizing the analytical area, a , will reduce the degree of spatial resolution when acquiring surface potential maps. Eq. 2.6 also suggests that increasing the primary beam energy will be beneficial in avoiding surface contamination.

Unfortunately, the secondary electron yield, δ , defined as $\delta = I_{SE}/I_p$, where I_{SE} and I_p are the secondary electron emission current and primary beam current respectively, also decreases with increasing primary beam energy [86], and so signal intensity will be sacrificed. This is because the range of the primary beam electrons scales with the primary beam energy, and thus less of the primary beam energy is dissipated at the surface.

An example of the dependence of beam parameters on the measurement of onset energies is shown in Figure 2.7. Here, onset energy line profiles were taken on a semiconductor grade p-doped Si (100) wafer (Silicon Inc. Boise, ID). Onset spectra are acquired from 256 discrete points along the line, which corresponded to a point-to-point distance of ~20 nm. The onset energy is then calculated by computing the maximum in the second derivative of the onset spectrum. The Si wafer provides a well-defined and homogeneous surface for such an

investigation. It is expected that under ideal conditions that such a line profile will be horizontal, and that any deviation from the ideal case is assumed to result from the measurement process and not the sample. The onset spectra shown in Figure 2.7 were collected under identical conditions, the only difference being the probe current used during acquisition of the spectra. The onset profile shown on the left of Figure 2.7 was taken with a probe current of 10 nA, and shows a 0.9 eV variation in the measured onset energy. This is in contrast to the profile shown on the right of Figure 2.7, which shows a substantially less variation in onset energy of 0.1 eV. We note that the nominal work function value for Si is 4.91 eV [101]. While both measurements exhibit a significant positive bias, the value obtained with the 1 nA beam is closer to this nominal value.

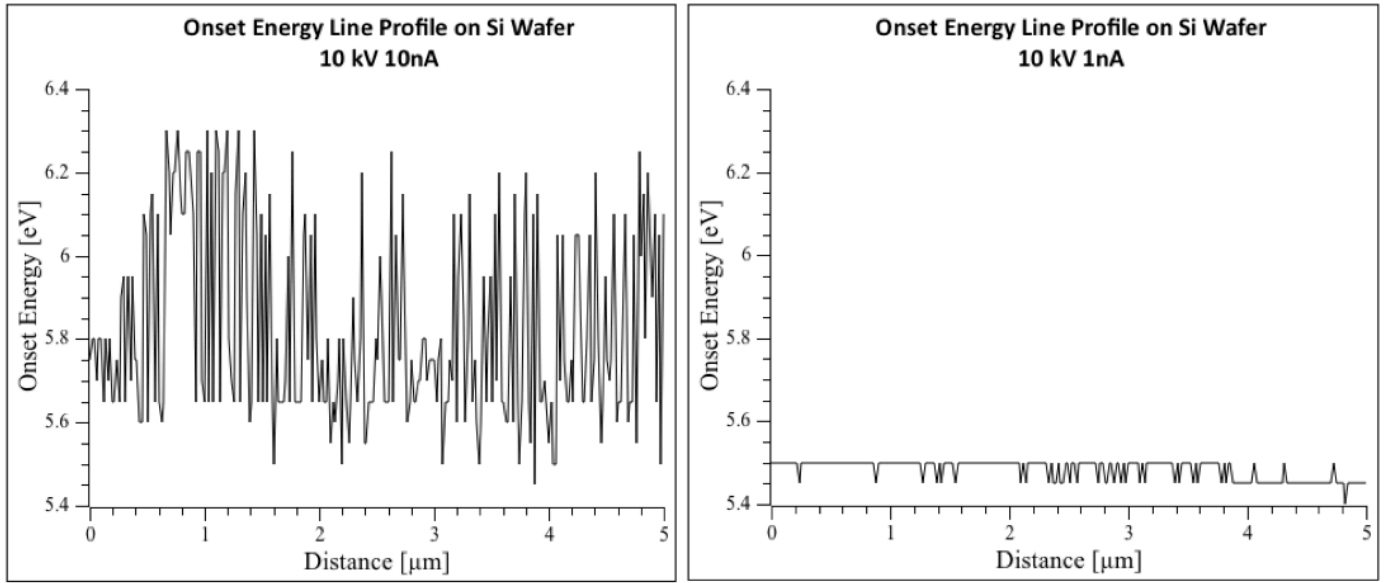


Figure 2.7: Onset energy line profiles taken on the surface of a Si wafer using two different probe currents: 10 nA (left) and 1 nA (right). $E_p=10\text{keV}$, $V_B=-9\text{V}$.

It is believed that the discrepancies observed between the two line profiles in Figure 2.7 is due to a buildup of a contamination layer during the measurement, as was observed in SEM

images. Figure 2.7 demonstrates that whatever advantage might exist in the use of large probe currents with regard to both precision and accuracy in determination of the onset energy, that the impact of the measurement process on the sample surface negates these gains.

As mentioned above, the use of a grounded metallic mask was found to have a significant impact on the onset spectrum. Shown in Figure 2.8 are two onset spectra taken from an Au (100) surface. The black curve was acquired in the presence of a circular Mo mask placed close to the sample surface. The red curve was acquired in the absence of this mask. We note that the red curve exhibits two onset energies. The first is around 12.5 eV, and is labeled as the secondary onset energy. The second is around 16 eV, and is significantly upshifted from the first onset energy. This is labeled as the primary onset energy.

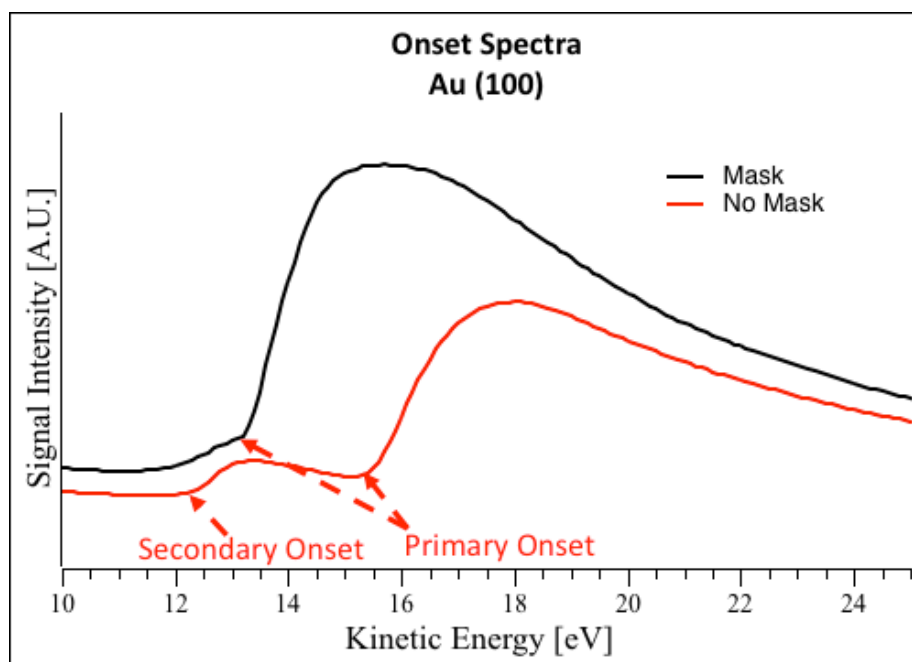


Figure 2.8: Comparison of onset spectra acquired in the presence and absence of a grounded Mo mask. $E_p=10\text{keV}$, $V_B=-9\text{V}$.

The low energy of the electrons required for the onset measurement are highly susceptible to scattering by the presence of fringe electrical fields, which may be present near the surface or within the microscope. This issue has previously been reported in the case of using the onset method to measure the potential difference at the step of a Cs thin film on a W substrate [99]. There, the large surface potential difference at the Cs/W interface (~ 3 eV) resulted in the presence of two energies of onset. In the present case, the single crystal Au surface is not expected to have such drastic differences in surface potential, and so it is not believed that the shift in the primary onset energy is related to the sample. The relative increase in primary onset energy in the absence of the mask (red spectrum), indicates that the secondary electrons near the onset energy are scattered away from the detector in the absence of the mask. Even in the presence of the mask (black curve), there appears to be a small increase in the signal intensity near the value of secondary onset. The overall signal intensity acquired in the presence of the mask is also larger, indicating that less secondary electrons were scattered away from the detector. Thus, it is believed that the mask acts as an electrostatic lens, which is able to guide secondary electrons to the detector. The efficacy of the lens will depend upon the sample bias voltage, the sample to mask distance, and the distance of the electron from the optical axis of the lens. It is believed that the presence of fringe fields will impact the accuracy in determination of the work function, and use of a metallic mask helps to mitigate this. The easiest parameter to alter the effect of the lens is the sample bias. However, we note that the resolution of the CMA scales with the measured kinetic energy of the secondary electrons. Thus, as the bias voltage increases, the spectral resolution decreases, which negatively impacts the accuracy in the determination of the onset energy.

It was noted earlier that the acquisition time of a surface potential map can be significantly reduced if the signal intensity, at a fixed E_{pass} (Figure 2.5), is monitored across a given region. Reduction of the acquisition time has the primary advantage of reducing the exposure of the surface to the electron beam. However, variations in the measured intensity of E_{pass} , may not strictly depend upon variations in the surface potential. In principle, the secondary yield, δ , may also contribute to the measured intensity at E_{pass} . It has been shown that the relationship between δ and Φ is not straightforward [108]. The secondary yield will depend upon beam parameters, i.e. accelerating voltage [86] or probe current, which are assumed to be constant during the measurement, and therefore cannot be responsible for observed differences in surface potential. δ will also depend upon characteristics of the sample such as composition and surface topography [86]. Such sample properties, may of course, vary across a given analytical region. In this regard, experiments were conducted to see if and to what extent, surface properties affecting the value of δ might impact surface potential imaging at a fixed pass energy.

Shown in Figure 2.9 are the results of an experiment, which demonstrate the possible impact of material differences in the measurement of changes in surface potential. Here, a thick Au film was deposited on a portion of a Fe surface, in order to produce a region with a different work function. We note that the value of δ and the work function, are larger for Au than Fe. An SEM image of the interface is shown in the left panel of Figure 2.9. The electron beam was scanned across the interface, schematically depicted by the dotted yellow line. Onset spectra, as well as the Au and Fe Auger signal intensities, were acquired at discrete points along this line. Their respective profiles are plotted in the right panel of Figure 2.9.

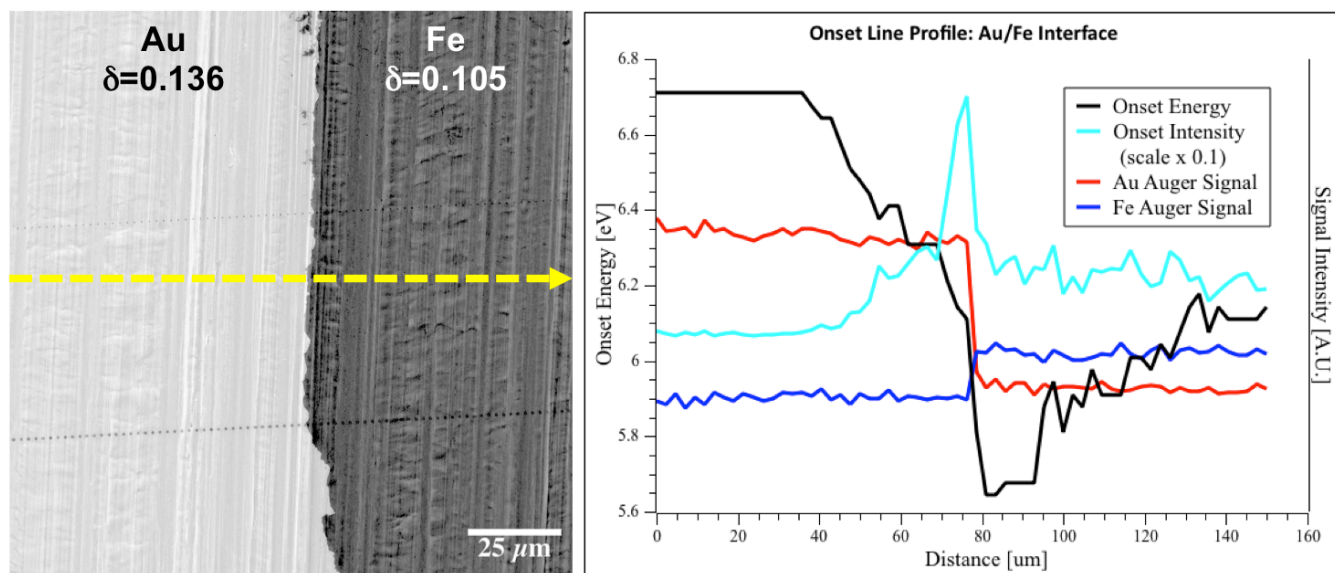


Figure 2.9: SEM image of an Au/Fe interface (left panel). The dotted yellow line indicates the scanning direction of onset and Auger line profiles (right panel) taken across the interface. $E_p=30\text{keV}$, $V_B=-17.9\text{V}$.

The onset energy (Figure 2.9, black line) was determined by the maximum in the 2nd derivative of the spectrum. The variation in the onset spectrum intensity (Figure 2.9, cyan line), was monitored by fixing the analyzer pass energy to 24.5 eV. We note that the intensity at this energy is inversely related to the work function. Namely, that the larger the onset *intensity*, the lower the work function. The onset energy shows a difference of about 0.6 eV, which is in good agreement with previously reported values [101]. The onset spectrum *intensity* increases as one passes from the Au to the Fe side of the interface. If differences in δ were significant, one would expect the opposite trend. Namely, that because δ is larger for Au than Fe [109], the onset spectrum intensity at E_{pass} could be larger on the Au side of the interface. The onset spectrum intensity profile in Figure 2.9 (cyan line) shows that this is not the case. Therefore, variations in δ across a sample surface due to material differences are not expected to impact the interpretation of surface potential data using this method. This data demonstrates that the onset

method can be used to accurately measure work function *differences* across a sample surface.

We note that while the Au and Fe Auger signal intensities (Figure 2.9 red and blue lines) show a rather sharp interface, that the onset energy profile is slightly broadened. It may be that this is due to charge segregation (contact potential) at the interface of two dissimilar metals.

The effect of the possibility for topographic contrast is shown in Figure 2.10. These data were acquired from a graphene coated Cu surface. This sample was selected due to the fairly large degree of surface topography, as evidenced by the terraced morphology shown in the SEM image in Figure 2.10 B. Figure 2.10 A is a surface potential map acquired at fixed pass energy from the same field of view as Figure 2.10 B. We see in the surface potential map that contrast exists at the edges of the terraces, as indicated by the white arrows (Figure 2.10 A). The top white arrow in Figure 2.10 A shows that the surface potential is lower at these edges relative to the surrounding area, i.e. at the top of the terrace. In the case of the region indicated by the bottom white arrow, the surface potential is higher at these edges with respect to the surroundings, and also the region indicated by the top white arrow. Moreover, when considering the entire field of view, it appears that the terrace edges on the lower portion of the terraces appear to systematically exhibit lower contrast with respect to the edges on the upper portion of terraces. While it might be expected that variations in the surface potential exist at atomic or nanometer sized steps, it is surprising that relative variations in the surface potential are not the same at the edges of these terraces. This might suggest that there is some type of shadowing responsible for what appears to be systematic contrast. We note that the analyzer in the microscope is coaxial to the primary beam, so that such shadowing cannot be explained by the relative geometry of the source and detector. Figure 2.10 C shows a higher magnification

surface potential map of a similar region. Again, contrast can be seen on either side of the terrace edges.

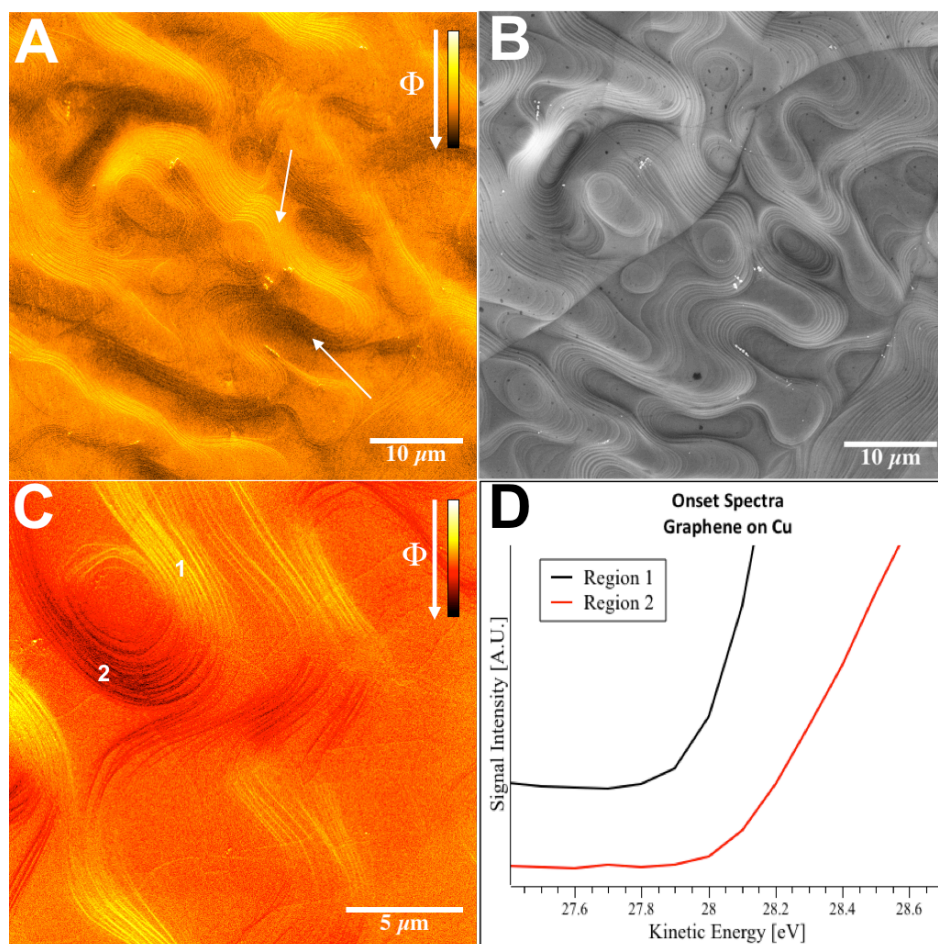


Figure 2.10: A: Surface potential map of a graphene coated Cu substrate $E_p=25\text{keV}$ $V_B=-20\text{V}$. White arrows indicate terrace edges, which exhibit a high degree of contrast. B: SEM image of the same field of view as A. C: Surface potential map of a graphene coated Cu substrate taken from a similar region as A, $E_p=25\text{keV}$ $V_B=-50\text{V}$. Onset spectra take from two contrasting sides of the terrace marked as 1 and 2 in C, $E_p=25\text{keV}$ $V_B=-25\text{V}$.

Onset spectra were acquired from two regions, labeled as 1 and 2 in Figure 2.10 C, which exhibited a high degree of contrast. The respective onset spectra are shown in Figure 2.10 D. The spectra exhibit a difference in onset energy of approximately 0.1 eV. Specifically, the surface potential from region 2 is 0.1 eV higher than from region 1. These relative differences

are in agreement with the contrast exhibited in Figure 2.10 C. Thus, it is believed that surface topography does not have a significant impact on the observed contrast in the surface potential map. It is not clear why the observed contrast shown in Figure 2.10 A appears to exhibit systematic variation. We simply note that the Cu substrates used to grown the graphene are very thin ($\sim 20 \text{ }\mu\text{m}$), and that the degree of plastic deformation of the substrate is likely substantial. The systematic variation in surface potential might be related to the underlying crystallographic texture of the substrate.

The data shown in Figure 2.10 illustrates the possibility for the use of the onset method to rapidly produce a map showing surface potential variations. The accuracy of the method can be improved in the following ways: First, by incorporating the ability to anneal samples in the UHV of the microscope, clean surfaces can be prepared without the need for Ar^+ sputtering. It is also believed that the ability to prepare clean surfaces will mitigate the impact of the electron beam on the measurement of the onset energy. Second, a specially designed lens to guide the low energy electrons of interest to the detector, may reduce what appears to be a systematic positive bias. Given that the energy of the electrons is critical in determining the energy of onset, the use of magnetic fields in such a lens poses a significant advantage over electrostatic fields. Nonetheless, these data suggest that the generation of surface potential maps by monitoring the variation in secondary electron emission intensity at a fixed pass energy is a viable way of determining active regions on a given surface. It was shown that variations in the secondary electron yield due to surface topography or material difference have little impact on observed differences in the onset emission intensity. We note that the experimental parameters found to produce accurate and reproducible results were primary beam energies in the range of

25-30 keV, probe currents in the range of 1-5 nA, and sample biases in the range of 25-50 V. This method was applied to the study of MnS inclusions in carbon steel, as well as graphene coated Cu surfaces. The detailed results of these measurements will be presented in the following chapters.

It was observed that contrast differences across the Au/Fe interface, as shown in Figure 2.8, was dependent upon the primary beam energy. This is exemplified in Figure 2.11, which shows two SEM images of the Au/Fe interface.

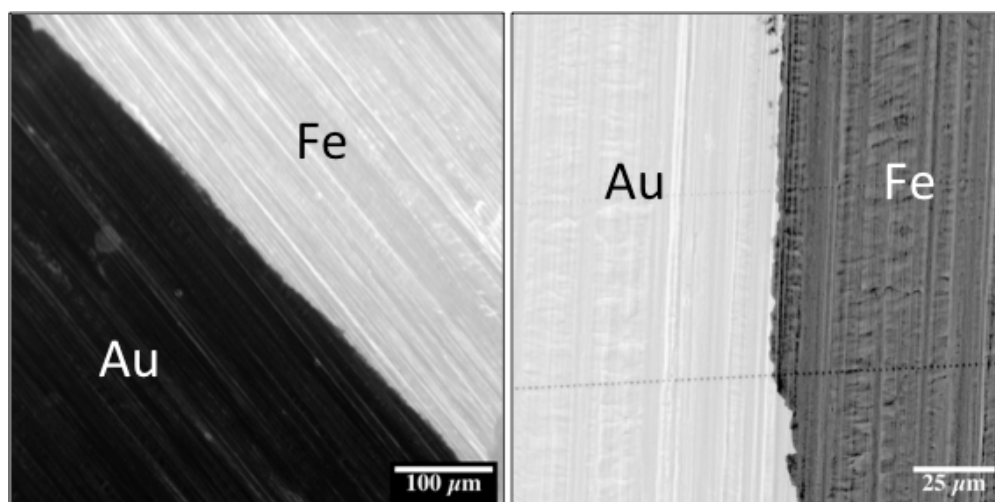


Figure 2.11: SEM images of an Au/Fe interface taken at 200 eV (left) and 30 keV (right) primary beam energies.

The SEM image on the left of Figure 2.11 was taken with a primary beam energy of 200 eV, whereas the SEM image on the right was taken with a primary beam energy of 30 keV. It can be seen that the contrast on either side of the interface is inverted between the two images. This is believed to be due to the relative contribution of the backscatter and secondary electrons to the imaging signal. In the case of the 30 keV image (Figure 2.11, right), the backscatter contribution, which scales with the atomic number [86], dominates. Thus, the Au side of the

interface in this image appears brighter. It is clear that in the case of the 200 eV image, that the contrast mechanism is not identical to the 30 keV image.

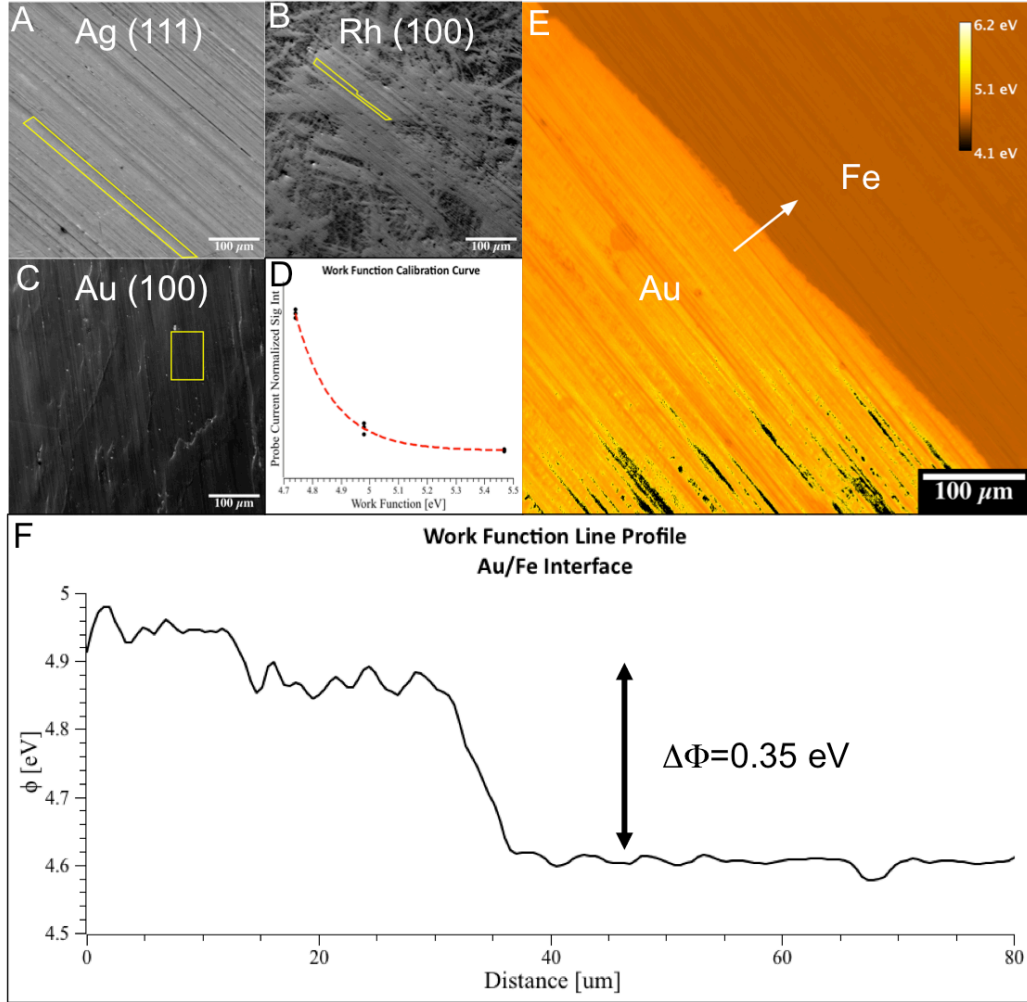


Figure 2.12: A-C: 200 eV calibration images taken from single crystal standards, yellow regions indicate integration regions used in the calibration. D: Resulting calibration curve, red line shows exponential fit to the data. E: Result of calibration curve (D) applied to the image shown in the left panel of Figure 2.11. Image shows surface potential difference across Au/Fe interface. F: Work function profile extracted along the white line shown in E.

While the secondary yield is known to increase with decreasing primary beam energy [86], based upon the data presented in Figure 2.9, it cannot explain the contrast observed in the 200 eV image in Figure 2.11. Nonetheless, given that the work function of Au is higher than Fe, it is

hypothesized that the observed contrast difference in the 200 eV image might be correlated to these work function differences.

The intensity values in the 200 eV SEM image were calibrated with respect to known standards. This is shown in Figure 2.12 A-C. Single crystal Ag, Rh, and Au surfaces were used to conduct the calibration. The integrated intensity within the clean regions (enclosed by the yellow lines shown in Figure 2.12 A-C) of the surface, was normalized to the measured probe current and integrated area. The resulting calibration is shown in Figure 2.12 D, which was fitted to an exponential curve. The nonlinearity of the curve is believed to arise from the nonlinear response of the detector (scintillator). This calibration was then applied to the image shown on the left of Figure 2.11. The result is the calibrated surface potential map shown in Figure 2.12 E. It shows that the work function is higher on the Au side, as it should be. A line profile was extracted from this image, and is shown in Figure 2.12 F. There is fair agreement between the measured potential of 0.35 eV and the nominal value of 0.6 eV [101]. We note that the noise level in the line profile from the Au side of the interface is higher, and is likely due to the intensity values being on the tail end of the calibration curve (Figure 2.12 D). This might also explain the observed inaccuracy in the measured potential difference. We note that the probe size of the 200 eV beam is large, $\sim 1\text{ }\mu\text{m}$, and thus is not suitable for high-resolution surface potential imaging. This method and data are presented here for the purposes of documentation. It suggests the possibility of using a calibrated microscope to rapidly determine work function differences at large length scales on a given surface.

CHAPTER THREE

CHARACTERIZATION OF MnS INCLUSION SURFACES

3.1 Experimental Methods

Samples of 1018 carbon steel were purchased as bars from NESSteel, Inc. (Tolland, CT). The elemental composition in wt.%, as reported by the manufacturer, is 0.14–0.16 C, 0.6–0.9 Mn, less than 0.004 P, less than 0.05 S and the balance Fe. These bars were then cut either parallel or perpendicular to the rolling direction of the steel to produce approximately 1x1 cm² coupons. The coupons were mounted on glass microscope slides using silicone glue and subsequently polished with silicon carbide polishing paper up to 1200 grit (2.5 μm), followed by a diamond slurry down to a smallest particle size of 0.1 μm. The samples were then rinsed with ultrapure deionized water, dried with dry nitrogen, and then unmounted and cleaned via sonication in acetone. The coupons were then introduced into a PHI 710 Integrated Auger Nanoprobe (see 2.3). Typical primary beam energies ranged from 5-20 keV, with probe currents from 1-10 nA. Auger spectra were quantified by using instrumental sensitivity factors [80] provided by Physical Electronics. Auger elemental maps were collected by monitoring variations in the difference in peak and background intensities from spectral regions of interest. To correct for spatial shifts in the electron beam during the collection of Auger data and depth profiles, an image registration algorithm (available in PHI's instrument control software) was used. As is standard practice in the collection of EBSD data, a 20-keV beam was used with the sample tilted to 70 degrees from the horizontal (i.e., electrons entered the surface at an approximate 20-degree grazing angle). Only data points where the confidence index [110] of the

acquired pattern was greater than 0.1 were used. A floated argon-sputtering gun was used to obtain depth profiling and related compositional changes within the surface of the sample down to depths of approximately 60 nm. Ar-ion energies of 500 to 1000 eV were used during depth profile measurements. An estimate of the sputtering rate was determined via depth profiles of standard 100-nm SiO₂ grown on Si wafers.

3.2 Surface Elemental Composition of MnS Inclusions

Figure 3.1 shows an SEM image of a typical “MnS” inclusion from a polished 1018 carbon steel sample, which was cut parallel to the rolling direction of the steel bar. Auger and EDX survey spectra were taken at locations both on the inclusion and on the steel surface (marked respectively as 1, 2 and 3). The spectra from regions 1 and 2 indicate that the inclusion is not solely composed of Mn and S, but contains other elements such as Fe, Cu, and O. The Ar peaks observed in regions 1 and 2 of the Auger spectra are a result of light sputtering (approximately 0.5 nm) to remove some of the environmental hydrocarbon contaminants typically present on any given surface. It is interesting to note that the Ar signal is only observed on the inclusion, despite the fact that the entire region was sputtered with Ar-ions. The observed C signal is believed to originate from environmental contamination left over after the light sputtering. The spectrum from region 3 was collected from an area outside of the inclusion, in the bulk ferrite phase. Evidence of a small *Cu-L* series X-ray peak is observed in the EDX spectrum, but not in the Auger spectrum. Its presence is likely related to the poor lateral resolution of EDX relative to AES, and likely originates from the inclusion. The elements shown in the spectra acquired from the inclusion in Figure 3.1 were commonly observed in this study. Their presence indicates that MnS inclusions are not a pure phase of Mn and S, but also

contain Fe, Cu, and O. A part of this work was devoted to further understand how these elements are incorporated into these inclusions, and how their presence or absence might affect the electrochemical behavior of the inclusion and surrounding interface.

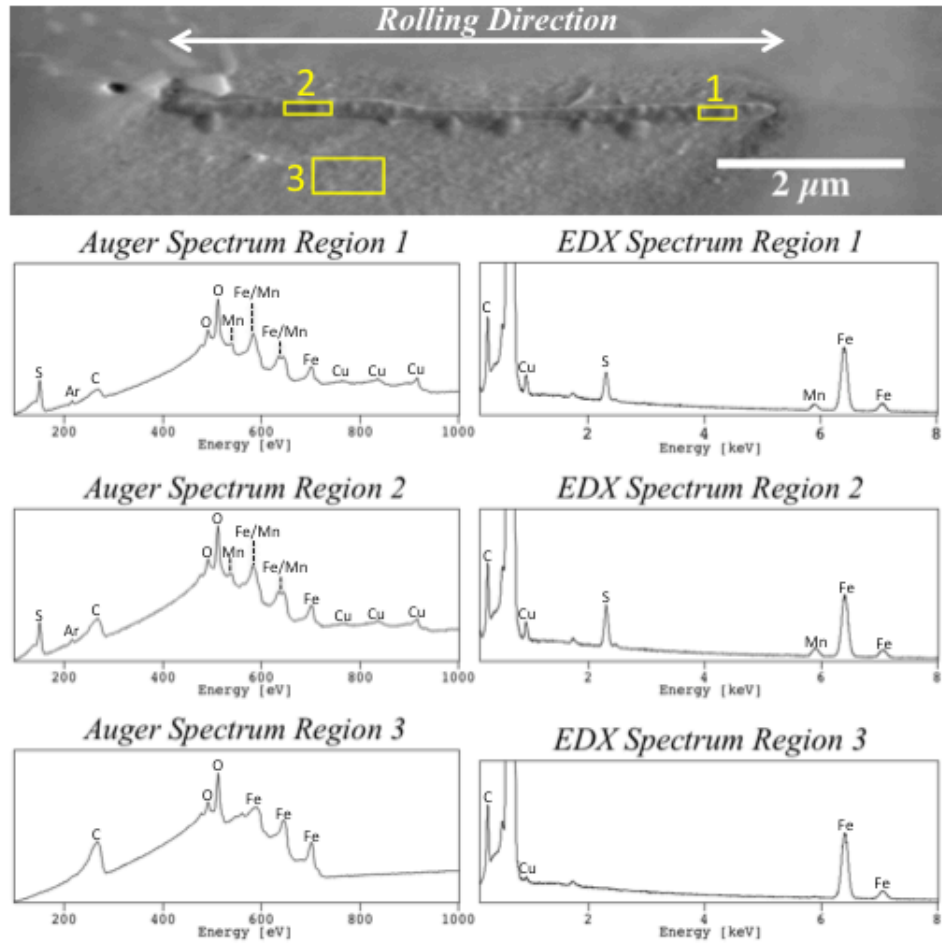


Figure 3.1: Top: SEM image of a MnS inclusion cut parallel to the rolling direction. Bottom: Auger and EDX spectra acquired from the regions marked 1, 2, and 3 in the SEM image (top). $E_p = 10$ keV.

Mn *LMM*, S *LMM*, Fe *LMM*, and O *KLL* Auger elemental maps and cross-sectional elemental line profiles are shown in Figure 3.2. The data were acquired from the same inclusion shown in the SEM image in Figure 3.1. Regions which are relatively enriched in Mn, can be observed on the right side of the inclusion. This enrichment is not observed in the S map,

demonstrating that Mn and S are not everywhere spatially correlated. Upon closer inspection of the SEM image (Figure 3.1), a nodular morphology appears to be associated with these Mn-rich regions.

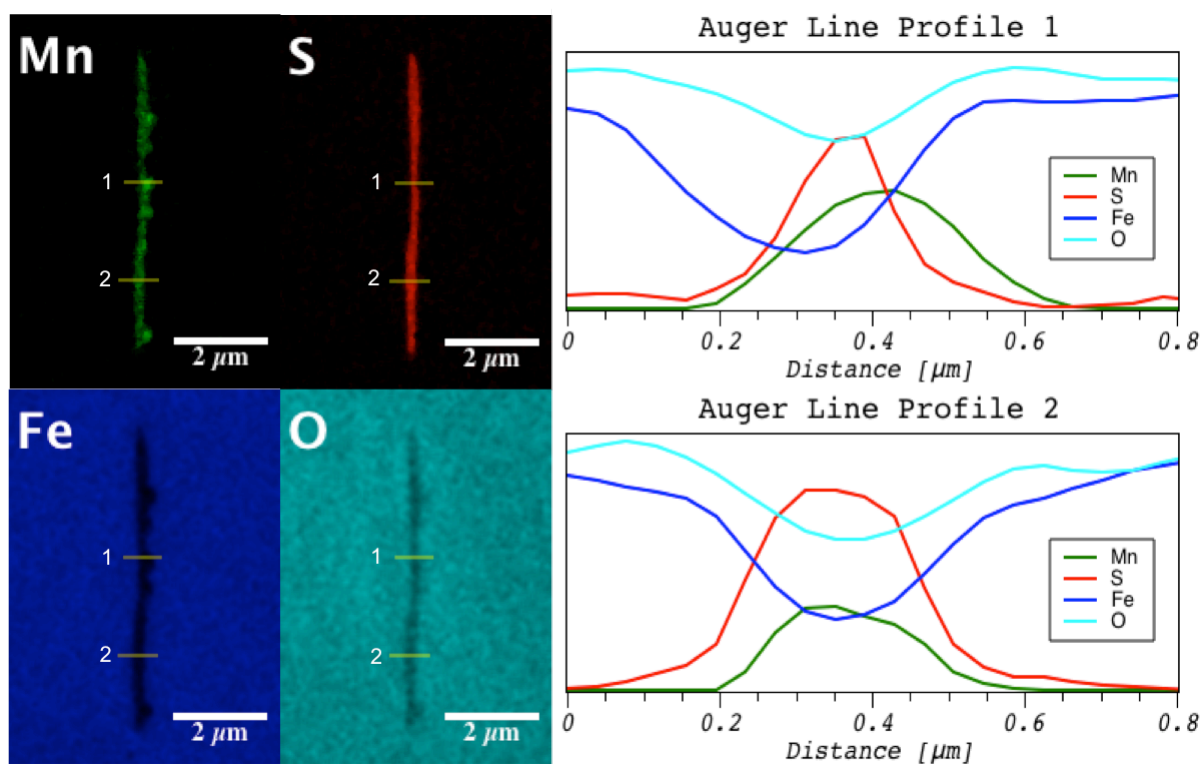


Figure 3.2: Left: Auger elemental maps acquired from a MnS inclusion (see SEM image Figure 3.1). Right: Auger line profiles taken from two regions, labeled as 1 and 2 in the Auger maps. The scan direction is from the left of the field of view to the right. $E_p = 10$ keV.

A cross-sectional line scan across one such nodule is shown in Figure 3.2 (Line Profile 1). The Mn signal profile is shifted toward the right side of the inclusion relative to the S, Fe, and O profiles. We also note that the Fe profile is asymmetric, with a larger concentration gradient (slope) on the right of the inclusion than on the left. These observations suggest that the chemical composition of the nodule is different from that of the bulk inclusion, specifically that the nodule is more akin to a metal oxide than to a metal sulfide. Line Profile 2 (Figure 3.2) does

not pass over such a nodule. Here, the Fe, Mn, S, and O signals are somewhat spatially correlated to one another, and the type of segregation between the Mn and S signals found in Line Profile 1 is not observed. In this case, however, S is observed to extend 100-150 nm beyond the Mn on either side of the inclusion. This suggests the presence of a sulfur-rich interface between the inclusion and the bulk ferrite phase. It is clear that the S content in the immediate surroundings of the inclusion is not exclusively associated with Mn. The solubility of S (as FeS) in a Mn-containing ferrite phase is extremely limited, and its presence is usually confined to interfaces. Rapid quenching of the steel may lead to the presence of FeS in the immediate surroundings of a “MnS” inclusion as well as the presence of Fe in solid solution in the “MnS” lattice [111].

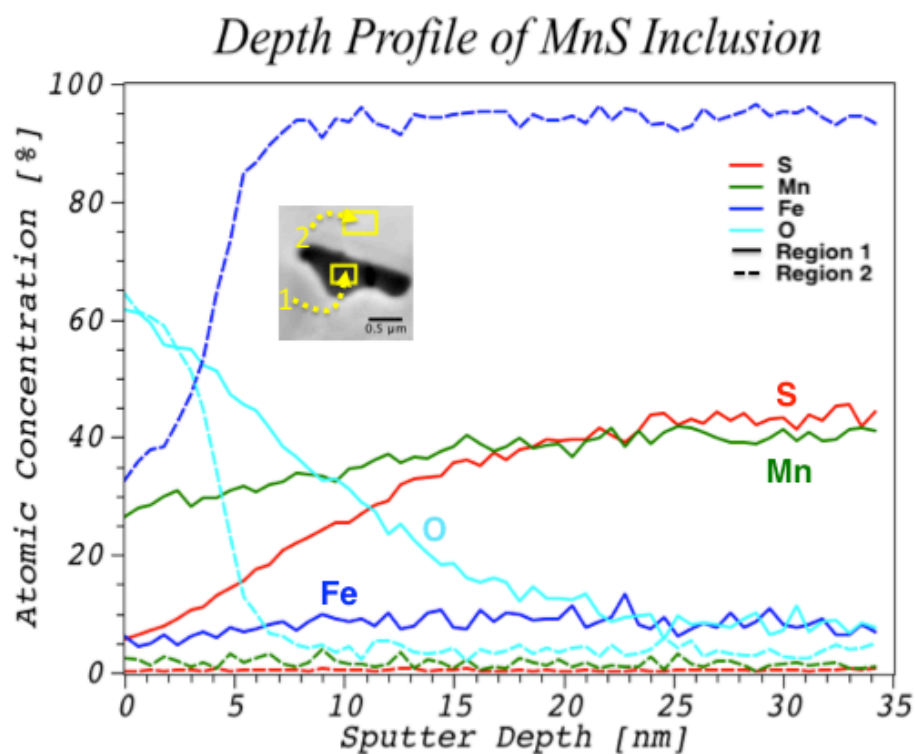


Figure 3.3: Auger depth profiles acquired from the two regions shown in the inset SEM image. Region 1 corresponds to the MnS inclusion shown in the SEM image, and region 2 corresponds to a nearby region of the steel surface. $E_p=10$ keV.

The presence of oxygen within inclusions is seldom discussed in the literature, and it is of interest to discern whether the oxygen peaks seen in the Auger spectra (see Figure 3.1) are restricted to the surface as a metal oxide, a component of the bulk “MnS” inclusion, or a mere environmental contaminant. To investigate this matter, Auger depth profiles were performed on an inclusion from a 1018 carbon steel sample cut perpendicular to the rolling direction. The Fe *LMM*, S *LMM*, Mn *LMM*, and O *KVV* Auger signals were monitored as a function of sputter time (proportional to depth in nm); the results are shown in Figure 3.3. The full lines are data obtained from within the inclusion (Region 1), while the dashed lines are data collected from the neighboring ferrite phase (Region 2). A 500 eV Ar⁺ ion beam was used during the depth profile. The O signal on the ferrite phase (Region 2) rapidly decreases and gives an estimated thickness of about 8 nm, in good agreement with typically reported values of native oxide thicknesses [112]. This is in contrast to the inclusion (Region 1), in which the O signal profile is significantly broader and persists after roughly 20 nm of sputtering. The decrease in the O signal within the inclusion is associated with a slow rise in the S signal, while both the Mn and Fe signals remain relatively unchanged. Moreover, the magnitudes of the slopes of the O and S profiles are similar. This indicates a *replacement* of O with S into the bulk of the inclusion, at an approximate proportion of 1:1. Both MnO and MnS are isometric, with lattice parameters differing by approximately 15% [113,114]; thus, it is reasonable to suggest that the observed O within the inclusion occupy previous S vacancies, and that the diffusion of O within the bulk of the inclusion occurs via hopping to neighboring vacancies. The occupation of S vacancies by O has been previously reported [115].

Shown in Figure 3.4 is a high-magnification SEM image and corresponding Mn *LMM*, S *LMM*, O *KLL* and Fe *LMM* Auger elemental maps of a small region within a MnS inclusion. The SEM image shows nodular like features, ~ 100 nm in size, within the inclusion. The corresponding Auger maps show that these nodules are depleted in S, and enriched in oxygen. Mn is seen throughout the inclusion, and the nodules are thus believed to be some type of Mn-oxide. Given the discussion above, it is likely that the nodules are MnO. Oxygen was still seen in Auger spectra taken from the inclusion even after extensive sputtering (>10 nm). Thus, the oxygen content seen in the nodules is believed to extend fairly deep below the surface, similar to the inclusion shown in Figure 3.3. Figure 3.4 shows that inclusion surfaces can be highly heterogeneous. It is not clear why the oxide phases are spatially segregated from the sulfide region of the inclusion. If the oxidation mechanism of the inclusion is, as suggested above, due to presence of S vacancies, then Figure 3.4 suggests that the vacancy content is or was concentrated within the oxidized regions. Nonetheless, it is clear that the absence of S is associated with the presence of MnO.

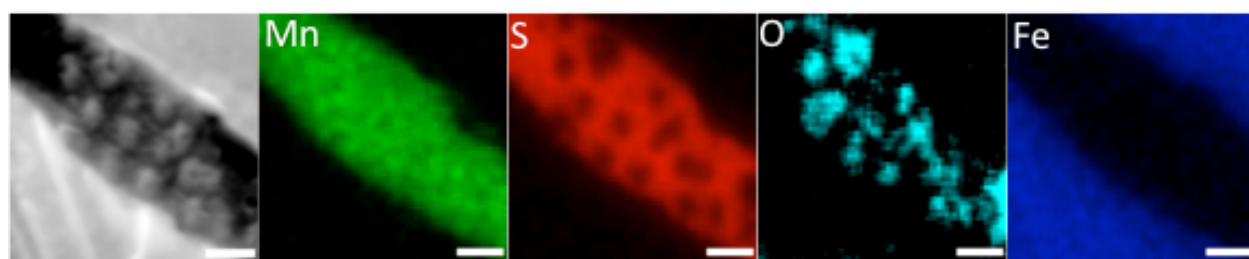


Figure 3.4: SEM image and Auger elemental maps acquired from a MnS inclusion, scale bar is 200 nm. Images indicate the heterogeneous distribution of O, believed to be MnO. $E_p=10$ keV

As discussed above, the observation of Cu within inclusions warranted further consideration. Shown in Figure 3.5 is an Auger depth profile acquired from a MnS inclusion, cut

perpendicular to the rolling direction, as shown in the inset. The Cu *LMM*, S *LMM*, Mn *LMM*, and Fe *LMM* signal intensities are shown as a function of depth. A 500 eV Ar⁺ ion beam was used during the depth profile. The Cu and S concentrations initially increase, and reach a plateau at a depth of ~ 2 nm below the surface. The ratio in atomic concentration between Cu and S in this region is ~ 2:1, and indicates that the Cu is present as Cu₂S. The Cu signal begins to decrease around 4 nm, and reaches the background level at around 6 nm. The S and Mn concentrations increase beyond the removal of Cu, and approach a ratio of 1:1, indicative of MnS. It is therefore believed that the inclusion was covered with a 5- 6 nm film of Cu₂S. This range of thicknesses of Cu₂S layers was observed on many inclusions studied. We note that the Mn content is negligible within the Cu containing film, which suggests that Cu replaces Mn. This is not the case for the Fe content, which is constant throughout the film, as well as the inclusion. An SEM image of the inclusion, post sputtering, is shown in the inset of Figure 3.5. A light feature can be observed near the bottom of the inclusion shown in the inset of Figure 3.5. EDX analysis from the inclusion indicates that this region is Cu containing, likely Cu₂S. The fact that Cu was observed with X-rays post sputtering, indicates that it forms the bulk composition in this region. Therefore, it is suggested that the bright feature is a separate Cu₂S phase (stringer), which coexists alongside the MnS inclusion. Because of its affinity for sulfur, the presence of Cu near sulfide inclusions is not surprising. However, it is noted that Cu₂S has a higher standard energy of formation than MnS [113].

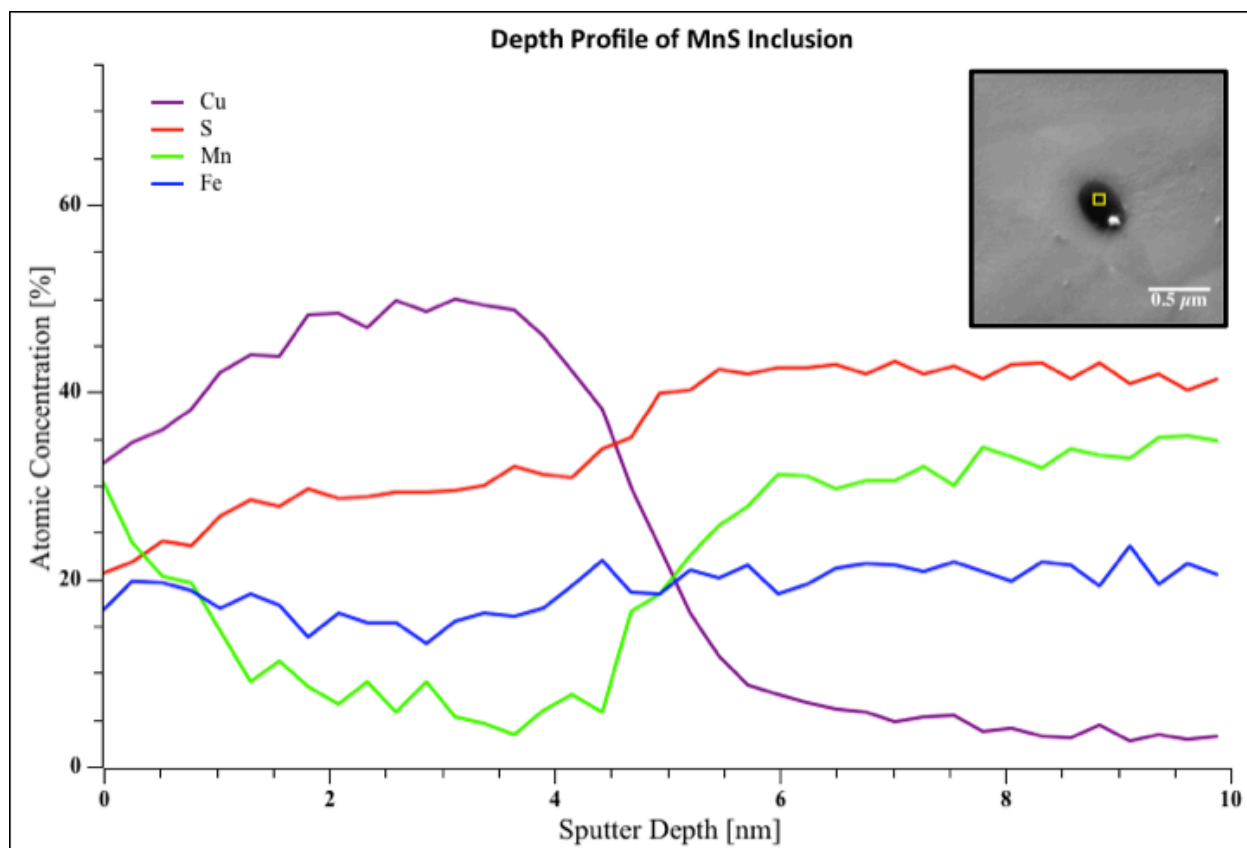


Figure 3.5: Auger depth profile taken from a MnS inclusion shown in the inset SEM image. A thin (5-6 nm) Cu_2S film is observed on the inclusion. $E_p=10$ keV

Segregation of phases was observed in Cu coated inclusions, similar to what is exhibited above in Figure 3.4. Shown in Figure 3.6 are S *LMM*, Cu *LMM*, Mn *LMM*, and O *KLL* Auger elemental maps of a Cu coated MnS inclusion. The images suggest the presence of two distinct phases: Cu_2S and MnO. The MnO phases are again present as discrete islands, as indicated by the white arrows. Depth profiles conducted on the inclusion demonstrated that the Cu is again present as a thin film. Thus, Cu appears to have been able to replace Mn except in the MnO phases. It is also possible that the isolated Mn regions were sources of S for growth of the Cu_2S film, which subsequently oxidized due to a depletion of S.

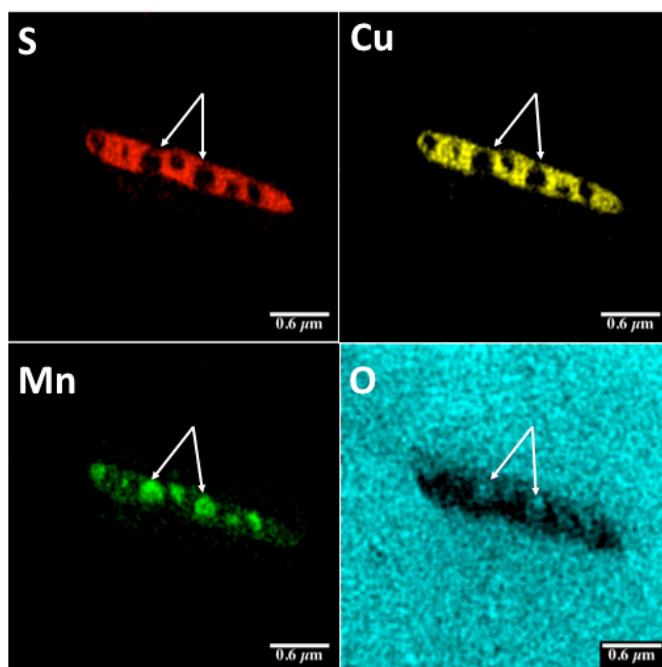


Figure 3.6: Auger elemental maps taken from a MnS inclusion. Images indicate the heterogeneous distribution of a Cu_2S film. $E_p=20\text{keV}$

Upon exposure to various corrosive environments, others have observed the presence of Cu_2S on MnS inclusions in stainless steels alloyed with Cu [25,32,116,117]. In these references, it was suggested that dissolved Cu-ions act to passivate some inclusions. EDX was used to characterize inclusions before exposure, and did not indicate the presence of Cu. However, this technique would be insensitive to the presence of a thin Cu_2S film, and it cannot be ruled out that such a film would be responsible for the observed passive behavior, and even act as a site for continued growth of a Cu_2S film. In the present case, it is not clear what the source of the Cu_2S film on a MnS inclusion might be. One possibility is that pure Cu_2S inclusions (e.g. bright region in the inset of Figure 3.5) are distributed within the carbon steel matrix, and act as a source of Cu. During sample preparation (i.e. cutting and polishing) of the steel coupon, the observed thin Cu_2S film may form, although it is not clear. Nonetheless, such surface heterogeneities of MnS

inclusions are likely to be a reality in commercial steels, as well as in corrosion experiments, and thus knowledge of their presence is of value.

3.3 Chemical Analysis of Inclusion Surfaces

As mentioned in section 2.3, since the kinetic energy of Auger electrons should depend upon the binding energy levels associated with the transition, it should be possible to extract chemical information from Auger spectra. It has been shown however, that rather poor agreement exists between the kinetic energy of Auger electrons and the calculated value using eq. 2.2 [85]. Moreover, the high degree of peak broadening, and rather poor spectral resolution of the CMA, makes the use of core-level Auger transitions difficult for the purposes of chemical analysis. Another strategy is to use Auger transitions involving valence band electrons. Because the electronic structure of the valence band will vary with chemical state, the line shape of these transitions can be used to identify various chemical species present on the surface. This has been demonstrated in the case of metal oxides [118]. Within the context of pitting corrosion, it is of value to be able to determine changes in the properties of the native oxide film at the inclusion/steel interface. Chemical changes might explain why the passive properties of the oxide film are compromised at this interface. Moreover, the low kinetic energies associated with these Auger transitions ($\sim 10\text{-}50$ eV), make them particularly surface sensitive.

Shown in Figure 3.7 is an example of the Fe *MVV* Auger transition, taken from a 1018 carbon steel surface. The direct and differentiated spectra are shown in the left and right panels of Figure 3.7 respectively. The black curve was taken in the presence of the native oxide layer on the steel surface. The red curve was taken upon removal of the oxide layer via Ar^+ sputtering, and thus represents metallic Fe. We see that in the case of the oxide two peaks are

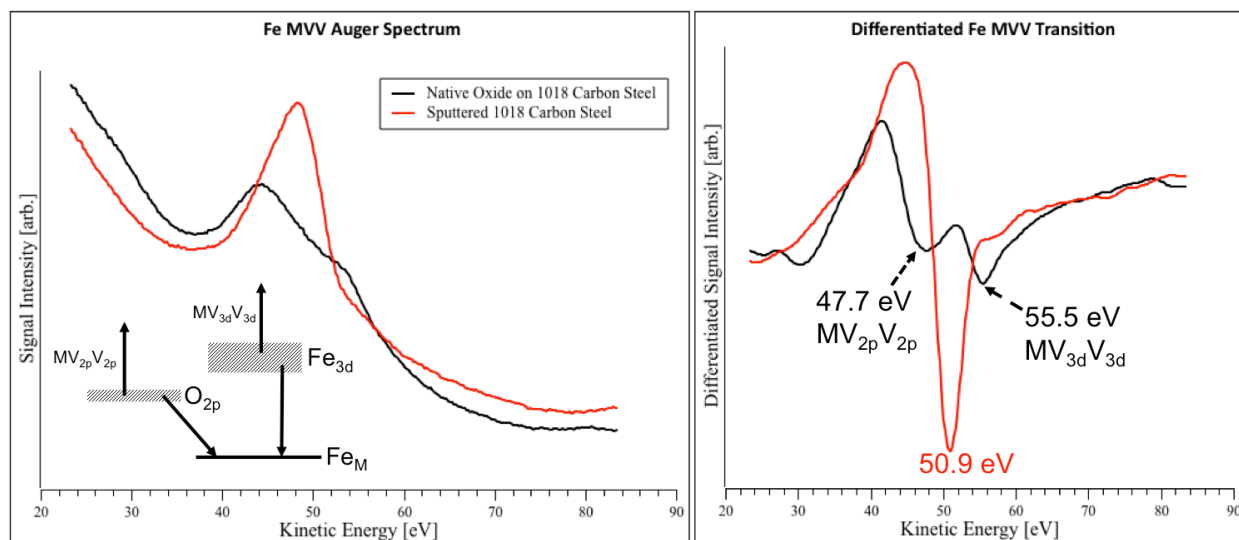


Figure 3.7: Fe MVV Auger spectra acquired from a 1018 carbon steel surface. Left panel: Direct spectrum. Right panel: Differentiated spectrum. Black/Red curves correspond to the native oxide/metallic surface respectively. $E_p = 2\text{keV}$.

present at 47.7 and 55.5 eV. The difference of 7.8 eV is in fairly good agreement with previously reported values for $\gamma\text{-Fe}_2\text{O}_3$ [119], which is believed to form on Fe surfaces at temperatures less than 200 C [6]. Upon removal of the oxide layer, a single peak at 50.9 eV is observed, in good agreement with the nominal value [120]. The peaks at 47.7 and 55.5 eV have been interpreted as transitions involving the 3d and 2p bands of Fe and O respectively, and the peak separation as being equivalent to double the 3d-2p band energy difference [118], and one may write the two transitions as $MV_{3d}V_{3d}$ and $MV_{2p}V_{2p}$, as indicated in Figure 3.7.

As discussed in section 3.2, it is believed that some regions of the inclusion surface are MnO, whilst others are MnS. Thus, it was desired to be able to distinguish between the two Mn species by use of low energy Auger electrons. Reference spectra were collected from various Mn containing surfaces, and are shown in Figure 3.8. The spectrum on the bottom of Figure 3.8 was collected from Mn metal (Sigma Aldrich), which possessed a native oxide layer.

Quantification of the Auger spectrum acquired from the native oxide, indicate that the atomic ratio of Mn:O was 1:1, and is thus believed to be MnO.

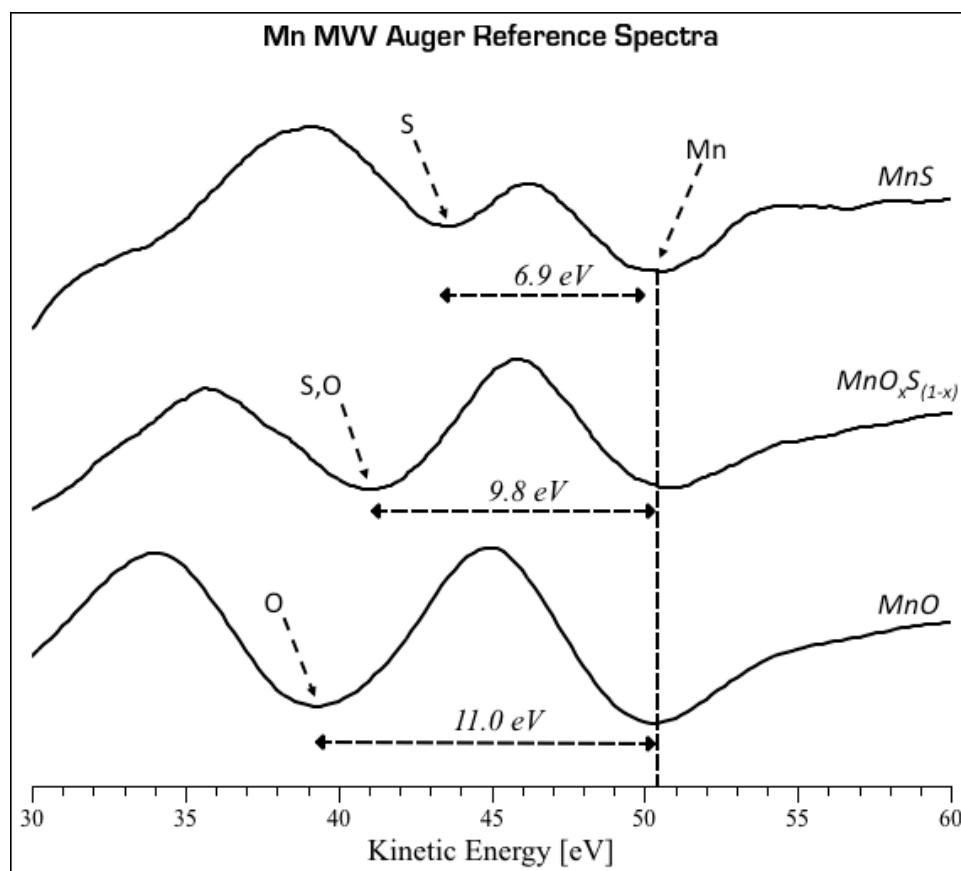


Figure 3.8: Differentiated Mn MVV Auger reference spectra acquired from MnO, $\text{MnO}_x\text{S}_{(1-x)}$, and MnS surfaces. For MnO and MnS spectra $E_p = 5$ keV. For $\text{MnO}_x\text{S}_{(1-x)}$ $E_p = 10$ keV.

The middle spectrum was collected from a MnS powder (Sigma Aldrich). The powder in the “as received” condition contained a significant amount of oxygen, which required extensive sputtering to remove. This is in agreement with the observation of a thick oxygen-containing layer on MnS inclusion surfaces (c.f. Figure 3.3). Thus, the middle spectrum in Figure 3.8 is believed to represent $\text{MnO}_x\text{S}_{(1-x)}$, i.e. that the O is in solid solution with S. The top spectrum in Figure 3.8 was acquired after removal of O, via extensive sputtering of the MnS powder, and is

believed to represent MnS. As in the case of the oxidized steel surface (Figure 3.7), a single Mn MVV peak is split into two when bound to O or S. The difference in kinetic energy between the two peaks appears to vary depending on the chemical state, from 11 eV in the case of the oxidized Mn metal surface to 6.9 eV in the case of MnS. Thus it appears that the peak separation decreases as the O content in MnS decreases. We note that the position of the high-energy peak (~ 50.5 eV), does not change between standards. Therefore, it is reasonable to suggest that this peak is related to the Mn 3d states and represents the $MV_{3d}V_{3d}$ transition. Likewise, the low energy peak is related to the O 2p and S 3p states and represents the $MV_{2p/3p}V_{2p/3p}$ transition. Previous UPS data taken from MnO and MnS surfaces [121,122], shows that the Mn 3d states are peaked at similar binding energies at 3.7-4 eV, while the O 2p and S 3p states are peaked at 7 and 6.3 eV respectively. This suggests that the separation of the peaks observed in the MVV transition should be larger in the case of MnO than in the case of MnS, which is confirmed by the reference spectra in Figure 3.8. However, in the case of MnO, the photoemission data indicate a difference in the Mn 3d and O 2p states of ~ 3 eV. The predicted peak separation in the Mn MVV spectrum would be 2 fold this value or 6 eV, which is much less than the observed difference of 11 eV. Thus, the simple picture shown in the inset in the left panel of Figure 3.7, does not sufficiently explain the observation of the two peaks in the Mn MVV transition. The same is true for the case of MnS. This discrepancy has been previously reported in the case of MnO [118]. Nonetheless, the spectra shown in Figure 3.8 are believed to be useful in ascertaining the chemical state of Mn within MnS inclusions.

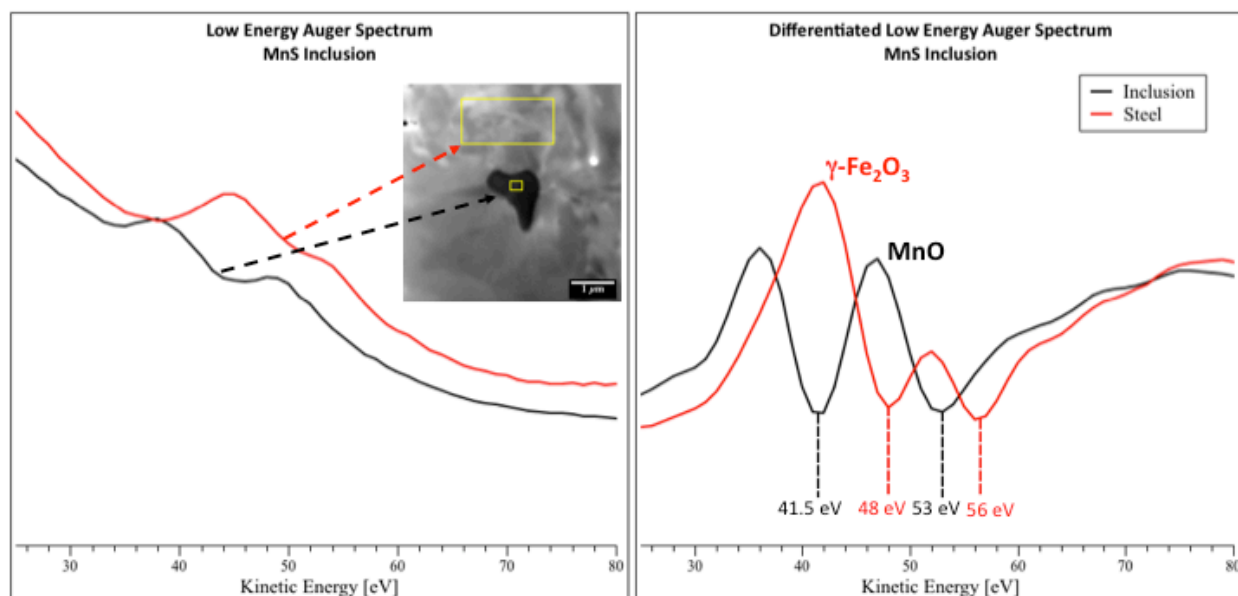


Figure 3.9: Fe and Mn MVV Auger spectra acquired from a MnS inclusion (black curve) and from a nearby region of the steel surface (red curve). Left: Direct spectrum. Right: Differentiated spectrum. SEM image of the analytical regions shown in the inset in the left panel. $E_p = 5$ keV.

Shown in Figure 3.9 are *MVV* Auger spectra acquired from the surface of an inclusion, and the neighboring steel surface (see left panel inset, Figure 3.9). Here, the spectrum taken from the inclusion (black curve, Figure 3.9) is shifted down in energy with respect to the spectrum taken from the steel surface (red curve, Figure 3.9). The peak energy difference in the spectrum taken from the inclusion is ~ 11.5 eV, in fairly good agreement with the reference spectrum for MnO (Figure 3.8), though we note that the resolution of the spectrum shown in Figure 3.8 is not as good as the reference. The peak separation in the spectrum taken from the steel surface is ~ 8 eV, in good agreement with the value obtained for γ -Fe₂O₃ (Figure 3.7). The high energy peak position in the Mn MVV spectrum at ~ 53 eV is slightly higher than reference spectra taken from pure Mn containing samples (Figure 3.8). This might be due to the fact that the inclusion contains a small amount of Fe, which would result in an upward shift of the d-

states. Figure 3.9 shows that there is sufficient differences in the peak positions, particularly with those associated with MnO and $\gamma\text{-Fe}_2\text{O}_3$ in the *MVV* spectrum, to be able to distinguish between the native oxide formed on the steel and the oxide(sulfide) present on the inclusion. This also implies that one can map the distribution of oxides on a steel surface.

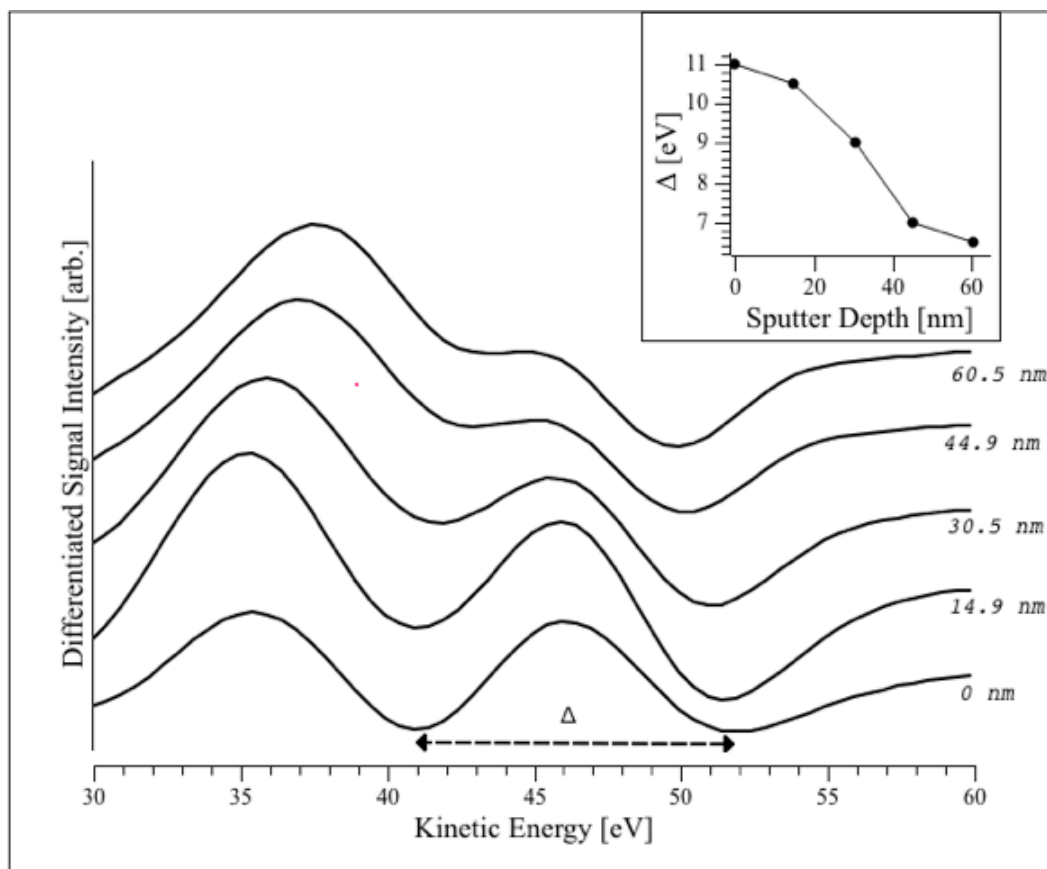


Figure 3.10: Differentiated Mn *MVV* spectra acquired from a MnS inclusion at various depths. Inset shows the change in the value of Δ , which is associated with the chemical state of Mn, as a function of depth. $E_p = 5\text{keV}$.

The Mn *MVV* transition was used to provide insight into the broad O depth profile observed on inclusion surfaces (c.f. Figure 3.3). In particular, it was desired to be able to identify the type of oxide present within the inclusion bulk. Shown in Figure 3.10 are Mn *MVV* derivative spectra collected at various depths below the surface of a MnS inclusion. Difference

in energy between the two peaks, marked as Δ in Figure 3.10, can be used to assess the change in chemical state of Mn within the inclusion. The inset shows Δ as a function of depth, which is observed to decrease from a value of 11.0 eV to 6.5 eV. The initial value of $\Delta=11.0$ eV agrees well with the reference spectrum for MnO (see Figure 3.7). As seen in Figure 3.10, Δ decreases to a value of 6.5 eV at a depth of approximately 60 nm, which is in good agreement with the MnS reference spectrum (see Figure 3.8). A value of Δ in between 11 and 6.5 eV, is believed to be related to the degree of substitutional oxygen present at the surface. Thus, the continuously decreasing value of Δ in Figure 3.10 is believed to reflect the decreasing number of substitutional oxygen atoms with increasing depth. We note that the position of the peak in the Mn *MVV* transition at ~ 52 eV, exhibits a downshift of over 1 eV with inclusion depth, in better agreement with the reference spectrum for MnS shown in Figure 3.8. As discussed above, this could be related to changes in the Fe content within the inclusion, although the depth profile data (not shown) does not indicate substantial differences in the Fe content. We hypothesize that the MnS inclusions formed during the metallurgical preparation of the steel are nonstoichiometric and contain S vacancies. This may be a kinetic effect related to the amount of available S during solidification of the inclusion. This is not unreasonable, as Mn is typically added in proportion to 10 times the expected S content. Another possible source of S vacancies is oxidation of surface S atoms, which result in the formation of volatile S compounds, i.e. SO, SO₂, etc. These vacancies may accommodate O atoms, and subsequent diffusion of O into the bulk occurs via these S vacancies. From thermodynamic considerations (free energy of formations) it appears that MnO is favored over MnS at room temperatures [113].

Thus, we suggest that the correct formulation of the composition of MnS inclusions may be written as $\text{Mn}_{(1-x)}\text{Fe}_x\text{S}_{(1-y)}\text{O}_y$. Given that the observed Fe signal remains constant through the depth profile on the inclusion (Figure 3.3), the value of x is not expected to vary significantly through the depth of the inclusion. In contrast, the O content (y) appears to vary considerably through the inclusion bulk. It appears that in some cases, oxidation of the inclusion surface is not homogeneous (c.f. Figure 3.4). Given the above discussion, this may be due to variations in the vacancy content within the bulk inclusion.

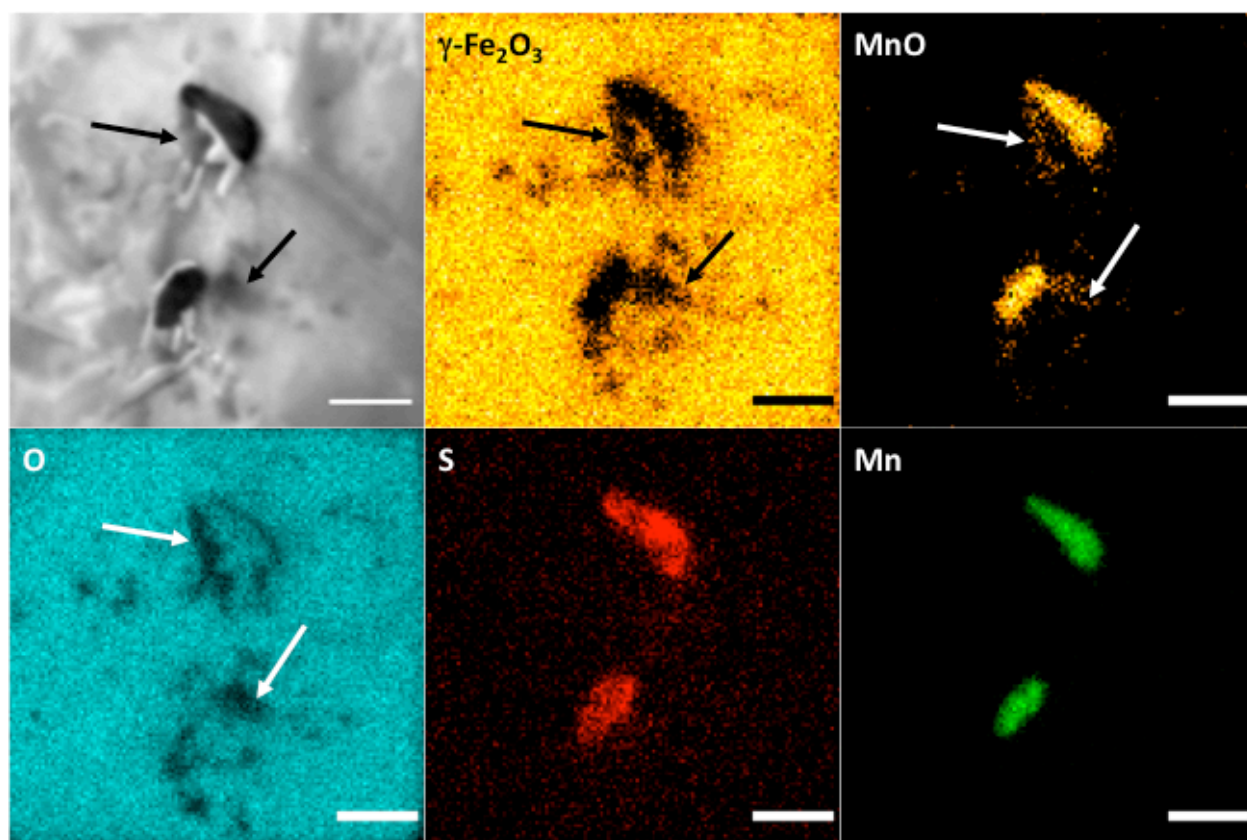
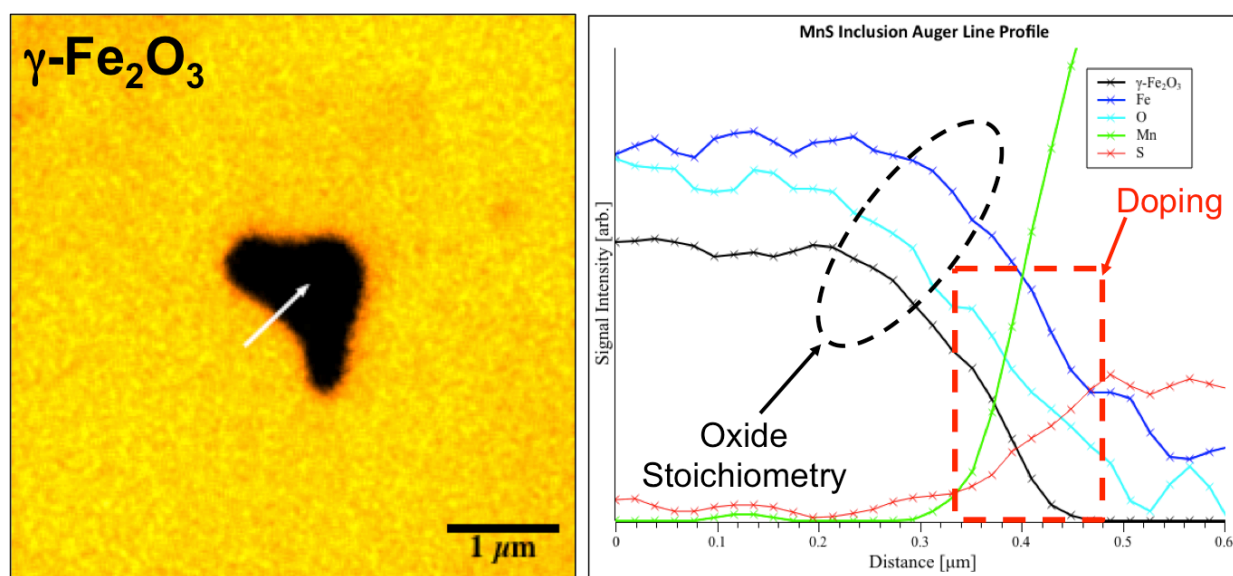


Figure 3.11: SEM image (top left) and Auger *chemical* and elemental maps acquired from a MnS inclusion. Scale bar is 1 μm . $E_p = 5\text{keV}$.

An example of an Auger *chemical* map is shown in Figure 3.11, in which a pair of MnS inclusions cut perpendicular to the rolling direction, are shown. The maps for $\gamma\text{-Fe}_2\text{O}_3$ and MnO

were acquired with peak positions of 44.4 and 37.5 eV (in the direct spectrum) respectively. Figure 3.11 also shows corresponding O *KLL*, S *LMM*, and Mn *LMM* Auger maps from the same field of view. The MnO map shows that both inclusion surfaces are completely covered in a layer of MnO. The γ -Fe₂O₃ map shows that the native oxide is not everywhere present on the steel surface, particularly near the inclusions, as indicated by the arrows. The O map indicates that the oxygen content is depleted (though not necessarily absent) in these regions. The Mn and S maps indicate that they are also not present. Spurious pixels in the MnO map appear to be spatially correlated with these oxygen-depleted regions.



3.12: Left panel: Auger chemical map of γ -Fe₂O₃ in the vicinity of a MnS inclusion. Right panel: Auger line profiles taken across the inclusion along the arrow indicated in the Auger map shown in the left panel. $E_p = 5$ keV

It is possible that these are related to Fe in the native oxide layer, and that the film in this region is either chemically or structurally distinct from other regions on the steel surface. This would manifest itself as a shift in the Fe *MVV* peak at 44.4 eV (see Figure 3.9), and thus appear as an

absence of the native oxide. This would also explain the presence of the spurious pixels in the 37.5 eV image. It is also conceivable that this region is not composed of Fe, O, Mn, or S, however it is difficult to speculate as to what other elements might be present.

The native oxide at the MnS/steel interface was studied in more detail by use of the Fe *MVV* Auger transition. Shown in Figure 3.12, is another Auger chemical map of a MnS inclusion. The left panel is the Fe *MVV* transition acquired at 44.6 eV, and is indicative of γ -Fe₂O₃. A depletion of the signal intensity is observed around the perimeter of the entirety of the inclusion/steel interface, similar to what is observed in Figure 3.11. A line profile was taken across the interface as indicated by the white arrow shown in the left panel of Figure 3.12. The signal intensities of γ -Fe₂O₃, Fe *LMM*, O *KLL*, Mn *LMM*, and S *LMM* are plotted in the right panel of Figure 3.12. The line profile shows that the decline of the native oxide signal is significantly broadened at the interface, and is approximately 250 nm in width, much larger than can be accounted for by the probe size (estimated to be < 50 nm). The decline in the γ -Fe₂O₃ signal at the interface could be related to thinning of the oxide, however one would expect to see an increase/decrease in the Fe and O Auger signals respectively, and both are observed to decrease. A more plausible explanation would be changes to the oxide stoichiometry. The observation of the simultaneous decrease in the Fe and O Auger signals would not be consistent with a change from Fe₂O₃ to Fe₃O₄ or FeO at the interface. Therefore, it is hypothesized that the change in stoichiometry is due to an increase in the number of cation and anion vacancies in the oxide film. It has been suggested that vacancies in the oxide film are responsible for its localized breakdown and initiation of pit growth [123]. Closer to the inclusion, the Mn and S Auger signals are observed along with the γ -Fe₂O₃ signal. These data suggest that the oxide contains

elements from the inclusion (i.e. Mn and S), which may occupy cation and anion vacancies. Fe_2O_3 has been shown to be able to incorporate both S and Mn [124,125]. The doping of Fe_2O_3 with S was shown to enhance the dissociation of water [124], which is believed to be the precursor to anodic dissolution of metal surfaces [126]. Thus the $\gamma\text{-Fe}_2\text{O}_3$ native oxide film at the inclusion/steel interface is believed to be highly defective, and contain a relatively large amount of both cation and anion vacancies. These may be occupied by elements originating from the inclusion, which in turn may affect the reactivity and electrochemical behavior in these regions.

3.4 Surface Potential Measurements of MnS Inclusions

Surface potential measurements using the onset method as described in section 2.4 were conducted on MnS inclusions. While the work was not extensive, a few results are worth mentioning here. Shown in Figure 3.13 is an onset energy line profile taken across the MnS inclusion shown in the inset. The scan direction is from the left of the field of view to the right. A *S LMM* Auger line profile is also shown as a point of reference for the inclusion. We first note that the work function on the inclusion surface is ~ 300 meV higher than the surrounding steel matrix. Given the interpretation presented in section 2.4, this implies that the inclusion is more noble in the electrochemical sense, than the surrounding matrix. In other words, the inclusion surface would form the cathode in a galvanic coupling with its steel surroundings. This is in agreement with Wranglen [35], who hypothesized that in carbon steels, the MnS inclusion surface is the site for cathodic reduction of H^+ , while active dissolution of the metal occurs at the metal/inclusion interface. As shown in Figure 3.13, there is a slight decrease of ~ 150 meV in the work function near the left side of the inclusion, as indicated by the arrow. This region corresponds to the inclusion/steel interface, as indicated by the decline in the *S LMM* Auger

signal, and indicated by the red circle in the SEM image. This implies that this interface is particularly susceptible to dissolution. We note that a smaller decline in the work function of ~ 50 meV is observed at the interface on the right side of the inclusion. It is therefore hypothesized that upon exposure to a corrosive environment, preferential dissolution will occur in the region indicated by the red circle in the SEM image of Figure 3.12. A slight broadening of the S signal is observed on the left side of the inclusion, and appears to be present in the low surface potential region. This data indicates that there is a region at the inclusion/steel interface which contains S, and which is believed to be corrosively active. Such a region may act as a source for dissolved S ions.

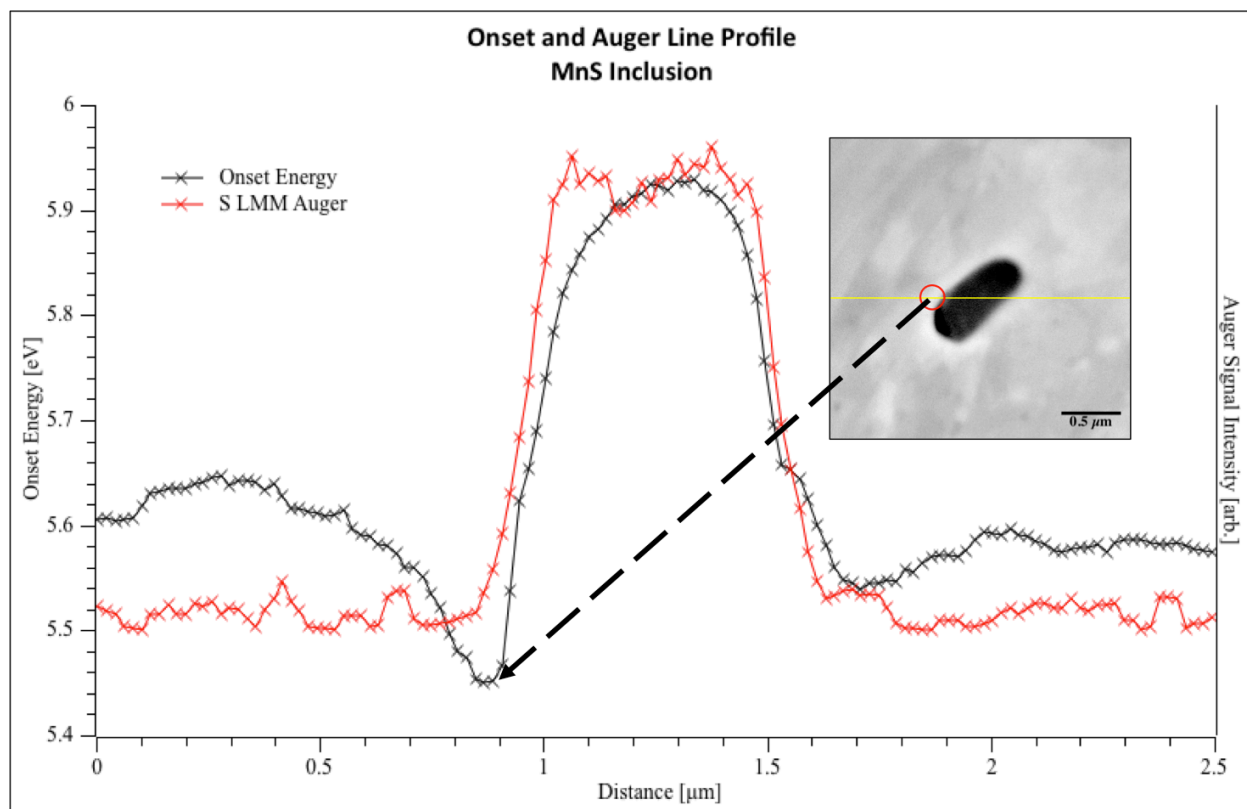
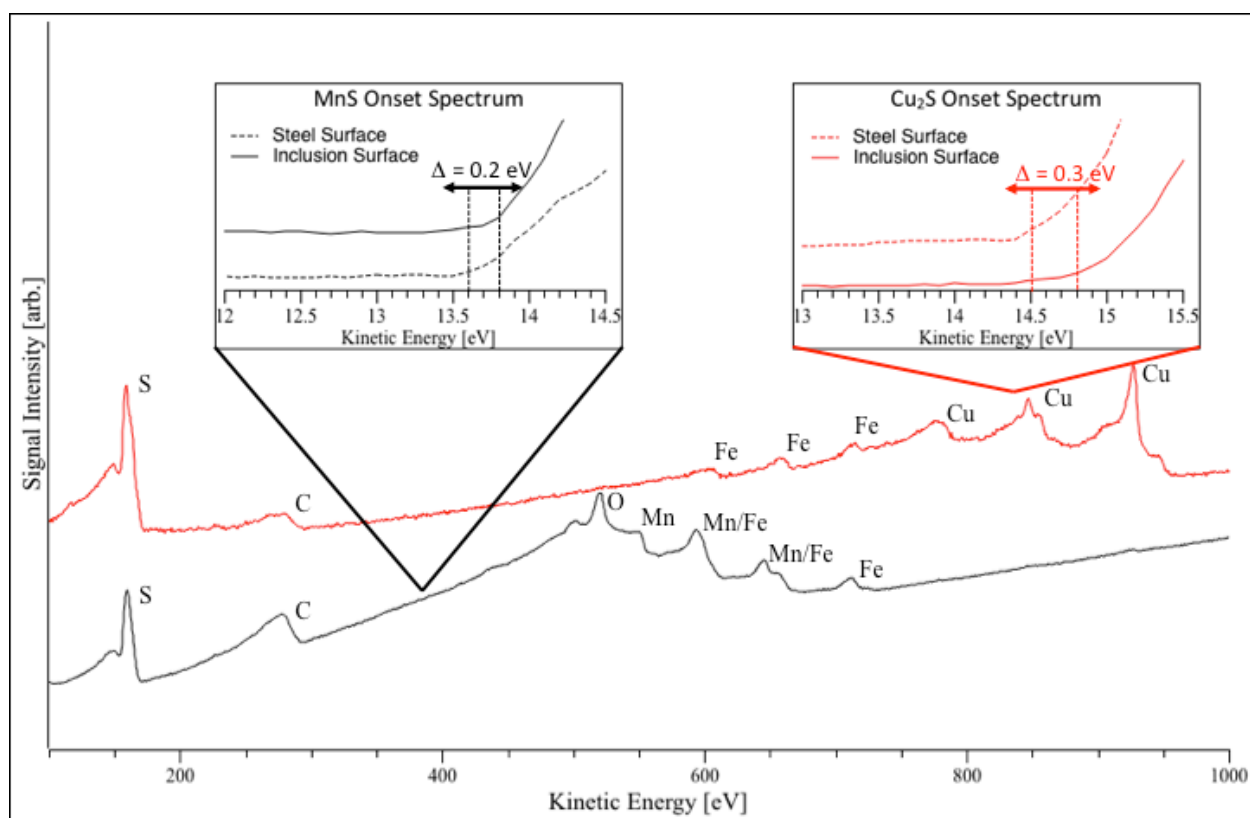


Figure 3.13: Onset and S Auger line profile taken across a MnS inclusion shown in the inset SEM image. The scan direction is from left to right. $E_p = 10$ keV. $V_b = -9.0$ V.

The onset method was employed to determine how the presence of a Cu_2S film on an inclusion surface might affect its electrochemical behavior. Shown in Figure 3.14 are onset and Auger spectra acquired from two different MnS inclusions. The black curves were acquired from an inclusion, which did not possess a Cu_2S film. The Auger spectrum acquired from this inclusion indicates that the composition of its surface was typical of those inclusions studied during this work.



3.14: Auger spectra acquired from a MnS inclusion surface containing Cu_2S film (red curve), and an inclusion surface without the Cu_2S film. Insets show onset spectra collected from each inclusion surface, as well as a nearby region of the steel surface. $E_p = 10 \text{ keV}$. $V_b = -9.0 \text{ V}$.

The red curves were acquired from an inclusion, which possessed a thick Cu_2S layer, as evidenced by the lack of Mn in the Auger spectrum. Onset spectra were acquired from both inclusions, as well as from a nearby region of the steel surface, and are shown as insets in Figure

3.14. In the case of the MnS inclusion which did not indicate the presence of Cu, the surface potential difference was found to be ~ 0.2 eV. In the case of the Cu_2S film, the difference is found to be ~ 0.3 eV. Thus it is believed that the presence of a Cu_2S film acts to ennoble the inclusion surface, and inhibit dissolution. This is in agreement with previous work, where it was shown that the deposition of dissolved Cu ions on MnS inclusion surfaces, increased the measured surface potential of the inclusion [25].

3.5 Crystallographic Study of Inclusion Surfaces

As discussed above, it was believed that some MnS inclusions were coated with a thick oxide layer, believed to be MnO. EBSD was employed in an attempt to distinguish between the presence of MnS and MnO phases on a MnS inclusion. Shown in the top panel of Figure 3.15 is a combined inverse pole figure (IPF) map of the MnS and MnO phases identified in the inclusion shown in Figure 3.1. Given the similarity of the Kikuchi patterns of the two crystalline structures, it was not possible to distinguish between the two phases with a reasonable degree of certainty. The presence of α -Fe (Ferrite) was not detected within the inclusion. Regions within the inclusion identified as MnS/MnO are believed to be crystalline (FCC MnS or MnO), while areas not associated with these phases are believed to be highly disordered. The crystalline regions of the inclusion are shown in the top panel of Figure 3.15 as the green colored areas. The crystalline regions exhibit a strong texture oriented in the $[101]$ direction, indicated by the color green in the top panel of Fig. 3.15. It is noted that the crystalline regions are not uniformly distributed, and that there is localized clustering along the length of the inclusion. Because of kinetic effects related to rapid cooling/quenching of the steel, loss of crystalline order may have occurred during the metallurgical preparation or the rolling of the steel.

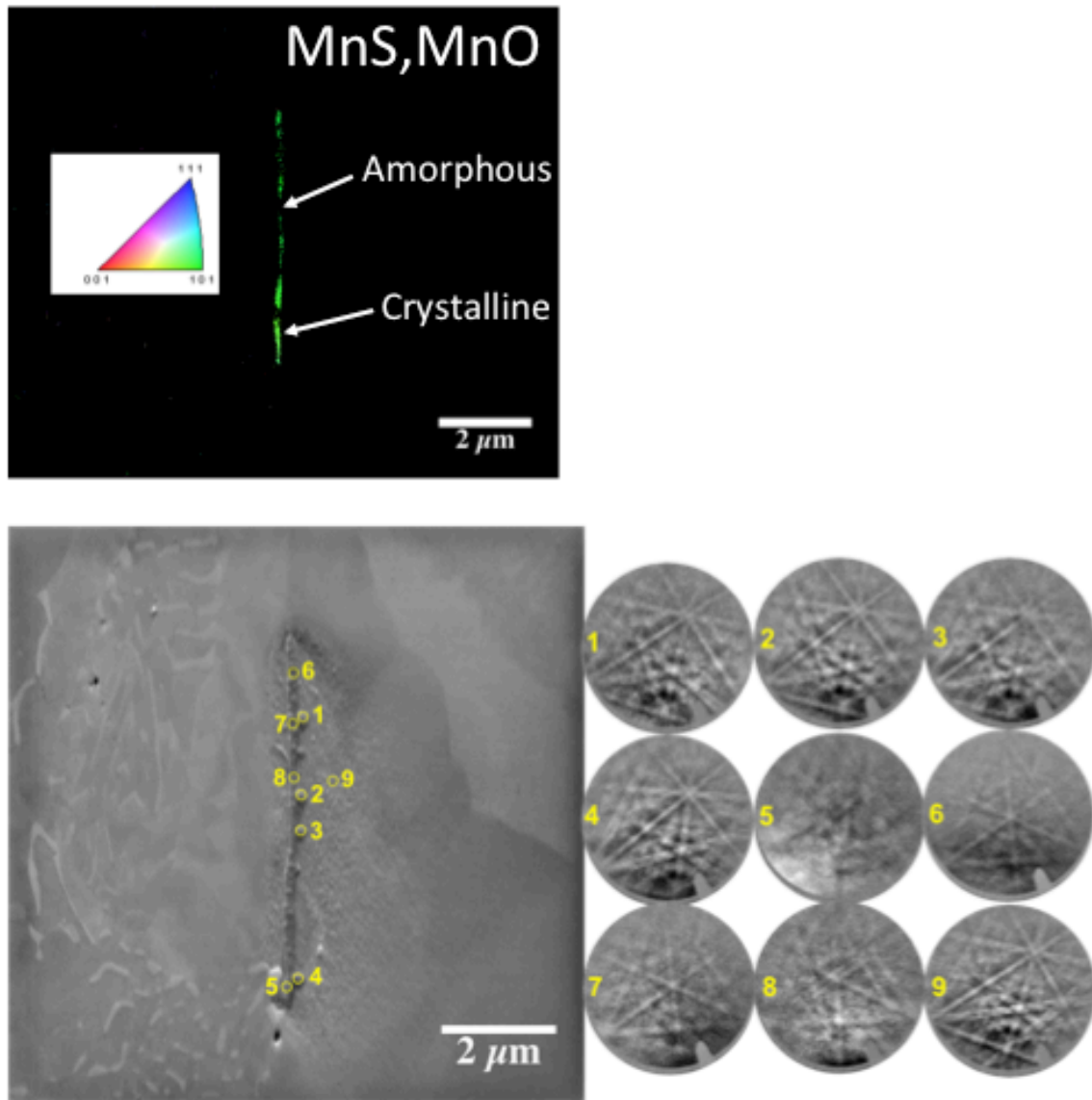


Figure 3.15: EBSD data acquired from a MnS inclusion shown in the SEM image on the bottom. Top: Combined orientation map of MnO and MnS phases indicating a strong (101) texture. Absence of indexed points indicates that the inclusion is amorphous in those regions. Bottom: SEM image of the MnS inclusion corresponding to the orientation map in the top of the figure. The right shows Kikuchi patterns acquired from 9 regions shown in the SEM image.

The bottom panels in Figure 3.15 show Kikuchi patterns taken at various locations within the inclusion, marked on the SEM image shown on the left. There is marked variation in pattern

quality in terms of band contrast throughout the inclusion. In particular, we note that regions 1-4, with nodular morphology (shown to be MnO), and the ferrite phase (region 9) exhibit good pattern quality. These patterns all suggest FCC crystal structure with $m3m$ point group symmetry on the inclusion and BCC on region 9. This is in contrast to other regions within the inclusion (regions 5-8), in which the pattern quality varies from fair to poor.

Transmission Electron Microscopy Analysis of the MnS/Ferrite Interface

Given the hypothesis that residual strain at the MnS inclusion/Ferrite interface is the underlying cause for the susceptibility of these regions to localized corrosion [34,41,46]. It was desired to image this interface using a transmission electron microscope (TEM). A TEM is capable of atomic spatial resolution, and so in principle structural disorder at the inclusion interface (if present) should be directly observable in such a microscope. A TEM requires samples to be electron transparent. For the current study, MnS inclusions from a sample cut perpendicular to the rolling direction were pre-selected using the Auger microscope described in section 2.3. The sample was then sent to a private company (TESCAN Pleasanton, CA) to extract the inclusion of interest and prepare a sample, which was electron transparent. The extraction was performed by milling out a lamella, which contained the inclusion of interest, with a focused Ga^+ ion beam (FIB) and welding it to a Cu finger. Once welded, the lamella was subsequently thinned with the same Ga^+ ion beam until electron transparent. The thinned sample was then characterized using the integrated Auger Nanoprobe. An SEM image of the inclusion of interest is shown in the left panel of Figure 3.16.

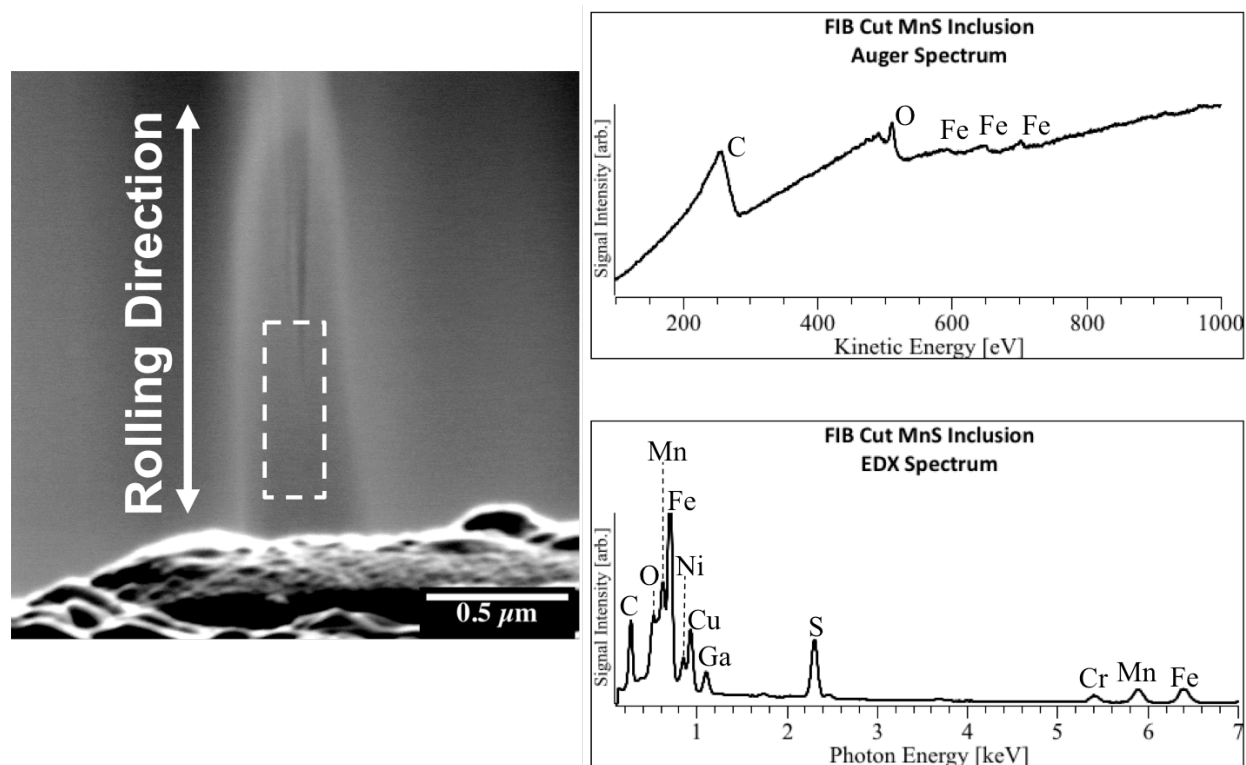


Figure 3.16: Left: SEM image of FIB cut of MnS inclusion. Right: Auger (top) and EDX (bottom) spectra acquired from the rectangular region of the inclusion indicated in the SEM image (left). $E_p=10$ keV.

The MnS stringer is in the center of the field of view, and the arrows in the left panel of Figure 3.16 indicate the rolling direction. An Auger spectrum was acquired from the region indicated by the dotted white rectangle, and is shown in the right panel of Figure 3.16. The spectrum only indicates the presence of C, O, and Fe. The carbon is due to environmental contamination, however the presence of Fe and O indicate that a residual amount of the steel matrix is still present on top of the inclusion. An EDX spectrum acquired from the same region is also shown in the right panel of Figure 3.16. The spectrum indicates the presence of Mn and S, and shows that the inclusion is indeed present beneath the surface. These data exemplify the difference between Auger and EDX spectroscopy, namely that Auger is insensitive to the bulk composition.

Fe, Cr, and Ni are also observed in the EDX spectrum, and primarily arise from the sample holder beneath the lamella, which is thinner than the excitation volume of the electron beam at this energy (a few hundred nm). Ga is also observed in the EDX spectrum, and likely originated from preparing the lamella with the Ga^+ FIB. When considering the objective of the TEM analysis, namely high-resolution imaging of the inclusion/steel interface, it is necessary that the imaging signal originate only from the interface, and that there is no contribution from a residual steel overlayer. The standard approach of EDX does not possess sufficient surface sensitivity to ensure this, and so Auger spectroscopy must be used.

The sample was then extensively sputtered with Ar^+ ions while periodically monitoring the Auger signal intensity for the presence of Mn and S. Shown in the left panel of Figure 3.17 are Auger spectra acquired from the inclusion (red curve), as well as from a region of the nearby steel surface (blue curve).

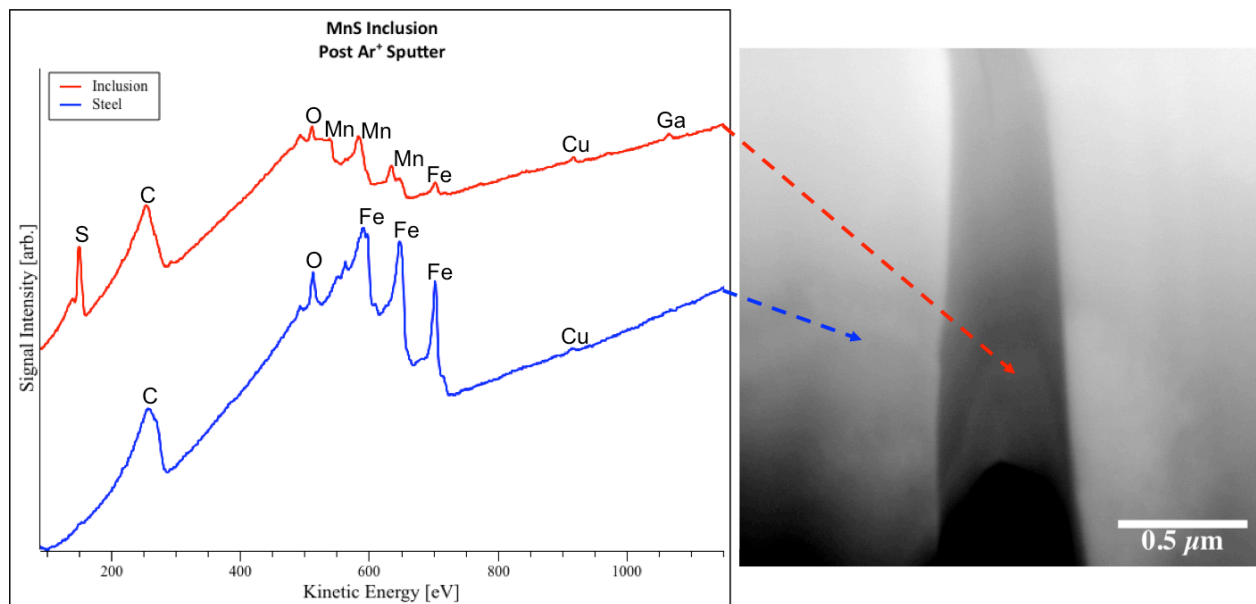


Figure 3.17: Left: Auger spectra acquired post sputtering from the same inclusion shown in Figure 3.16 (red line) and a nearby region of the steel surface (blue line). Right: SEM image of MnS inclusion post sputtering. $E_p=10$ keV.

An SEM image of the inclusion after sputtering is shown in the right panel of Figure 3.17. The S and Mn signals are now observable, indicating that the steel overlayer has been removed.

The Fe observed in the spectrum acquired from the inclusion is believed to be a component of the inclusion (c.f. Figure 3.1), and not a remnant of the steel overlayer. We note that the presence of O and C observed in both spectra could not have originated from the Ar^+ ion beam used in the Auger microscope, since the sputtering was conducted under UHV conditions. If present as a surface contaminant or oxide, these would not be observed after extensive sputtering. Thus, the C and O are believed to originate from the relatively poor vacuum present in the FIB microscope used to prepare the lamella, and are likely implanted into the inclusion and steel matrix. The Ga observed in the spectrum acquired from the inclusion (red curve), is also believed to be implanted Ga from the FIB. It is worthwhile noting that Ga is not observed in the spectrum acquired from the steel surface (blue region). The Cu observed in both spectra in Figure 3.17 is believed to be debris from the Cu finger that the lamella is welded to, and was within the sputtered region ($2 \times 2 \text{ mm}^2$). Figure 3.17 shows that while the use of Auger spectroscopy along with Ar^+ sputtering is a viable way to ensure removal of the steel overlayer, and that challenges still exist in preparing such samples for TEM analysis. Because the ultimate objective is to determine the presence of structural defects at the inclusion/steel interface, careful consideration of the sample preparation process is necessary. In particular, one must be confident that the observation of a structural defect (i.e. dislocation) did not originate from the thinning of the lamella with the FIB.

The method described above was applied to both sides of the lamella prior to conducting the TEM analysis. The lamella were sent for TEM analysis to the NanoEarth user facility at

Virginia Polytechnic and State University (Blacksburg, VA). Shown in Figure 3.18 are example TEM images from the analysis. Figure 3.18 A is a low magnification TEM image of the MnS inclusion shown in Figure 3.17. The bright region seen near the right side of the inclusion is believed to be a hole in the lamella resulting from the sample preparation process.

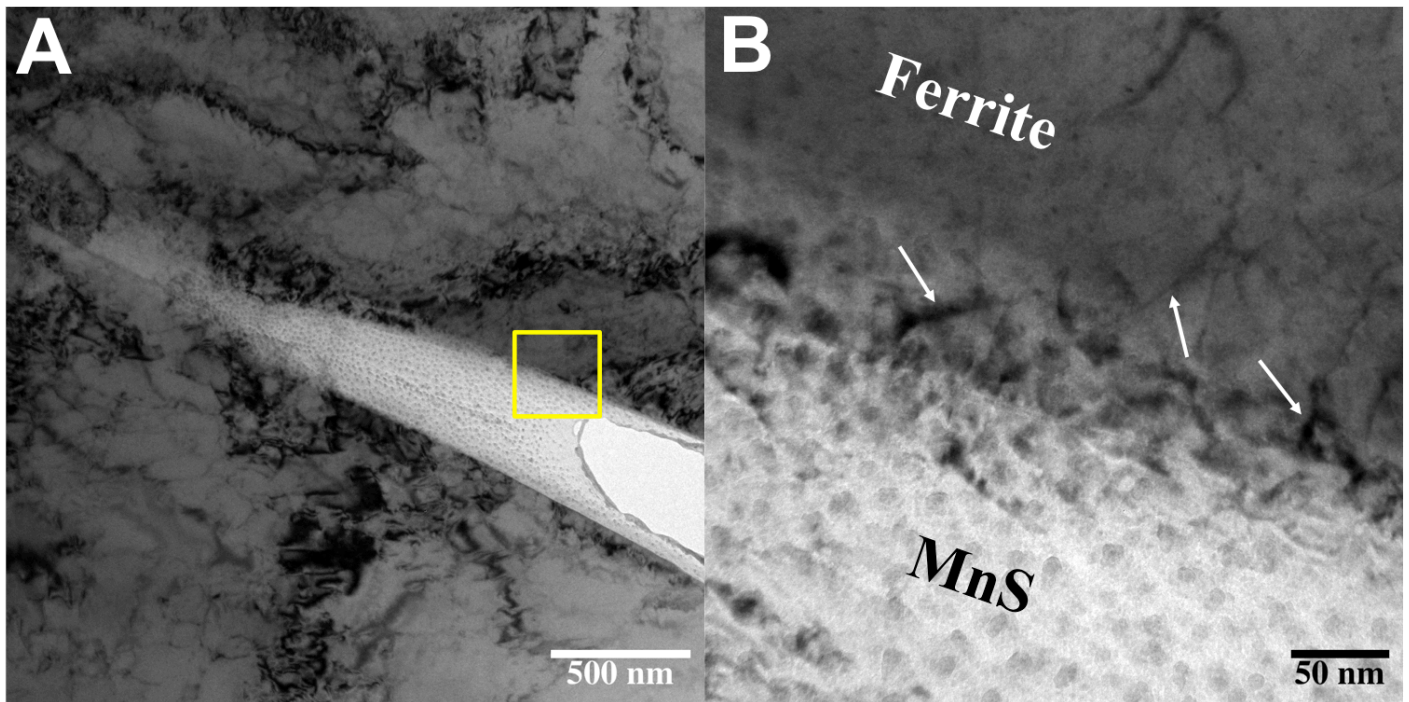


Figure 3.18: TEM images of the MnS inclusion shown in Figures 3.16 and 3.17. A: Low magnification image of the lamella. The yellow box indicates the inclusion/steel interface shown at high magnification in Figure 3.18 B. $E_p=200$ keV.

Figure 3.18 B is a high magnification image of the inclusion/steel interface indicated by the yellow box in the image of Figure 3.18. The MnS inclusion is the bright area in the lower part of the image. The ferrite phase is located in the dark region near the top of the image. The interface, and region of interest, is near the middle of the image and exhibits a contrast somewhere between the MnS and Ferrite. This region is estimated to be ~ 70 nm in width. A network of dark lines can be observed in the interfacial region. These are believed to be

dislocations in the Ferrite lattice [127]. Some of the dark regions are fairly thick, indicating a large dislocation density. Figure 3.18 B indicates that the inclusion/ferrite interface is highly disordered and strained. As mentioned above, it is hypothesized that the relatively large degree of strain at this interface is responsible for the high susceptibility of these regions to localized corrosion.

3.6 Conclusions and Future Outlook

The results of the above work can be summarized as follows:

1. MnS inclusions are not pure phases of Mn and S, but contain other elements such as Fe, O, and Cu. Thus the name “MnS inclusion” is somewhat misleading. Fe and O were found to be present both on the surface and within the bulk of inclusions. Fe is believed to be in solid solution with Mn, whereas O is believed to be in solid solution with S. Thus it is believed that the composition of MnS inclusions may be written as $\text{Mn}_{(1-x)}\text{Fe}_x\text{S}_{(1-y)}\text{O}_y$. While the Fe content was found to be relatively constant within the bulk of the inclusion, this was not the case with O and S. Therefore in this formulation of the inclusion composition, the value of y is a function of depth below the inclusion surface. Cu was observed as a thin (~ 5 nm) film, believed to be Cu_2S , on some inclusion surfaces.
2. The spatial distribution of Mn, S, Cu, and O across the inclusion surface were observed to be heterogeneous. Oxygen enriched regions, approximately 100 nm in size, were observed on some inclusion surfaces, and correlated with a nodular morphology. These regions were found to be S depleted, and believed to be MnO. Cu enriched regions were found to correlate with Mn depleted areas on some inclusion surfaces. The Cu enriched regions are believed to be thin films of Cu_2S .

3. Depth profiling revealed that oxygen is present tens of nanometers below the inclusion surface, and suggests a replacement of S with O within the inclusion bulk. In other words, MnS inclusions appear to possess a surface oxide, which is much thicker than those formed on metal surfaces. It is believed that this oxide is formed after the surface is exposed to air, and not during the metallurgical preparation of the steel. The oxidation of metal sulfide surfaces has not been extensively reported in the literature, nonetheless it is hypothesized that oxidation of the inclusion occurs via occupation of S vacancies by O. Diffusion of O within the inclusion bulk may occur via hopping of O atoms to neighboring vacancies. It is not clear if the vacancy content within the inclusion is constant in time, or if loss of S might occur at the inclusion surface, thereby generating additional vacancies. As noted above, MnO is thermodynamically favored over MnS.
4. It was demonstrated that low energy Auger transitions involving valence band electrons could be used to distinguish between oxide species, i.e. γ -Fe₂O₃ and MnO, present on the steel surface. Mn *MVV* Auger spectra were used to determine changes in the chemical state of Mn within the bulk of MnS inclusions.
5. The onset method was used to measure work function differences between inclusion and steel surfaces. It was found that the work function of inclusion surfaces were several hundred meV larger than nearby regions of the steel. In the context of electrochemistry, this implies that MnS inclusion surfaces are more noble than the nearby Fe surfaces, and may therefore form efficient galvanic couples. It was also demonstrated that the work function difference of a Cu₂S film relative to the nearby steel surface was more positive

than an inclusion without such a film. It is concluded that the presence of a Cu_2S film, acts to ennoble the inclusion surface.

6. The inclusion/steel interface was found to possess characteristics different from both the inclusion and steel phases. Auger electron spectroscopy revealed the presence of S in a region spatially distinct from the inclusion. Use of the Fe MVV Auger transition to monitor changes in the native oxide ($\gamma\text{-Fe}_2\text{O}_3$) at the inclusion steel interface revealed a broad (~ 250 nm) intensity profile. It is believed that the oxide film becomes increasingly nonstoichiometric (i.e. defective) at this interface, and that elements from the inclusion (Mn and S) may be incorporated into the film. Onset measurements revealed a ~ 150 meV decrease in the surface potential at an inclusion/steel interface, implying that this region was more susceptible to dissolution than the neighboring steel surface. This is in agreement with reported observations that localized corrosion initiates at the inclusion/steel interface.
7. A MnS inclusion was prepared for TEM analysis of the inclusion/steel interface. AES is deemed necessary to ensure that only the inclusion/steel interface contributes to the imaging signal. Auger spectra revealed evidence from the preparation of the lamella with the FIB, and indicates that extreme care in preparation of the sample is necessary in order to properly interpret the resulting TEM data. TEM images of the inclusion/steel interface indicate a high dislocation density, and support the hypothesis that the interface is highly strained, and that this strain is responsible for localized dissolution at the inclusion/steel interface.

As discussed in section 1.4, S is believed to play several detrimental roles during the pit *growth* process. Therefore it is hypothesized that a possible distinction between active and inactive inclusions, is the *availability of S*. Availability is meant in regard to both the total S present within the inclusion and its interface, and also with respect to the S *chemically available* for dissolution. It is hypothesized that the S availability will have a significant impact on the pitting kinetics at a given MnS inclusion. This work has demonstrated that the S content on inclusion surfaces is highly variable. Some inclusion surfaces were found to be S depleted, and believed to be entirely coated with a thin film of MnO. Other inclusion surfaces exhibited small, localized regions of S depletion, also believed to be MnO. While others did not exhibit significant variation in the S content across their surfaces. Thus we may envision MnS inclusion surfaces in carbon steels as possessing a variable degree of O doping. At this point it is not clear how various electrochemical quantities (i.e. equilibrium potential or dissolution kinetics), might be affected by the O content on a MnS inclusion surface, and if for example, MnO exhibits passive properties. It would be of value to conduct electrochemical studies on well-defined MnS surfaces with varying degrees of oxygen doping. In a similar spirit, it was previously suggested that the Fe content in a MnS inclusion has an impact on its pitting behavior, specifically that those inclusions rich in Fe were more resistant to corrosion [27]. We have also shown that there appears to be a replacement of O for S within the bulk of the inclusion. At this point, it is not clear if the inclusions are born S deficient, or if S depletion is an integral part of the inclusion oxidation mechanism. Nonetheless, it is reasonable to suggest that variations in the bulk S content will impact dissolution kinetics of the nearby steel surface, simply due to the limited availability of S. The presence of a Cu₂S thin film, observed on some inclusion surfaces, is

expected to exhibit passive properties. Such an inclusion is not anticipated to be a significant source of available S, and thus is hypothesized to be inactive.

With regard to the initiation of localized corrosion at the inclusion/steel interface, the work presented here demonstrates that the native oxide exhibits changes at this interface. It is suggested that the oxide stoichiometry, as well as incorporation of inclusion elements into the oxide are responsible for the observed changes. These hypotheses were in part, based on Auger chemical analysis using the Fe MVV transition. In principle, the use of Auger transitions involving valence band electrons is a viable method to monitor chemical changes at the small length scales of an inclusion interface [85]. However, more work must be done to properly interpret these spectra. Given that the substrate at these interfaces is known to be strained, it would also be of interest to see if changes in the native oxide can be correlated with this residual strain.

CHAPTER FOUR

STUDY OF GRAPHENE COATED Cu SURFACES

4.1 Experimental Methods

CVD grown graphene on polycrystalline Cu were purchased from ACS Material (Pasadena California) and Graphena (San Sebastián, Spain). All x-ray photoelectron and x-ray excited Auger electron spectra were acquired with the XPS instrumentation described in section 2.2. XPS data were background subtracted using a Shirley type background procedure. Peak fitting of XPS spectra was accomplished using a mixed (90/10) Gaussian/Lorentzian peak profile. Peak positions and widths were assigned based on values obtained from the literature. Electron energy loss spectra, Auger spectra, and Auger maps were acquired using the integrated scanning Auger nanoprobe described in section 2.3.

4.2 Characterization of Graphene Coated Cu Surfaces

The development of CVD methods for graphene growth has allowed for high quality and large coverage graphene films to be routinely grown on a variety of metallic substrates [52]. Raman spectroscopy has become a routine method for determining the presence and quality of graphene films [128]. AES, being a surface sensitive technique, is also a prime candidate for characterization of thin graphene films. AES has been used to determine the thickness of graphene layers on SiO₂ by considering the attenuation of Auger electrons originating from the substrate [129]. In addition to characterizing the presence and quality of graphene films, an understanding of the interaction between graphene overlayers and various substrates is relevant

for use of graphene as a protective film. Using density functional theory (DFT), Khomyakov et. al. showed that the Dirac cone of graphene on Al, Cu, Ag, Au, and Pt substrates remains intact, and that a shift in the Fermi level occurs due to charge transfer [130]. They deemed this type of interaction as physisorption, due to the preservation of graphene's electronic structure, and a weak bond of the carbon atoms to the substrate. ARPES measurements of graphene on a variety of noble metal surfaces have shown, that in addition to a shift in the Fermi level due to charge transfer, that in some cases, a small gap of a few hundred meV is opened up at the Dirac point [131–133]. In the case of Co, Ni, Pd, and Ti substrates, a strong interaction leads to significant changes to the electronic structure of the graphene overlayer, consistent with chemisorption [130]. Here, we present a unique feature in the Cu *LMM* Auger transition in CVD grown graphene on polycrystalline Cu substrates, and show that its subsequent suppression is related to coupling of the graphene overlayer to the surface. It is also demonstrated that this feature can be used to map graphene domains with a high degree of spatial resolution.

Shown in Figure 4.1 are raw spectra of the Cu *LMM* Auger transition acquired from CVD grown graphene on Cu. The black curve was acquired after UHV annealing of the sample up to 700 C to remove oxygen present at the graphene/Cu interface [75]. The red curve was acquired after the graphene overlayer was removed via sputtering with 2.5 keV Ar⁺ ions. A broad feature centered around 895 eV is observed on the low kinetic energy side of the Cu *LMM* peak, shown in the inset of Figure 4.1. Upon sputtering (red curve), the inset shows that the broad feature is no longer visible. Thus, it was hypothesized that the feature in the Auger spectrum was related to the presence of graphene.

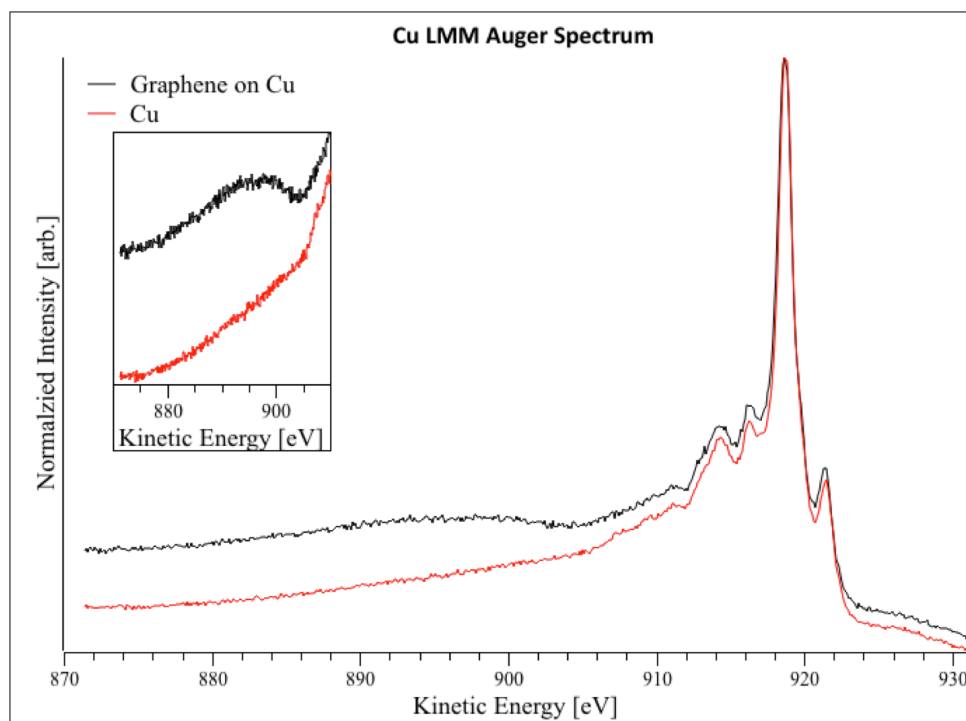


Figure 4.1: X-ray excited Cu *LMM* Auger transition of a graphene coated Cu surface. Black line corresponds to the sample after UHV annealing to 700 C. Red line corresponds to the sample after removal of graphene via Ar^+ sputtering. The inset shows a broad feature centered around 895 eV only present in the graphene coated sample.

Given that the observed feature is on the low kinetic energy side of the Cu *LMM* peak, it is reasonable to suggest that it is due to losses that the Cu *LMM* Auger electrons experience upon passing through the graphene overlayer. Figure 4.2 compares the low kinetic energy side of the Cu *LMM* Auger transition and the Cu $2p_{1/2}$ photoelectron line. Both should exhibit this broad feature if indeed it is related to some type of loss. In Figure 4.2 A, the energy loss relative to the Cu *LMM* and Cu $2p_{1/2}$ peak positions are shown. The intensities are normalized to the respective peak intensities. In the case of monolayer graphene on Cu (black and red curves), there is good agreement in the position and intensities between the Cu *LMM* and Cu $2p_{1/2}$ spectra.

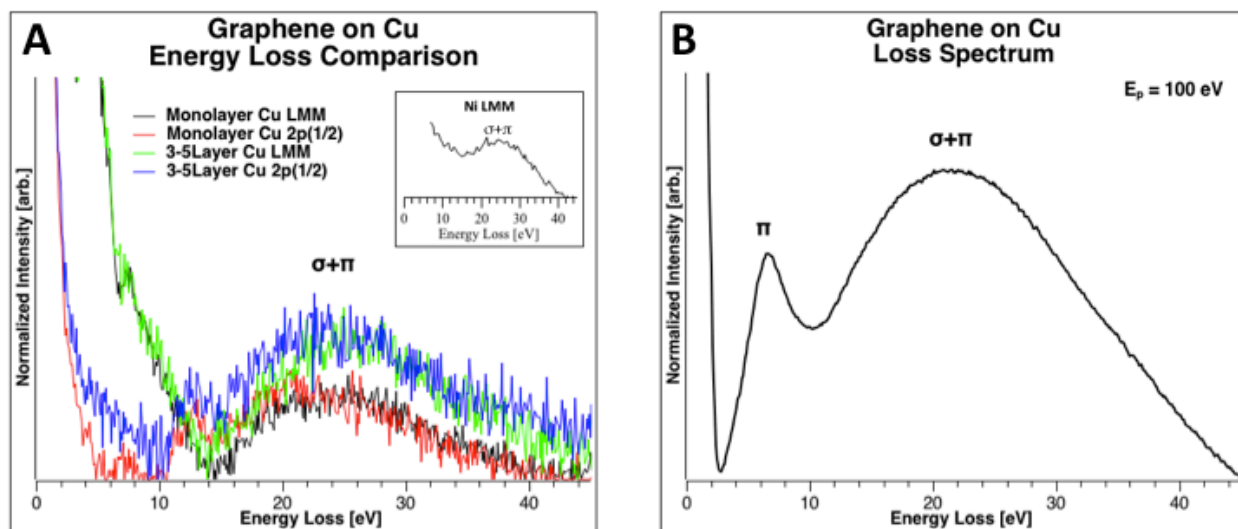


Figure 4.2: (A) Comparison of the low kinetic energy side of the Cu *LMM* Auger and Cu $2p_{1/2}$ photoelectron line. Black and red lines were acquired from monolayer graphene, while blue and green lines were acquired from 3-5 layer graphene. Energy loss is relative to the respective peak position. Signal intensity is normalized to the respective peak intensity. Inset shows loss feature of electron beam excited Ni *LMM* Auger transition collected from few layer graphene on Ni (B) EELS spectrum collected from monolayer graphene on Cu. Primary beam energy is 100 eV.

In the case of the spectra collected from 3-5 layer graphene on Cu, there is also good agreement between the Cu *LMM* and Cu $2p_{1/2}$ (green and blue curves) spectra. The normalized intensity of this feature increases as the number of overlayers is increased. Though broad, the peak position is ~ 23 eV. Shown in Figure 4.2 B is an electron energy loss spectrum (EELS) acquired from a monolayer graphene on Cu sample using a primary beam energy of 100 eV. Here, the characteristic losses labeled as π and $\sigma + \pi$ are observed at 6.5 eV and ~ 22 eV, and correspond to plasmon excitations in graphene, as has been previously reported [134]. The $\sigma + \pi$ loss value is in good agreement with the losses observed in the Cu *LMM* and Cu $2p_{1/2}$ spectra (Figure 4.2 A). While in principle, the π plasmon loss at ~ 6.5 eV should also be observable in the photoelectron data (Figure 4.2 A), it is not discernible from the inelastic background. A similar feature was observed in the Ni *LMM* Auger spectrum acquired from many layer graphene grown on a Ni

substrate (Grapene Laboratories Inc. Ronkonkoma, NY). This is shown in the inset of Figure 4.2 A, the position of the feature relative to the Ni *LMM* peak is similar (~ 23 eV) to the data presented in Figure 4.2 A for the case of Cu, and shows that its presence does not depend upon the substrate. We therefore attribute the observed feature in the Cu *LMM* Auger transition as being due to losses of the Auger electron via the excitation of a $\sigma + \pi$ plasmon.

It was observed that in some cases, the $\sigma + \pi$ loss peak could be attenuated by annealing the sample in ultra high vacuum. An example is given in Figure 4.3, in which spectra of the $\sigma + \pi$ loss peak (Figure 4.3 A), O 1s (Figure 4.3 B) and C 1s (Figure 4.3 C) photoelectron lines, and the Cu *LMM* Auger transition (Figure 4.3 D) were collected at temperatures of 200 C (red line), 400 C (green line), and 600 C (cyan line). At 200 C, the C 1s peak position is 284.3 eV, which is indicative of sp^2 C-C bonding, and typical of graphitic carbon. The O 1s spectrum shows a component at 530.3 eV, which is related to Cu_2O [135]. There exist other components at higher binding energy, which are associated with carbon-oxygen bonding [75], and are likely related to environmental contamination present on the surface. At 400 C, the C 1s peak is still positioned at 284.3 eV, indicating no major change to the graphene overlayer. The O 1s spectrum shows a singular component at 530.2 eV, still believed to be Cu_2O . The components associated with carbon-oxygen bonding are no longer observed, and believed to have volatilized into the vacuum. At 600 C, no oxygen is detected in the O 1s spectrum. The Cu *LMM* Auger spectrum indicates that the substrate is metallic, i.e. not oxidized. The C 1s spectrum shows an upshift of ~ 0.3 eV to 284.6 eV. The $\sigma + \pi$ loss peak is completely suppressed, and no feature in the spectrum is observed above the background level (note difference in scale).

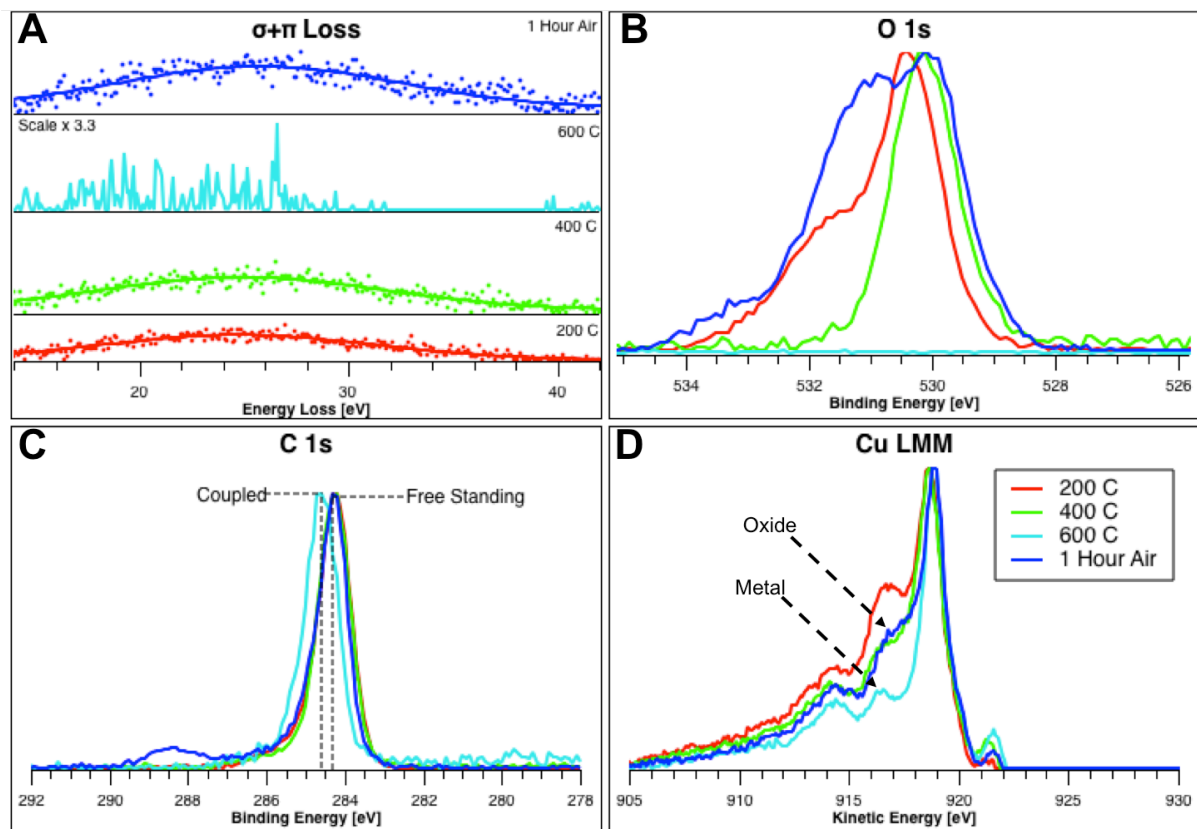


Figure 4.3: Evolution of the $\sigma+\pi$ loss (A), O 1s photoelectron spectrum (B), C 1s photoelectron spectrum (C), and Cu LMM Auger spectrum (D) with increasing temperature. Spectra were collected at 200 C, 400 C, 600 C, and after 1 hour in air (red, green, cyan, and blue lines respectively). The solid lines in the $\sigma+\pi$ loss spectra (A) correspond to a Gaussian fit of the data.

The suppression of the $\sigma+\pi$ loss peak is also observed upon cooling the sample to room temperature (not shown here). Removal of the sample from the UHV, and exposing it to air at room temperature for 1 hour (Figure 4.3 blue lines), causes a return of the $\sigma+\pi$ loss feature. This is also accompanied by a shift in the C 1s binding energy back to 284.3 eV. The O 1s spectrum also indicates the presence of Cu oxide and carbon-oxygen bonding.

While these data suggest that the loss feature might be related to the presence of oxygen, the feature was still observed in some samples after annealing in UHV at temperatures at and

above 600 C. Shown in Figure 4.4 are XPS spectra taken at 600 C of two different CVD graphene on Cu samples, respectively labeled as 1 and 2. The spectra from sample 1 (black lines) are identical to those presented in Figure 4.3, and are shown for the purposes of comparison.

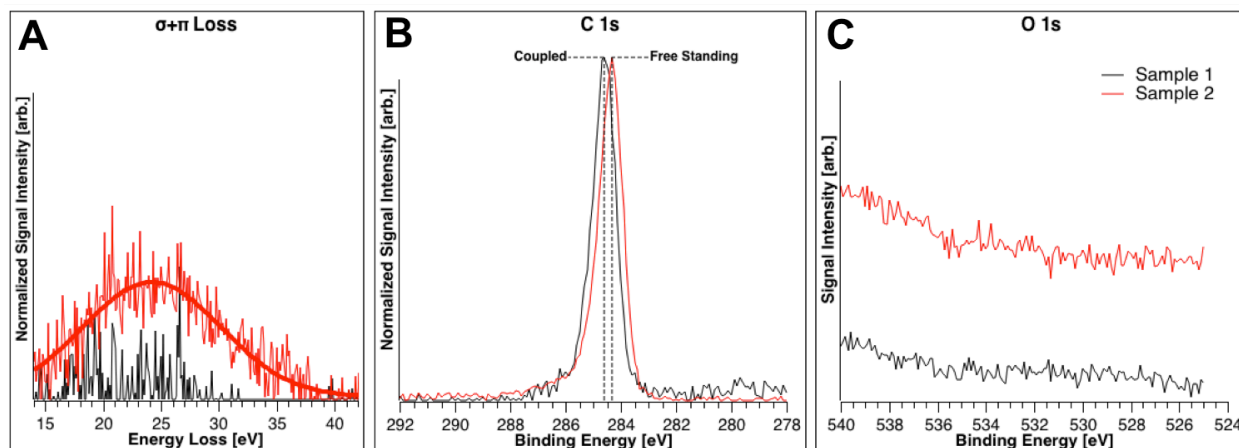


Figure 4.4: Comparison of the $\sigma+\pi$ loss (A), C 1s photoelectron spectrum (B), and O 1s photoelectron spectrum (C) taken from two different graphene on Cu samples labeled as Sample 1 (black curves) and Sample 2 (red curves). The red solid line in the $\sigma+\pi$ loss spectra (A) corresponds to a Gaussian fit of the data.

Figure 4.4 A shows that unlike in the case of sample 1 (black line), the $\sigma + \pi$ loss feature in sample 2 (red line) is not completely suppressed at 600 C. Comparison of the O 1s spectra (Figure 4.4 C) indicates that there is no discernable O peak in either sample. However, the C 1s spectra (Figure 4.4 B) shows significant differences in the C 1s binding energy. The C 1s peak binding energy of sample 2 (red line) is located at 284.3 eV, which is indicative of C-C sp^2 bonding, and does not exhibit the same increase in binding energy to 284.6 eV, as in the case of sample 1 (black line). These data suggest that the suppression in the $\sigma + \pi$ loss feature is correlated to the observed upshift in the C 1s binding energy.

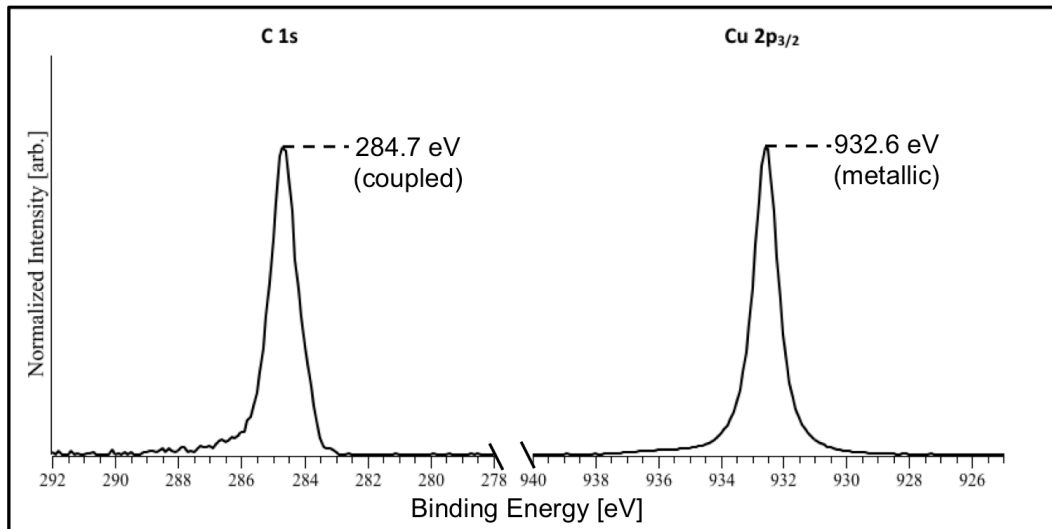


Figure 4.5: XPS spectra acquired from graphene on Cu post annealing at 600 C in UHV.

Previous XPS studies have attributed the increase in binding energy of the C 1s photoelectron line, beyond sp^2 bonded carbon, to charge transfer or “coupling” of the graphene overlayer to the substrate [74,75]. It was suggested that in the case of graphene on Cu, charge transfer occurs from the substrate to the graphene, resulting in an upward shift of the Fermi level. This results in a subsequent increase in the C 1s binding energy, in good agreement with the results shown in Figure 4.3 C at 600 C. In order to observe this increase in the C 1s binding energy, samples needed to be UHV annealed to temperatures exceeding 500 C to remove a layer of intercalated oxygen, present in all air exposed samples [74,75]. The intercalated oxygen is believed to inhibit charge transfer between the substrate and graphene overlayer. Such is the case in the spectrum shown in Figure 4.3 C at i.e. 400 C (green lines). Here, the C 1s binding energy at 284.3 eV, indicative of sp^2 bonded carbon, suggests that the graphene overlayer behaves as a freestanding film. The intercalated oxygen is evidenced by the presence of Cu_2O observed at 530.3 eV in the O 1s photoelectron spectrum. It is not until oxygen is no longer

detected, that a shift in the C 1s binding energy is observed. If the shift in the C 1s binding energy is indeed due to charge transfer and a shift in the Fermi level, one would expect to observe similar shifts in the entire photoelectron spectrum. Figure 4.5 shows XPS spectra acquired from a graphene on Cu sample UHV annealed to 600 C. The C 1s peak position at 284.7 eV indicates that coupling to the substrate has occurred. The Cu 2p_{3/2} photoelectron peak position at 932.6 eV is indicative of metallic Cu [136]. If a shift in the Fermi level was responsible for the binding energy shift in the C 1s spectrum, then the Cu 2p_{3/2} photoelectron peak position is expected to occur at 932.9-933.0 eV, which is not observed. Thus it is believed that the core level shift in the C 1s binding energy is due to bonding of the graphene overlayer with the Cu substrate. A core level shift in the Cu 2p_{3/2} is not observed, as only a small proportion of the signal originates from the graphene/Cu interface. The observation of the simultaneous suppression of the $\sigma + \pi$ loss peak and increase in the C 1s binding energy at 600 C (Figure 4.3), indicates a significant change in the electronic structure of the graphene overlayer upon coupling. It is thus not clear whether graphene is physisorbed or chemisorbed to the surface. Previous ARPES experiments of graphene coated Cu surfaces, in which the graphene electronic structure was observed to remain intact, were conducted with the known presence of oxygen [132,133]. In order to definitively conclude that the electronic structure remains unchanged, measurement of the C 1s binding energy can be used to ensure that coupling has occurred. In some cases (c.f. Figure 4.4, sample 2), it appears that coupling is inhibited, despite the removal of oxygen. This may be due to differences in the defect content, excessive wrinkling of the graphene film, or perhaps to differences in the substrates between the two samples. It is therefore proposed that the intensity of the observed $\sigma + \pi$ loss peak is inversely related to the

degree of coupling between the graphene and metal substrate, i.e. the more intense the loss, the more decoupled the graphene overlayer is from the substrate. In regard to Figure 4.3, upon removal of oxygen at 600 C (cyan lines), coupling of the graphene to the substrate is achieved and accompanied by suppression of the $\sigma + \pi$ loss feature. Upon exposure to air (Figure 4.3 blue line), oxygen disrupts coupling to the substrate and intercalates, which is accompanied by the return of the $\sigma + \pi$ loss feature.

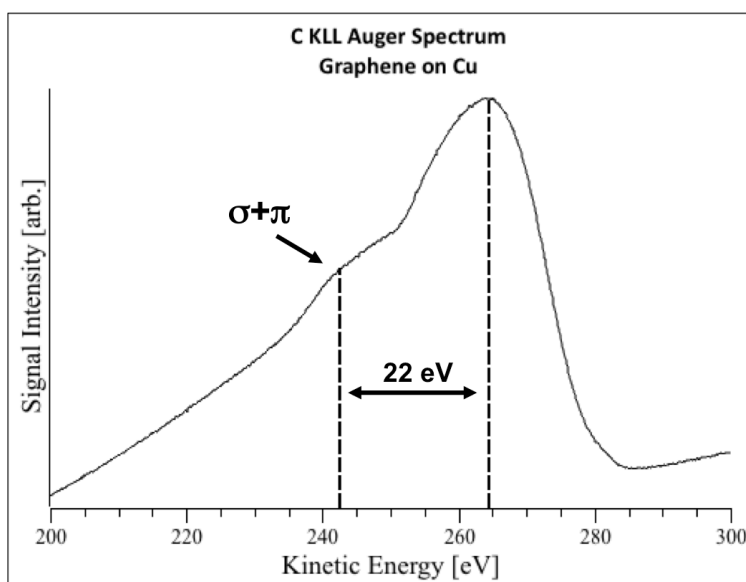


Figure 4.6: C *KLL* Auger spectrum acquired from graphene on Cu. The spectral feature at ~242 eV is believed to be the same loss observed in the Cu *LMM* and Cu 2p_{1/2} spectra (c.f. Figure 4.2)

The above observations also provide some insight into the nature of the interaction between the intercalated oxygen atoms and both the Cu substrate and graphene overlayer. In particular, one may ask whether the oxygen atoms in the intercalated layer interact with the Cu substrate, or graphene overlayer? Considering the spectra collected at 400 C shown in Figure 4.3 (green line), we see that the O 1s photoelectron spectrum indicates the presence of Cu₂O. The simultaneous observation of the $\sigma + \pi$ loss peak and C 1s peak binding energy at 284.3 eV

indicates that the intercalated oxygen layer strongly interacts with the Cu substrate and not the graphene overlayer.

There exists a well-known feature in the *C KLL* Auger spectrum acquired from graphitic surfaces. This feature presents itself as a slight hump on the low kinetic energy side of the peak. Shown in Figure 4.6 is an example spectrum acquired from a graphene on Cu surface, which exhibits this feature. The position of the feature is approximately 22 eV relative to the peak position, in good agreement with the loss feature observed in the Cu *LMM* and Cu $2p_{1/2}$ spectra (c.f. Figure 4.2). Auger transitions involving valence band electrons have been interpreted as a self-convolution of the density of states near the Fermi level [85]. Since the *C KLL* (or *KVV*) Auger transition involves valence band electrons, the spectral signature shown in Figure 4.6 had previously been interpreted as a feature in the graphite density of states [137]. However, its position at about 240 eV could not be accounted for by modeling the peak shape as a convolution of the density of states [137]. Therefore it is proposed that the observed feature in the *C KLL* spectrum is the same $\sigma + \pi$ plasmon loss observed in both the Cu *LMM* Auger transition and Cu $2p_{1/2}$ photoelectron line (c.f. Figure 4.2). This feature is then superimposed on a self-convoluted density of states, and must be accounted for, if attempting to extract information concerning electronic structure from the *C KLL* line shape.

Given the existence of a unique feature in the Auger spectrum of graphene coated surfaces, one may use a scanning Auger microscope to image the distribution and degree of coupling of graphene to such a surface at nanometer length scales. Here, we briefly show an example of such an experiment. Shown in Figure 4.7 are SEM and Auger maps of graphene on a

Cu surface. A mask was placed on the sample so that a selected area could be sputtered to remove the graphene.

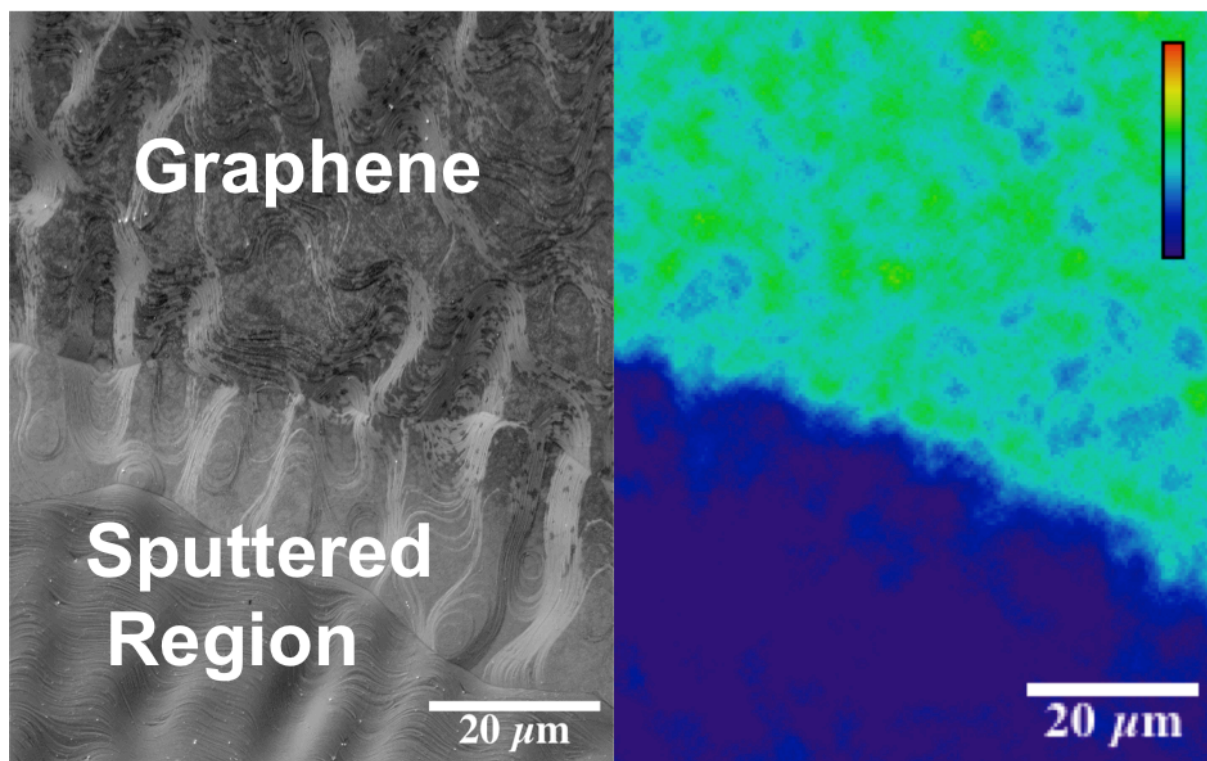


Figure 4.7: SEM image of graphene on Cu (A) and corresponding Auger map of the Cu *LMM* $\sigma + \pi$ loss peak (B). $E_p=10$ keV.

A field of view containing both the sputtered and graphene coated region was selected. The SEM image in Figure 4.7 A indicates the region where the sample was sputtered, and where the graphene film was still present. The Auger map (Figure 4.7 B) is from the same field of view, and is a measure of the $\sigma + \pi$ loss peak intensity normalized to the Cu *LMM* peak intensity. Given the above discussion, this is correlated to the degree of coupling of the graphene film to the substrate, and not *necessarily* related to its presence. However, because oxygen is believed to intercalate any air-exposed sample, the graphene film (where present) is expected to be decoupled and capable of being detected with this method. Figure 4.7 shows that this is a viable

method for mapping the spatial distribution of graphene. Use of this method may provide a means to image physical and chemical heterogeneities of graphene coated surfaces with nanometer spatial resolution. It is noted that simply mapping the distribution of C is not sufficient for identifying the presence of graphene, given that C is present on any surface due to environmental contaminants. A common method for mapping the distribution of graphene is Raman spectroscopy [128], however the spatial resolution is in most cases diffraction limited, and so cannot be performed with the high spatial resolution offered by electron beam based methods.

Imaging of graphene surfaces using a scanning electron microscope requires a low energy ($\sim < 500$ eV) beam, such that the signal is dominated by contributions from the graphene film. Show in Figure 4.8 A and 4.8 B are example scanning electron microscope images of a graphene on Cu surface, imaged with a 125 eV electron beam. One can see various domains, which exhibit bright/dark contrast. It could be suggested that they are indicative of changes in the crystallographic orientation of the substrate, however the morphology of the domains is not consistent with the observed morphology of the substrate grain boundaries. Loss spectra are shown in Figure 4.8 C, and were acquired from the dark and light regions indicated in Figure 4.8 B. In the case of the dark region, a substantial π plasmon peak is observed, which is not the case in the loss spectrum acquired from the light region, where the π plasmon loss intensity is much smaller. On the other hand, the $\sigma + \pi$ loss intensity is higher in the spectrum from the light region. Given the above interpretation, this implies that lighter regions shown in Figure 4.8 A and B are less coupled to the substrate than darker regions. This is supported by Auger spectra shown in Figure 4.8 D, which were acquired from regions of similar contrast. The spectra

indicate that light regions are correlated with the presence of Cl. Cl was observed on some graphene coated samples, and is believed to originate as a contaminant in the substrate. More insight into its presence is provided in section 4.3, where it will be shown that Cl is intercalated between the Cu substrate and graphene overlayer.

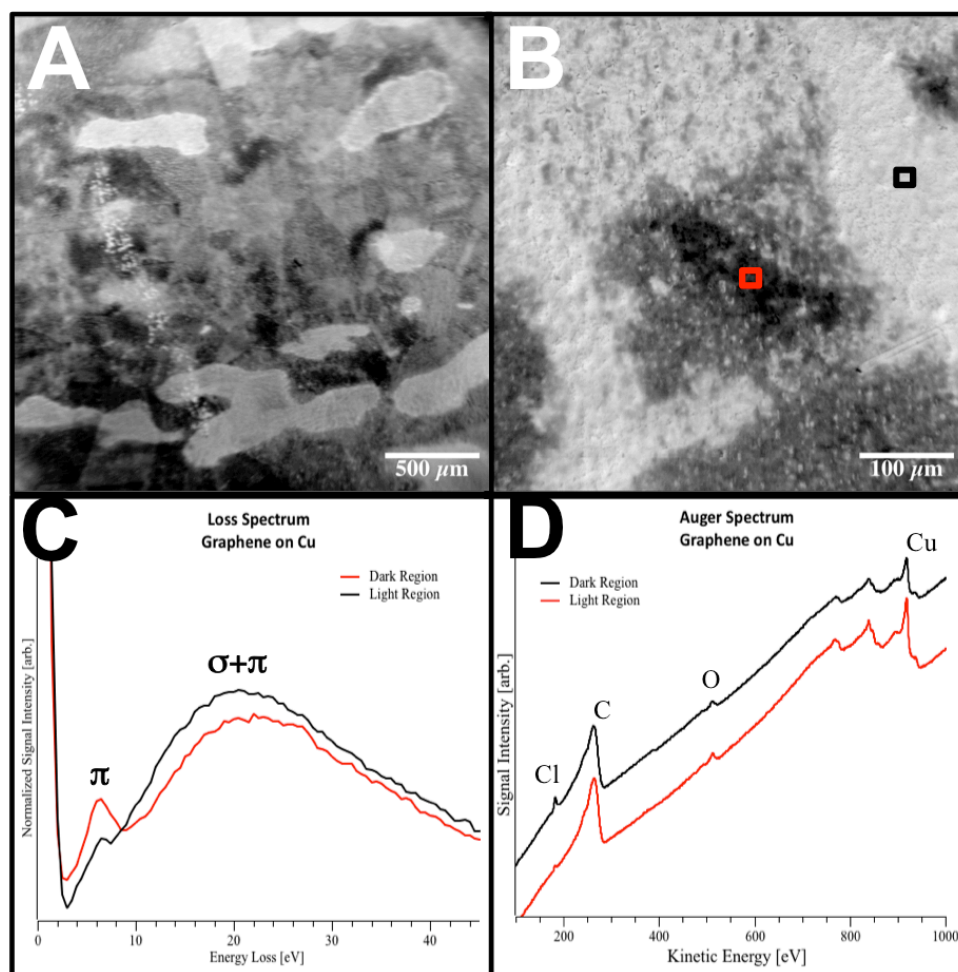


Figure 4.8: A,B: Low energy electron microscope images of graphene on Cu ($E_p = 125$ eV). C: EELS spectrum acquired from the dark/light regions shown in B as red/black boxes respectively. $E_p = 125$ eV. D: Auger spectra acquired from similar regions of bright/dark contrast. $E_p = 5$ keV.

The loss spectra shown in Figure 4.8 C acquired from these regions, support this hypothesis.

The presence of an intercalant, such as Cl, would be expected to decrease the degree of coupling

between the graphene and Cu substrate, and thus enhance the $\sigma + \pi$ loss feature. Moreover, the subsequent suppression of the π loss feature from these regions indicates direct interaction between the Cl atoms and the graphene overlayer, as supported by XPS spectra shown in section 4.4.

4.3 Oxidation of Graphene Coated Cu Surfaces

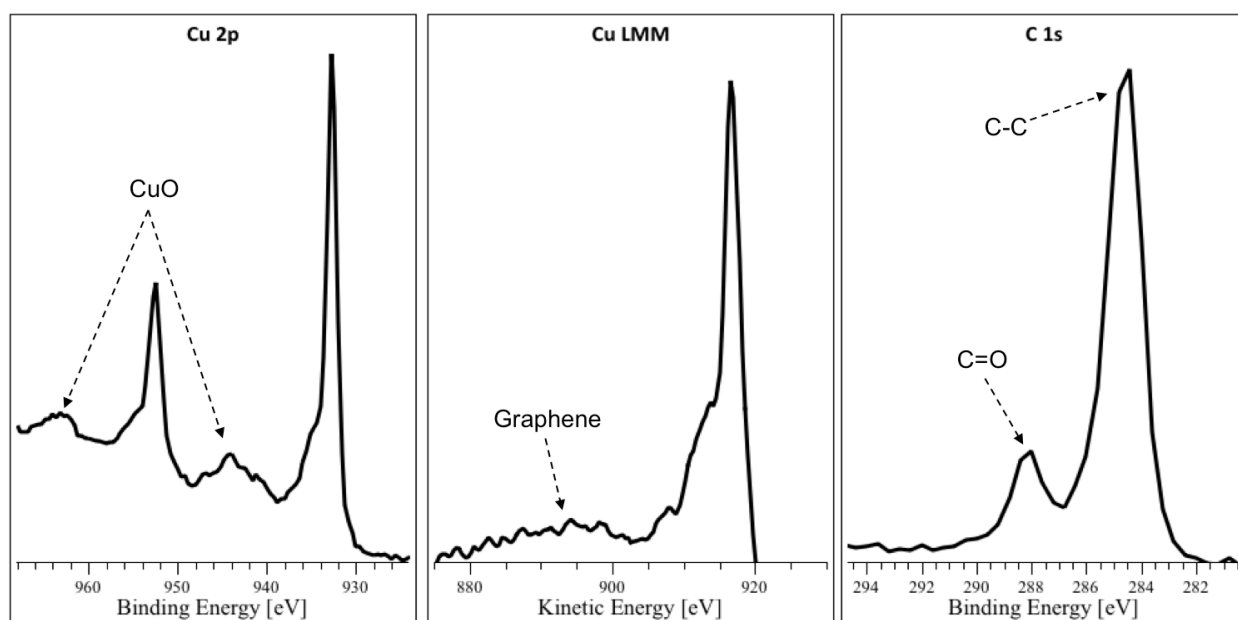


Figure 4.9: XPS spectra acquired from graphene coated Cu foil exposed to air at 200 C. for 30 minutes.

Shown in Figure 4.9 are XPS spectra acquired from a graphene coated Cu foil exposed to air at 200 C for 30 minutes. The Cu 2p spectra show shake-up features characteristic of CuO [136]. The Cu *LMM* Auger transition indicates the presence of graphene via the $\sigma + \pi$ loss feature discussed in section 4.2. The C 1s spectrum exhibits two main features, one at ~288 eV, which is indicative of C=O bonding [138,139]. This peak was observed on many samples, which exhibited substrate oxidation, and its importance will be discussed below. A second peak

at 284.4 eV is indicative of sp^2 C-C bonding, which is consistent with the observation of free standing graphene. These data indicate that the graphene overlayer fails to protect the substrate against oxidation at these temperatures. While the graphene overlayer is still present, it cannot be concluded from these data if oxidation has occurred in the regions which still contain a graphene film.

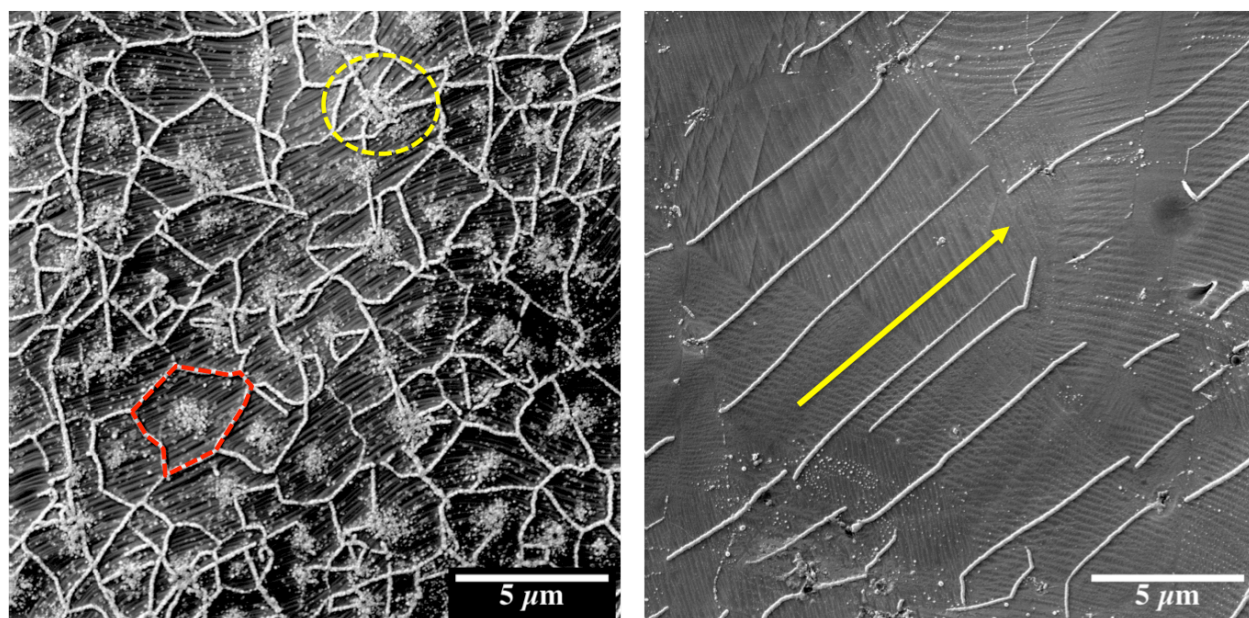


Figure 4.10: SEM images showing oxidation of graphene coated Cu foils exposed to air at 200 C for 30 minutes. Left: SEM image exhibiting two types of localized oxidation: grain boundary (indicated by red line) and filamentous (indicated by yellow line). $E_p = 10$ keV. Right: Growth of oxide filaments. Yellow arrow indicates growth direction. $E_p = 25$ keV.

Shown above in Figure 4.10 are SEM images showing the oxidation of graphene coated Cu foils. Both images indicate that oxidation is localized to specific regions of the surface. The left image in Figure 4.10 exemplifies two broad categories of localized oxidation observed in this work. The first appears to be oxidation at grain boundaries in the graphene overlayer, and is indicated by the red line shown in the left image of Figure 4.10. Oxidation at graphene grain boundaries has been previously reported, and has even been exploited as a method for

characterizing size and distribution of graphene domains [140,141]. That preferential oxidation occurs at graphene grain boundaries is not surprising, as these regions are expected to be highly disordered, and ineffective in isolating the substrate from the environment.

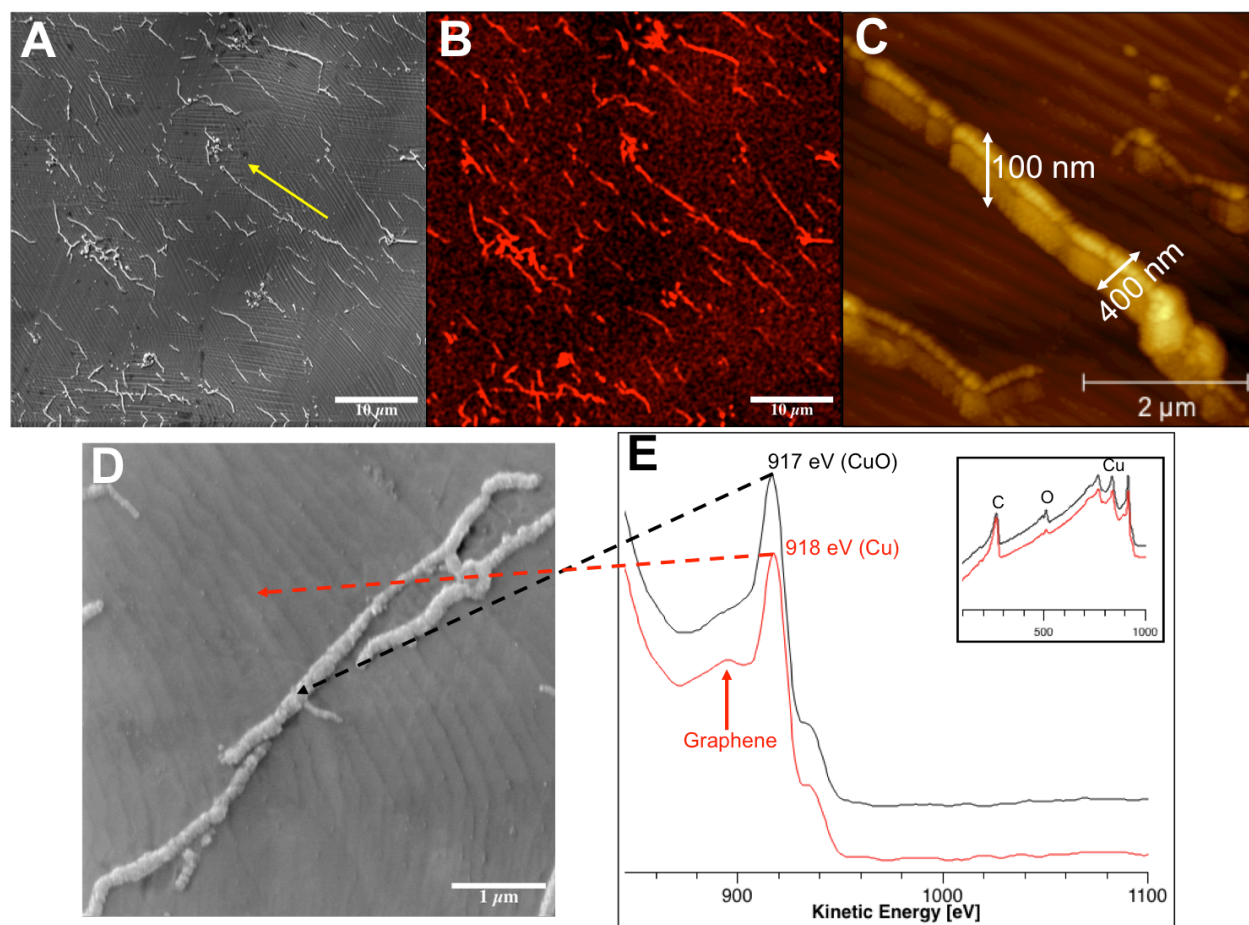


Figure 4.11: Graphene coated Cu substrate oxidized in air at 200 C for 1 hour. A: SEM image of filamentous structures growing on a graphene coated Cu substrate. Yellow arrow indicates direction of growth. $E_p = 10$ keV. B: O K- α EDX map of oxide filaments acquired from the same field of view as A. $E_p = 10$ keV. C: AFM image of oxide filament. D: SEM image of oxide filament from which the Auger spectra shown in (E) were acquired. $E_p = 30$ keV.

The second category is the growth of oxide filaments, shown in the right image of Figure 4.10.

These filaments appear to nucleate at particular regions on the surface, i.e. at the center of graphene domains as indicated by the yellow circle in the left image of Figure 4.10. The oxide

filaments appear to grow along a specified direction, as indicated by the yellow arrow shown in the right image of Figure 4.10.

The oxidation mechanism resulting in the growth of such filaments has not been reported in the literature, and thus warranted further investigation. Shown in Figure 4.11 is an example of a graphene coated Cu foil oxidized for 1 hour at 200 C in air. An O K- α EDX map (Figure 4.11 B) acquired from the same field of view shown in the SEM image in Figure 4.11 A, confirms that the filaments are composed of oxygen, believed to be CuO. An example AFM image of a filament indicates that they are roughly 100 nm tall and 400 nm thick. (Figure 4.11 C). Cu *KLL* Auger spectra, taken from a single filament and from a nearby region indicated in Figure 4.11 D, are shown in Figure 4.11 E. The peak position of the Cu *KLL* transition from the filament (917 eV) and the nearby region (918 eV), indicate the presence of oxidized Cu (likely CuO) and metallic Cu respectively [142]. The feature at ~894 eV, shown in the spectrum taken from a region nearby the filament (red curve, Figure 4.11 E), is the $\sigma + \pi$ loss feature and indicative of the presence of graphene. These data suggest that regions of the substrate still covered by the graphene film are not oxidized, and that oxidized regions no longer possess a graphene film. Oxidation of the substrate therefore appears to be *localized* to the observed filamentous structures, which appear to grow along a particular direction.

These observations raised two questions. The first is why the substrate appears to oxidize only in selective areas, and whether this is random or if some property of the graphene film or substrate makes it particularly susceptible to oxidation in these regions. The second concerns the directed growth of the filament, and whether this is related to the same property responsible

for localized oxidation of the substrate, or if this is some manifestation of the kinetics of the oxidation process. The work presented below is an attempt to answer these questions.

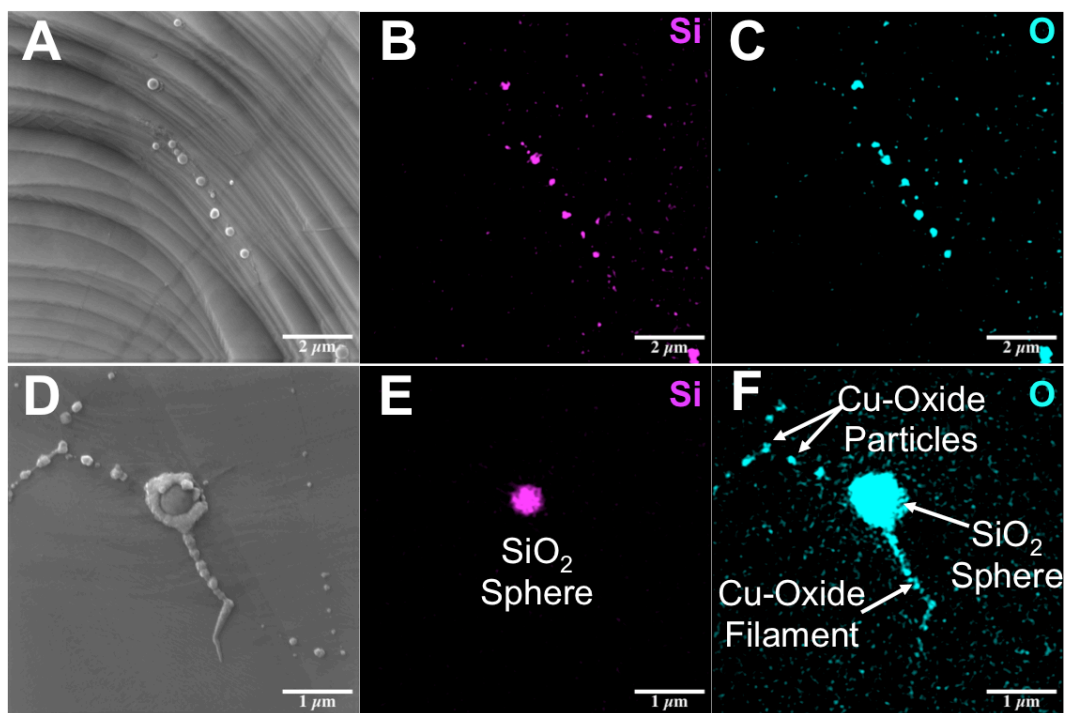


Figure 4.12: A: SEM image of SiO₂ spheres observed on graphene coated Cu surface. $E_p = 25$ keV. B,C: Si and O EDX maps respectively of the same FOV shown in A. $E_p = 25$ keV. D: SEM image of oxide filament growing on graphene coated Cu. $E_p = 30$ keV. E,F: Si and O EDX maps respectively of the same FOV shown in D. $E_p = 30$ keV.

Shown in Figure 4.12 A is an SEM image of small spheres, ~ 200 nm in diameter, observed on a graphene coated Cu surface. EDX data (Figures 4.12 B and C) indicate the presence of Si and O. It is believed that these are quartz particles originating from the CVD growth process, a known issue previously reported [143]. Figure 4.12 D shows an SEM image of a similar surface exposed to air for 1 hour at 200 C. A filamentous structure is observed to grow from what appears to be a sphere-like perturbation in the graphene film. EDX data

(Figures 4.12 E and F) reveal that the filament is a Cu oxide (believed to be CuO). Both Si and O are observed in the region of the sphere-like perturbation. It is believed that this is associated with the same quartz particles observed in Figures 4.12 A-C.

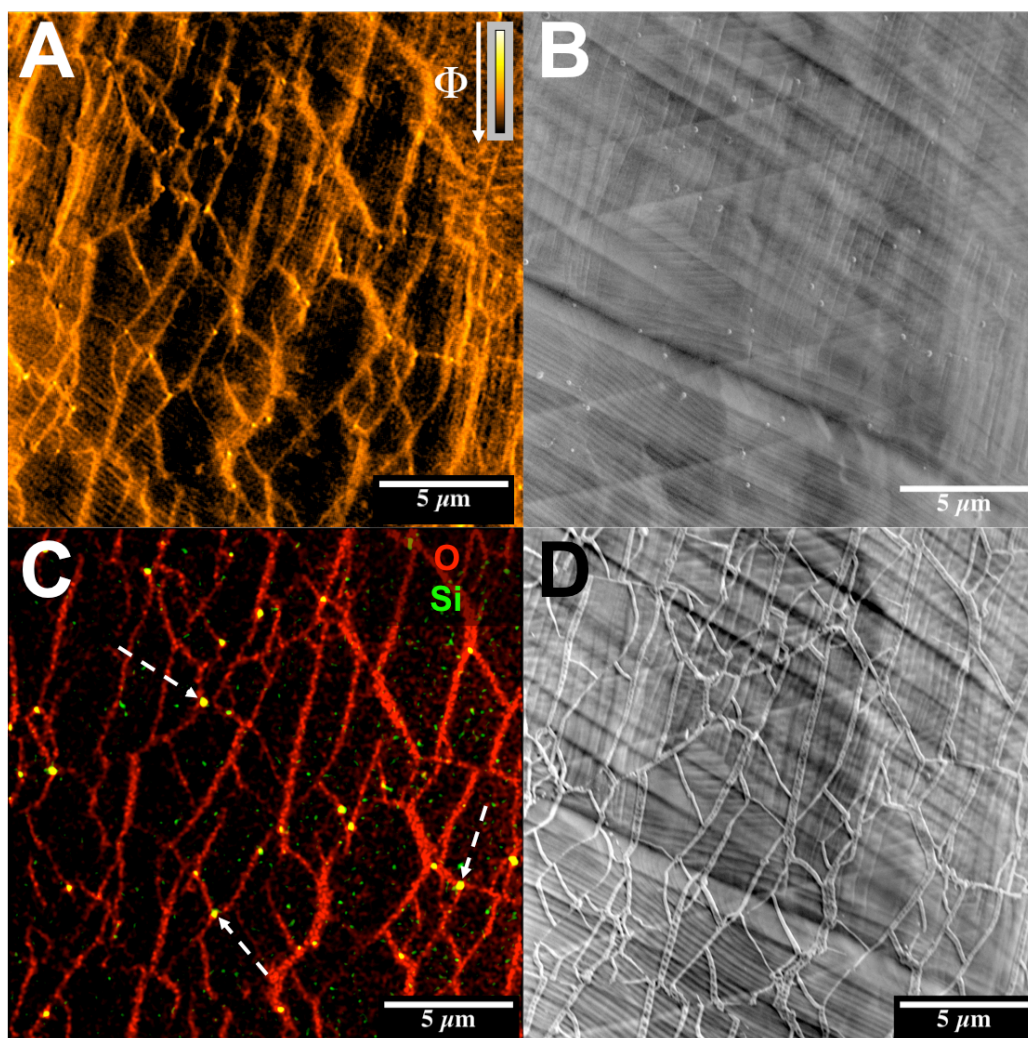


Figure 4.13: A: Surface potential map of graphene on Cu, $E_p=25$ keV, $V_B=-50$ V. B: SEM image of the same field of view shown in A. C: EDX map of the same field of view shown in A and B, post exposure to air at 200 C for 5 minutes. Image is an overlay of the O (red) and Si (green) distribution. $E_p=10$ keV D: SEM image of the field of view shown in C.

What these data suggest is that the graphene overlayer does not provide complete coverage in the neighborhood of the SiO₂ spheres, exposing the underlying substrate in these

regions. Upon exposure to air at 200 C, the substrate is locally oxidized in the region surrounding these spheres, which appear to be a nucleation point for growth of a CuO filament. Indicated in Figure 4.12 F is the presence of small oxide particles not associated with Si (Figure 4.12 E), believed to be some type of Cu-oxide, which have begun to grow in the vicinity of the quartz sphere.

Shown in Figure 4.13 A is a surface potential map of a freshly prepared graphene on Cu foil. Note that bright/dark contrast corresponds to regions where the surface potential is lower/higher. A network of low surface potential regions can be observed on the sample surface. These features are not observable in the corresponding SEM image (Figure 4.13 B). The sample was subsequently heated in air at 200 C for 5 minutes, and the same field of view shown in Figures 4.13 A and B are shown in Figures 4.13 C and D post oxidation. Figure 4.13 C is a red/green overlay of O(red) and Si(green) K- α EDX maps. Figure 4.13 D shows an SEM image of the corresponding field of view. Figures 4.13 C and D indicate the growth of CuO filaments within this region. There is excellent agreement between the regions of low surface potential and localized oxidation of the Cu substrate. Small yellow dots indicated by the white arrows in Figure 4.13 C indicate the presence of both Si and O. These are believed to be the same SiO₂ particles shown in Figure 4.12. Figure 4.13 shows that surface potential mapping can be used to identify and predict reactive regions on solid surfaces. Unlike in the case shown in Figure 4.11 A, the observed substrate oxide growth does not appear to be directed along a particular direction, but rather appears to encapsulate domains. Two possible explanations are offered in regard to this observation. The first is that the domains represent grain boundaries in the graphene overlayer. An alternative explanation is that the oxidized domains originated from a

network of intercalated oxygen. The SiO₂ particles shown as yellow dots in Figure 4.13 C would be regions of the film, which would allow oxygen to intercalate at the Cu/Gr interface. We note that oxide filaments connect the SiO₂ particles. The onset map in Figure 4.13 A then represents a network of intercalated oxygen beneath the graphene, which was present prior to exposing the surface to air at 200 C. This then suggests that the presence of intercalated oxygen decreases the surface potential of the graphene overlayer, which in turn enhances substrate oxidation.

To test the hypothesis that intercalated oxygen decreases the surface potential of a graphene coated Cu surface, an attempt was made to deliberately intercalate oxygen. To do this, a 1 mm hole was sputtered at the center of a graphene coated Cu film. The sample was then heated in air at 200 C for 5 minutes with the intent of driving oxygen intercalation at the interface of the sputtered region and graphene coated surface. Shown in Figure 4.14 A is an SEM image of this interface. The division between the sputtered and graphene coated surface is indicated by the dotted yellow line in Figure 4.14 A. Shown in Figure 4.14 B is a surface potential map from the same field of view as Figure 4.14 A. Low surface potential channels can be observed, which originate at the interface. Auger spectra were acquired from low and high surface potential regions, and are shown in Figure 4.14 C as the black and red curves respectively. The Oxygen *KLL* transition is observed in both regions, however is slightly more intense in the low surface potential channel. A peak at ~ 456 eV is observed only in the spectrum acquired from the low surface potential region. It is not consistent with the O *KLL* Auger series, as the peak at 456 eV should be the least intense [120], which is not observed. Another possibility is that the peak is attributed to Antimony (Sb).

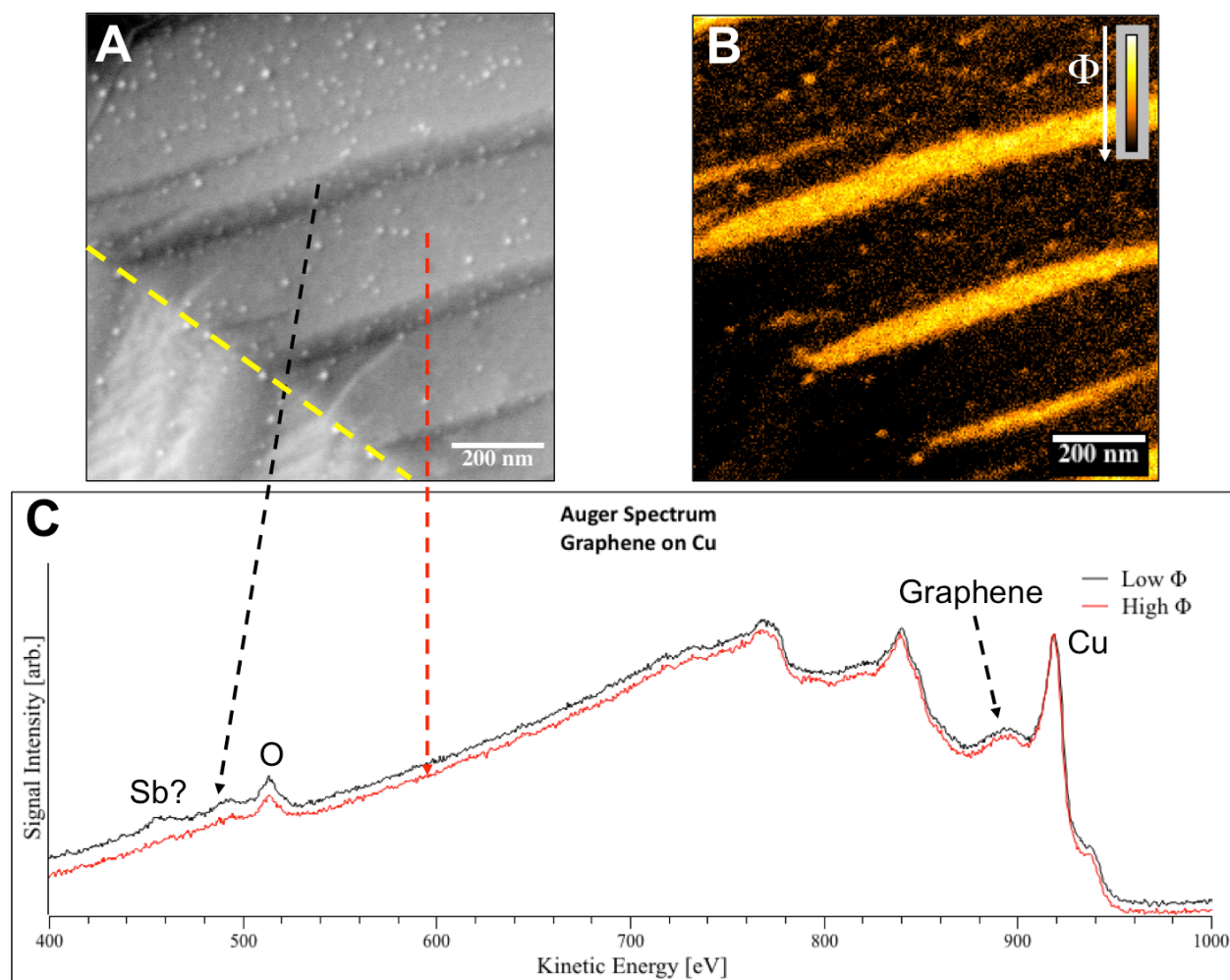


Figure 4.14: A: SEM image of graphene on Cu exposed to air at 200 C for 5 minutes. The dashed yellow line indicates the boundary between a graphene coated region (right) and uncoated region (left). $E_p = 25$ keV. B: Surface potential map acquired from the same field of view shown in A. $E_p = 25$ keV $V_B = -50$ V. C: Auger spectrum acquired from regions of low surface potential (black curve) and high surface potential (red curve). $E_p = 25$ keV.

While unlikely, we note that XPS spectra acquired from similar samples suggest the possibility for the presence of Sb. Shown in Figure 4.15 are XPS, Auger, and EDX spectra acquired from a graphene on Cu sample UHV annealed to 700 C. Three peaks are observed in the O 1s photoelectron spectrum shown in Figure 4.15 A. A peak at 532.8 eV is associated with C-O [139]. The two additional peaks at 536.8 and 527.6 eV are those possibly attributed to Sb.

The nominal values of the Sb $3d_{3/2}$ and $3d_{5/2}$ peaks are 537.6 and 528.3 eV respectively [136]. The peak positions shown in Figure 4.15 A differ considerably from the nominal values of Sb by 0.7-0.8 eV, however their difference of 9.3 eV is in fairly good agreement. The observed peak positions in Figure 4.15 A are also not consistent with reported chemical shifts for Sb [136]. Auger and EDX spectra acquired from similar samples, shown in Figure 4.15 B and C, did not indicate the presence of Sb. Both Auger and XPS are expected to have similar limits of detection, however XPS may in some cases be considered more sensitive. EDX data acquired from this region did not indicate the presence of Sb. However, if only present at the Gr/Cu interface, EDX would not be sensitive enough to detect it.

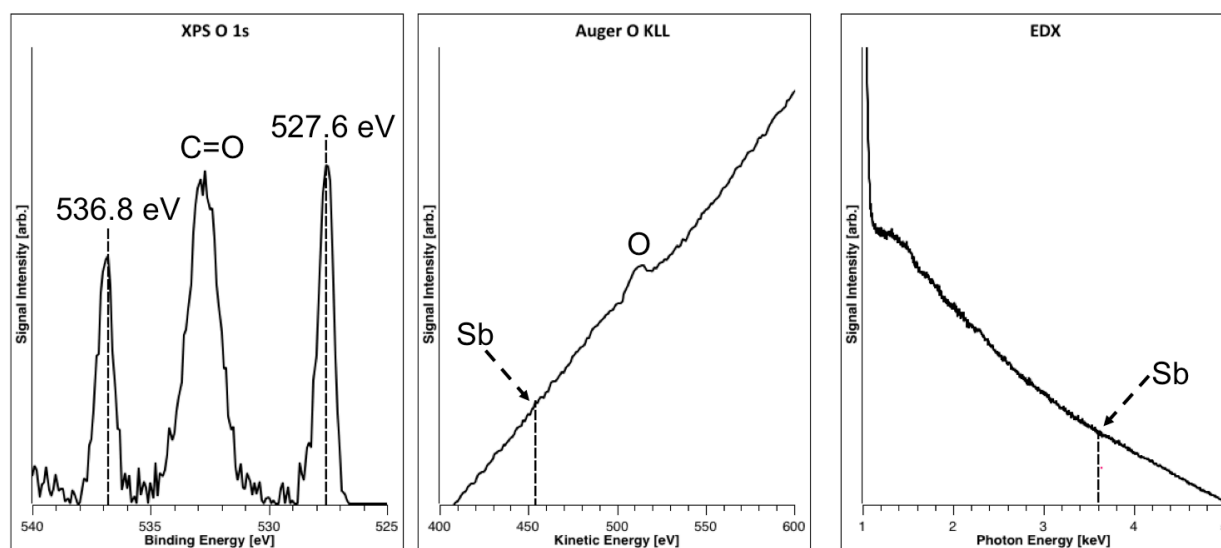


Figure 4.15: Graphene on Cu UHV annealed to 700 C. Left: O 1s XPS spectra. Middle: Auger spectrum showing the O *KLL* peak, and the nominal peak position of the Sb *MNN* transition. $E_p = 5$ keV. Right: EDX spectrum showing the nominal peak position of the Sb $L\alpha$ X-ray transition. $E_p = 5$ keV.

Cu foils used as the substrate material to grow graphene films were obtained from the same company, which provided the CVD graphene on Cu samples for these studies (ACS Material Pasadena, California). These foils are considered to be similar with regard to the

impurity content of the substrates used to grow the graphene films. The uncoated Cu foils were UHV annealed to 700 C, and XPS spectra acquired from these samples did not indicate the presence of the two peaks at 536.8 and 527.6 eV. If Sb were present as an impurity in the Cu foil, its detection via XPS would be expected. Therefore, the two peaks observed in the XPS spectra are not believed to be related to Sb, but to the presence of oxygen. The peaks at 536.8 eV and 527.6 eV are hypothesized to be O 1s photoelectron lines associated with C and Cu respectively. The peak at ~456 eV in the Auger spectrum acquired from the low surface potential region (black curve, Figure 4.14 C) is believed to be related to the O 1s peaks observed in the XPS spectra (left panel Figure 4.15). Regardless, the data shown in Figure 4.14 B and C shows that heterogeneities present at the Cu/graphene interface alter the surface potential. The intensity of the $\sigma + \pi$ loss feature is larger in the spectrum acquired from the low surface potential region suggesting the presence of an intercalant (believed to be oxygen).

Previous ARPES measurements of graphene on Cu (100) surfaces indicated the presence of two electron doped levels, one associated with charge transfer due to interactions between the Cu substrate and the graphene film, and another assumed to be due to the presence of intercalated oxygen [132]. The doping level due to intercalated oxygen was observed to be ~0.3 eV higher than the doping level associated charge transfer. Thus we interpret the observed low surface potential regions shown in Figures 4.13 A and 4.14 B as being due to the presence of a network of intercalated oxygen. Others have observed inhomogeneities in the surface potential on graphene surfaces, and have claimed that they result from charged impurities beneath the graphene [144]. There have also been claims that these inhomogeneities are responsible for increased reactivity of graphene [145,146]. Our observations provide direct evidence of

enhanced reactivity of graphene surfaces due to surface potential variations caused by heterogeneities, i.e. intercalated species or substrate impurities. It is believed that the observation of directed growth of oxide filaments (c.f. Figure 4.10), is indicative of a diffusion path of the intercalated species.

4.4 The Inhibition of Oxidation of Graphene Coated Cu Surfaces

It was observed that some graphene coated Cu foils exhibited resistance to oxidation. Shown in Figure 4.16 are the Cu $2p_{3/2}$ and C 1s XPS spectra acquired from two different graphene coated Cu samples, labeled as sample 1 and sample 2, indicated by the red and black curves respectively. Both samples were exposed to air at 200 C for 30 min. In the case of sample 1, the Cu $2p_{3/2}$ spectrum reveals the presence of CuO, indicating oxidation of the substrate. This is not observed in the case of sample 2 (black curve). Comparison of the C 1s

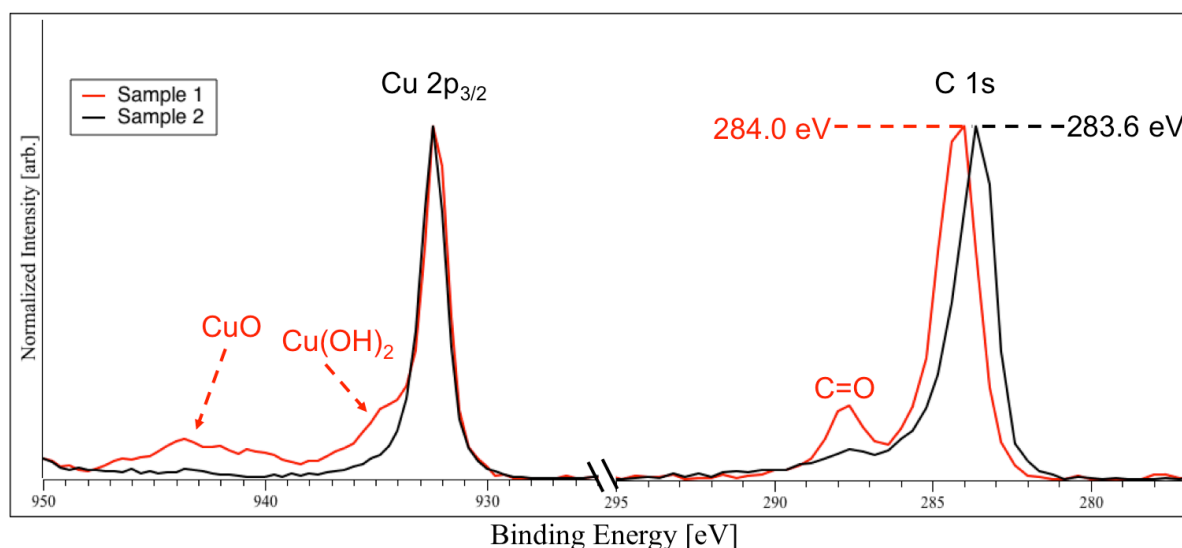


Figure 4.16: XPS spectra acquired from two different graphene coated Cu surfaces. Both exposed to air at 200 C for 30 min.

spectra between samples 1 and 2 reveals two significant differences. The first is the presence of a peak at ~ 288 eV, which is indicative of C=O bonding [138,139], and is quite prominent in the sample which exhibited substrate oxidation (sample 1). This suggests that the adsorption of O on the graphene surface is a critical step in substrate oxidation. The second difference is the peak binding energy in the C 1s spectrum. Sample 1 exhibits a peak position at ~ 284 -284.4 eV, which is indicative of sp^2 C-C bonding. The peak position in the C 1s spectrum from sample 2 is downshifted 0.6 -1 eV relative to sample 1. It was thus hypothesized that this binding energy shift was related to sample 2's resistance to substrate oxidation. One possible explanation for the differences in the C 1s binding energy in samples 1 and 2 is the defect content of the graphene overlayer. It has been shown that the presence of C vacancies in graphitic carbon results in a downshift in the C 1s peak position beyond sp^2 carbon (284.4 eV) [147]. While it is perhaps counterintuitive to suggest that a defective graphene film is more resistant to oxidation, it was shown by Vinogradov *et. al.* that the deliberate introduction of defects inhibited oxygen intercalation in graphene coated Ir (111) [148].

Experiments were conducted whereby defects were deliberately introduced into the graphene overlayer via Ar^+ ion sputtering. Graphene on Cu samples were annealed at 600 C in UHV to remove environmental contaminants as well as intercalated oxygen. The samples were then allowed to cool to RT. Following the procedure given in [148], the introduction of defects into the graphene film was conducted via sputtering with 300 eV Ar^+ ions. XPS spectra of the C 1s photoelectron line were collected after 30 second sputtering intervals. Shown in Figure 4.17 are the results of such an experiment. The left panel shows C 1s spectra acquired at various stages of the defect introduction process. The black curve was acquired after UHV annealing,

and the peak position at 284.9 eV indicates coupling of the graphene film to the substrate. The red curve shows that upon sputtering with 300 eV ions, a significant downshift of the C 1s binding energy to 283.9 eV is observed. This corresponds to a total sputtering time of 180 s and a total dose of $\sim 10^{14}$ Ar⁺ ions.

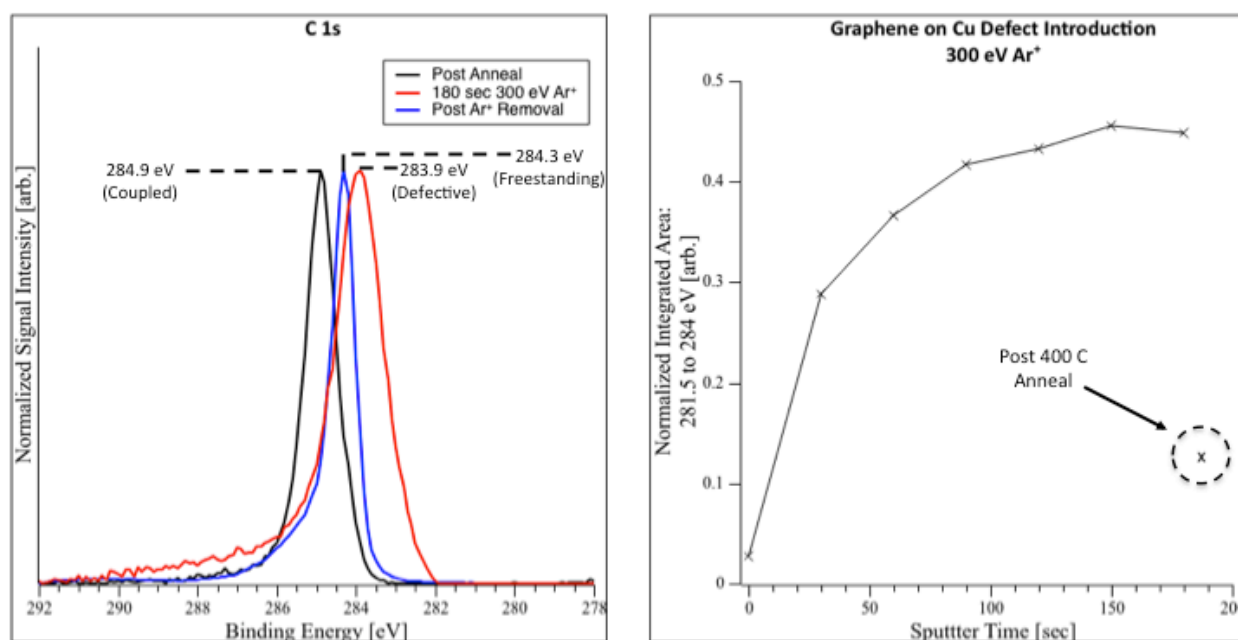


Figure 4.17: Left panel: C 1s XPS spectra acquired from graphene on Cu. The black curve was acquired after UHV annealing to 700 C. The red curve was acquired after 180 sec sputtering with 300 eV Ar⁺ ions. The blue curve was acquired after removal of Ar⁺ via UHV annealing to 400 C. Right panel: Integrated area of the C 1s spectrum from 281.5 to 284 eV normalized to the total integrated area of the C 1s peak as a function of sputter time with 300 eV Ar⁺ ions. The value of the data point indicated by the dotted circle was acquired after UHV annealing to 400 C.

As the C 1s binding energies related to the presence of C vacancies in graphitic C are ≤ 284.0 eV [147], a qualitative measure of the defect content in a given graphene film is the integrated area under the C 1s curve from 281.5 to 284 eV, normalized to the total C 1s peak area. This quantity is shown as a function of sputter time in the right panel of Figure 4.17, and is

observed to increase with increasing sputter time. This suggests the creation of vacancies via 300 eV Ar⁺ ions. The curve in the right panel of Figure 4.17 is observed to plateau after 120 seconds of sputtering. This is to be expected, since the probability of an Ar⁺ ion striking a C atom in the graphene lattice decreases with increasing vacancy content.

After exposure to the low energy Ar⁺ beam, Ar was observed in the XPS spectrum. It was found that the Ar could be removed via UHV annealing to ~ 400 C. The C 1s spectrum shown in the left panel of Figure 4.17 indicates a shift in the C 1s peak position to 284.3 eV, consistent with sp² C-C bonding. The portion of the C 1s peak attributed to the defect content is also observed to decrease upon annealing, as indicated by the arrow in the right panel of Figure 4.17. We note that it is still larger than its pre sputter value. There are two possible explanations for this observation. Either the chemical shift observed in the C 1s spectra upon sputtering (left panel Figure 4.17) is not related to the creation of defects but instead to an interaction between the C atoms in the graphene film and Ar, or the observed chemical shift is due to the creation of a defective film and the process of annealing to 400 C heals the defects. Previous XPS experiments whereby graphite was bombarded with Ar⁺ ions did not indicate a shift in the C 1s binding energy [149,150]. Moreover since Ar is a noble gas, it is not expected to interact strongly with the graphene surface. It is therefore believed that the observed shift in the XPS spectra upon Ar sputtering shown in Figure 4.17 is due to the creation of a defective graphene film, whereby the sp² network of the graphene is disrupted. Upon annealing to 400 C to remove Ar ions, the sp² network is somewhat restored, and the film is partially healed.

The deliberate action of producing defective graphene coated Cu surfaces via Ar⁺ sputtering was not observed to inhibit oxidation of the substrate. It is noted that Ar⁺ ion beam

energies down to ~ 20 eV were used in an attempt to produce defective graphene films. None of the films exhibited resistance to oxidation, which was observed to preferentially occur within the sputtered regions. The observed down shift in the C 1s binding energy was only observed at ion beam energies ≥ 300 eV. Therefore, the C 1s binding energy shift observed in Figure 4.16 is not attributed to the presence of a defective film.

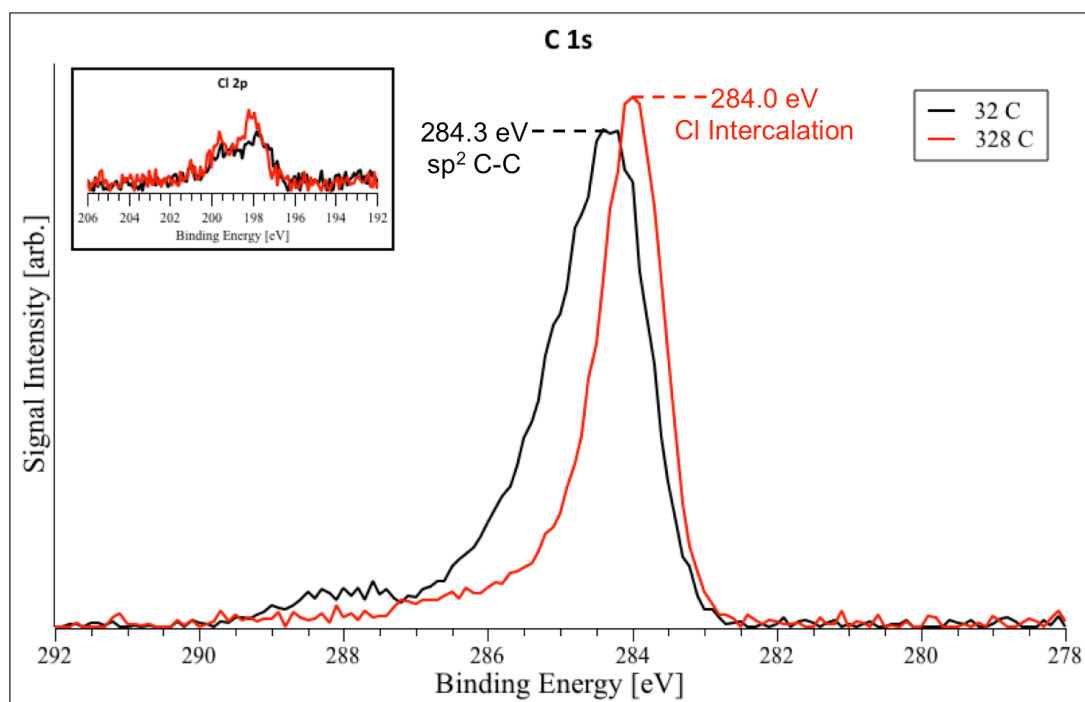


Figure 4.18: C 1s XPS spectrum acquired from graphene on Cu. The black curve was acquired at nearly room temperature (32 C), red curve was acquired after UHV annealing to 328 C. Inset shows the Cl 2p spectrum acquired under identical conditions.

During the analysis of defective graphene films which had been oxidized in air at 200 C, it was observed that regions which exhibited resistance to oxidation, were also found to contain Cl. XPS spectra acquired from these regions indicated a downshift in the C 1s peak position, similar to what is shown in Figure 4.16. Therefore, it was hypothesized that Cl might play a role in the oxidation resistance of graphene coated Cu foils. Cl contamination had been observed in

some of the graphene coated Cu samples used in this study. These samples were selected to test this hypothesis. Shown in Figure 4.18 are C 1s XPS spectra acquired from such a sample at 32 C (black curves) and 328 C (red curves), the inset shows corresponding Cl 2p spectra. At 328 C, a shift in the C 1s peak position is observed from 284.3 to 284 eV. A downshift in the C 1s peak position is first observed at ~ 300 C. A similar shift is not observed in the Cu 2p photoelectron spectrum, and indicates a strong interaction of Cl with the graphene film. The Cl 2p spectrum is shown in the inset of Figure 4.18, and the peak position of the Cl 2p_{3/2} is ~ 198 eV. The shift in the C 1s binding energy of 0.3 eV is in good agreement with similar experiments previously conducted with graphene grown on Ir (111) [151]. The peak position of the Cl 2p_{3/2} is also in good agreement [151]. In the current work, downshifts in the C 1s peak position up to ~ 0.8 eV to 283.6 eV were observed. Differences in the C 1s peak binding energy are attributed to the availability of Cl for intercalation.

The question of how Cl is incorporated into the graphene film naturally arises. Several possibilities exist, namely that Cl is bound on the vacuum side to the graphene film, that Cl is incorporated into the graphene as a substitutional defect, or is intercalated between the Cu substrate and graphene overlayer. Previous LEED measurements conducted on graphene coated Ir (111) surfaces indicated that a decoupling of the graphene film was correlated with the observed shift in the C 1s photoelectron spectrum upon chlorination. It was thus concluded that Cl had intercalated the graphene/Ir interface lifting the film from the substrate. This was also supported by evidence of changes in the Ir 4f photoelectron spectrum attributed to the intercalated Cl. Others have suggested that Cl binds directly to graphene grown on Cu and Si substrates, i.e. that the graphene film is functionalized and of the form Cl/G/substrate [152,153].

However the binding energy in the C 1s spectrum in these studies was observed to increase upon chlorination, opposite to the trend observed in the present work. We note that in the case of a Si substrate, the difference in the observed binding energy shift could be due to the difference in the substrate, and that in the case of graphene coated Si surfaces, Cl does not intercalate. Thus it is believed that in the present work, the observed shift in the C 1s binding energy shown in Figure 4.17 is due to the intercalation of Cl. Previous work showed that Cl intercalation (functionalization) results in hole doping of graphene [151–153], and suggested that the degree of doping appears to depend on the substrate. In the case of graphene coated Cu surfaces, the shift in the Fermi level was found to be ~ 0.6 eV [151].

Upon heating the Cl intercalated graphene coated Cu surfaces, oxidation of the substrate was observed to be inhibited, similar to what is observed in sample 2 shown in Figure 4.16. Thus it is the presence of Cl, not a defective film, which is believed to be responsible for the enhanced protection against oxidation. Shown in Figure 4.19 A is an Auger map of the Cl *LMM* intensity acquired from a Cl intercalated graphene on Cu sample exposed to air for 30 minutes at 200 C. Cl intercalation was achieved by heating the sample in UHV to ~ 320 C, similar to what is shown in Figure 4.18. Figure 4.19 A indicates that the Cl is not homogeneously distributed across the surface, but rather that regions of depletion and enrichment are observed. Auger spectra taken from Cl depleted and enriched regions are shown in the black and red curves of Figure 4.19 B respectively. Oxygen is observed in the Cl depleted regions, but *not* in the enriched regions. The inset in Figure 4.19 B shows the $\sigma+\pi$ loss intensity from the same two regions, and indicates that graphene is present in both areas. The intensity of the loss in the Cl enriched region (red curve) is higher, indicating a greater degree of decoupling of the graphene

from the Cu substrate, and further evidence that Cl is intercalated. Figure 4.19 is direct evidence that Cl intercalation inhibits oxidation of both the substrate and graphene overlayer. The observation of Cl depleted regions in Figure 4.19 A, supports the hypothesis that there is a limited availability of Cl for intercalation in these samples, and explains the observed variability in the C 1s peak position upon intercalation.

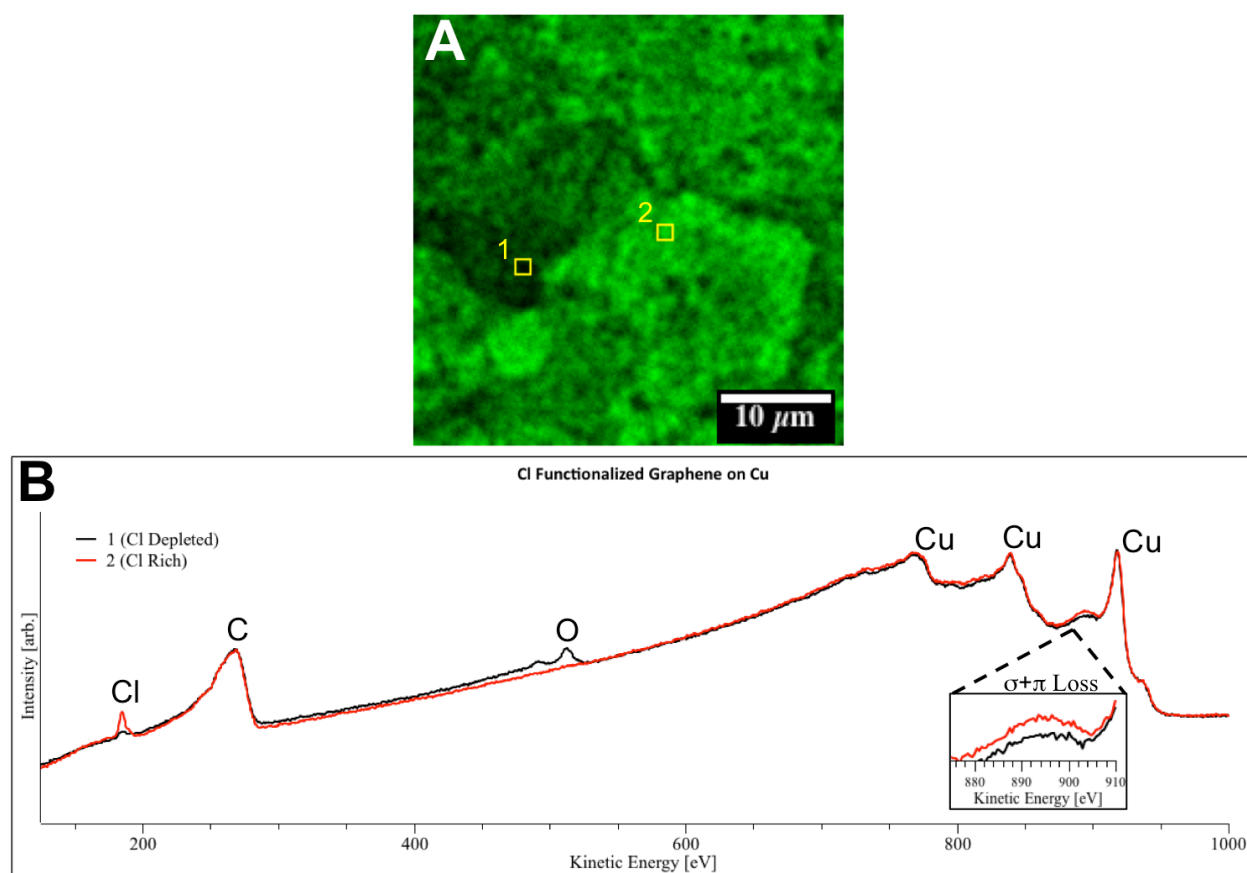


Figure 4.19: Cl intercalated graphene coated Cu foil exposed to air at 200 C for 30 minutes. A: Cl LMM Auger map. B: Auger spectra acquired from a Cl depleted region labeled 1 in the Auger map (black curve) and Cl enriched region labeled 2 in the Auger map (red curve). Inset shows the $\sigma+\pi$ loss peaks from the same two regions. $E_p=25$ keV.

As shown in Figure 4.16, the inhibition of substrate oxidation is associated with the absence of a peak in the C 1s spectrum at ~ 288 eV, associated with ketone/carbonyl groups (C=O) [138,139]. This suggests that the formation of C=O bonds at the graphene surface are a precursor in oxidation of the substrate, and that intercalation of the graphene film with Cl inhibits formation of the C=O bond. As has been suggested, etching of graphene proceeds via the adsorption of O to the graphene surface, and subsequent desorption as CO [73]. In other words, removal of the graphene overlayer during oxidation occurs from top to bottom, and not bottom to top. For example as discussed in section 4.3, intercalated oxygen was believed to be responsible for subsequent oxidation of the substrate. It could be suggested that the intercalated oxygen directly etches the graphene overlayer, a bottom to top mechanism. However, the data presented in Figure 4.3 shows that the intercalated oxygen layer can be removed at temperatures far exceeding 200 C without destroying the graphene film. Cl intercalation may serve two important roles in the inhibition of substrate oxidation. The first is that it inhibits O intercalation, which as suggested in section 4.3 is believed to be responsible for localized oxidation of the substrate. The second is that unlike in the case of O intercalation, Cl intercalation does not enhance the reactivity of the graphene overlayer, but rather appears to possess an inhibiting effect.

4.5 The Properties of Intercalated Water

The interaction of water with graphene coated metal surfaces is directly relevant in understanding the efficacy of such films to protect against corrosion. As discussed in section 1.5, a commonly proposed failure mechanism of graphene coated metal surfaces involves the intercalation of water. However, it is not clear what role the intercalated water plays in the

failure of graphene films. Given that intercalated water is confined to an interface of atomic dimension, it is reasonable to hypothesize that its behavior is different when compared to water at the interface between a bare metal surface and bulk solution. Here we present some preliminary results, which provide some insight into the interaction of intercalated water with graphene coated Cu surfaces.

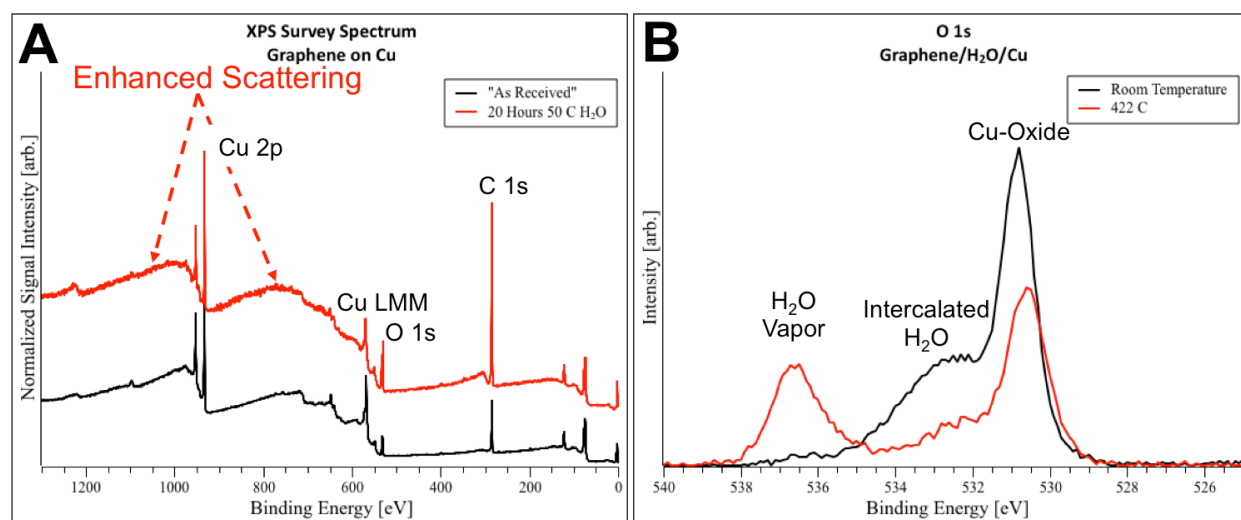


Figure 4.20: XPS spectra of water intercalated graphene on Cu. A: Survey spectra comparing graphene on Cu in its “as received” condition (black line) and after 20 hours intercalation at 50 C (red line). B: O 1s photoelectron spectra acquired from an intercalated sample at room temperature (black line) and at 420 C (red line).

Water intercalation was achieved by immersing graphene coated Cu foils in ultra-pure DI water (Millipore, $\sim 18.2 \text{ M}\Omega \text{ cm}$). Water temperatures ranged from room temperature to $\sim 50 \text{ C}$. Evidence for water intercalation was provided by XPS. Shown in Figure 4.29 are XPS spectra of water intercalated graphene on Cu foils. Figure 4.20 A shows survey spectra comparing graphene on Cu in its “as received” condition (black line) with a similar sample exposed to water at 50 C for 20 hours (red line). A relative increase in the background in the water exposed sample on the low kinetic energy side of the Cu 2p photoelectron lines and Cu LMM Auger

series is observed. The increase in the background is interpreted as being due to the presence of intercalated water, which results in an enhancement in the inelastic scattering of the Cu 2p photoelectrons and Cu LMM Auger electrons.

Shown in Figure 4.20 B is an O 1s photoelectron spectrum acquired from a similar water intercalated sample. At room temperature, two broad features can be observed. One associated with the presence of Cu-Oxide, and a second believed to be indicative of intercalated H₂O. A more detailed analysis of the O 1s spectrum is provided below. When the sample is heated to ~420 C, the intensity of the intercalated H₂O peak decreases and a new peak is observed at 536.6 eV. This peak is believed to be indicative of H₂O vapor trapped beneath the graphene overlayer. Its peak position is in good agreement with previous ambient pressure XPS experiments conducted at pressures of 1 Torr H₂O [154]. At ~600 C no water vapor is observable in the O 1s spectrum, and is believed to have been expelled into the vacuum. The C 1s peak is still observed post annealing, indicating that the graphene overlayer is still present. The data in Figure 4.20 is direct spectroscopic evidence that H₂O may intercalate graphene coated metal surfaces, and that this intercalated layer is stable (at room temperature) even under UHV conditions. Intercalated water was found to be stable in the UHV for at least 60 hours. It was found that water intercalation could be achieved within 1 hour at temperatures of ~45 C. At room temperature, intercalation was observed to occur within a time period of ~ 12 hours.

Shown in the top panel of Figure 4.21 is a high-resolution O 1s photoelectron spectrum acquired from a water intercalated graphene on Cu sample. The spectrum was fitted with the following 5 peaks: CuO at 529.9 eV [135] (purple line), Cu₂O at 530.5 eV [135] (red line),

$\text{Cu}(\text{OH})_2$ at 531.2 eV [155] (blue line), molecular water adsorbed on the Cu surface $(\text{H}_2\text{O})_{\text{ads}}$ at 532.5 eV [154,156,157] (green line), ether C-O bonding at 533.7 eV [148] (cyan line).

The evolution of the components in the O 1s spectrum was monitored at sample temperatures of 28 C (RT), 50 C, 100 C, and 200 C, and is shown in the bottom panel of Figure 4.21. Here, the amount of a particular species is determined as a percentage of its fitted area to the total area under the O 1s curve. At 50 C, a slight decline in the Cu_2O component (red line, bottom panel Figure 4.21) is observed to correlate with a slight increase in the $\text{Cu}(\text{OH})_2$ component (blue line, bottom panel Figure 4.21). At 100 C, the $\text{Cu}(\text{OH})_2$ component decreases, and continues to decline at 200 C. This is associated with a corresponding increase in Cu_2O , and suggests the conversion of $\text{Cu}(\text{OH})_2$ to Cu_2O via, $\text{Cu}(\text{OH})_2 + 3\text{Cu} \rightleftharpoons 2(\text{Cu}_2\text{O}) + 2\text{H}_{\text{ads}}$ or $\text{Cu}(\text{OH})_2 + 3\text{Cu} \rightleftharpoons 2(\text{Cu}_2\text{O}) + \text{H}_2$. The XPS instrument used in this study cannot directly detect H [158], and so it cannot be stated with sufficient confidence, which if any of the above two reactions occur. Similar experiments conducted with graphene grown on Ni substrates indicated H bonding to the graphene overlayer upon dissociation of water, and was associated with a significant modification of the C 1s peak shape [159]. No such modification of the C 1s peak shape was observed in the present case.

The $(\text{H}_2\text{O})_{\text{ads}}$ content (green line, bottom panel Figure 4.21) is constant throughout the entire temperature range up to 200 C. This is in stark contrast to previous experiments conducted on Cu (110) using ambient pressure XPS [154]. In that work, Cu (110) surfaces were exposed to partial H_2O pressures of 1 Torr. Complete dissociation of water was observed between 155-180 C. Previous experiments in UHV suggest that water irreversibly dissociates on Cu as well as most metal surfaces [157,160]. The dissociation of water at metal surfaces is

suggested to be a precursor to corrosion [161]. The data shown in Figure 4.21 suggest that graphene stabilizes the adsorption of H_2O on the Cu surface. The C 1s peak binding energy is observed at ~ 284.7 eV throughout the entire temperature range shown in Figure 4.21, and suggests a strong coupling of the graphene to the intercalated water layer, similar to what is observed when coupled to a bare Cu surface (c.f. Figure 4.5).

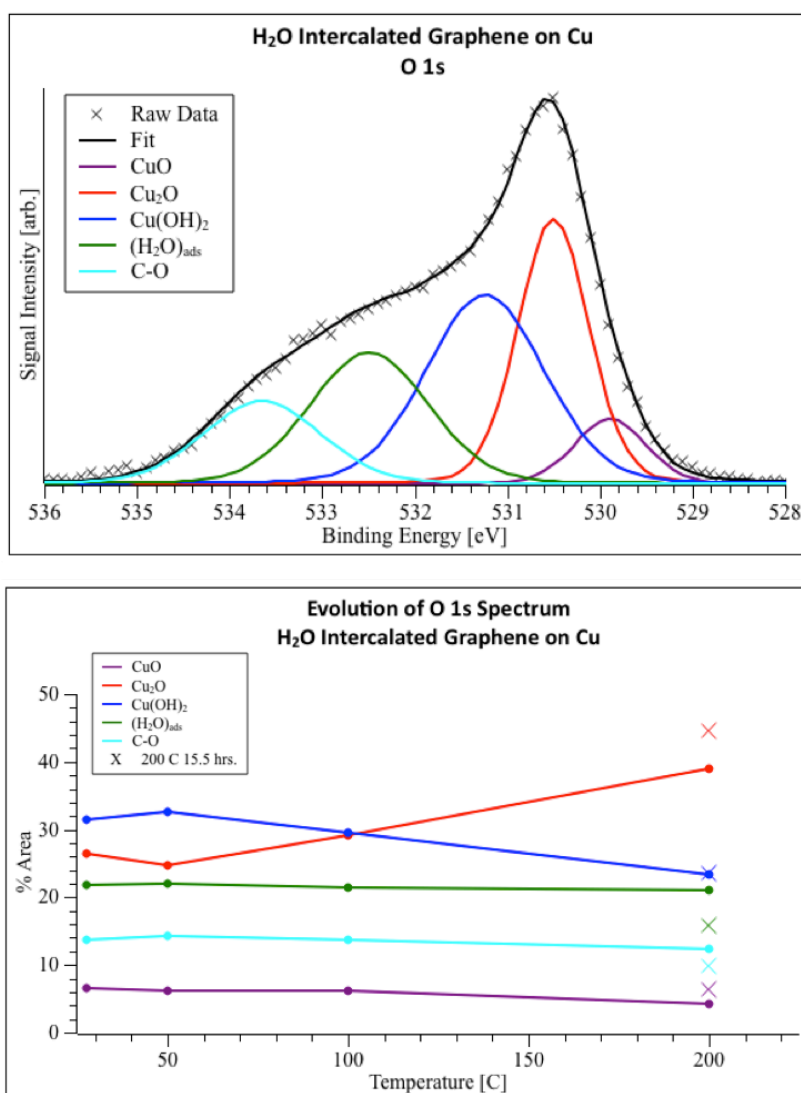


Figure 4.21: Top panel: O 1s photoelectron spectrum acquired from water intercalated graphene on Cu. The spectrum has been fitted with 5 components indicated by the various colors in the figure. Bottom panel: Evolution of the O 1s spectrum with temperature. The colors refer to the same fitted components shown in the spectrum in the left panel.

Upon heating to 200 C, the sample temperature was maintained for 15.5 hours in UHV. An XPS spectrum was subsequently acquired from the sample, and the results are indicated by the 'X' symbol in the bottom panel of Figure 4.21. An increase is observed in Cu_2O , as well as a slight increase in CuO . This is accompanied by a decrease in $(\text{H}_2\text{O})_{\text{ads}}$. No change is observed in the $\text{Cu}(\text{OH})_2$ component. This suggests that oxidation of the Cu surface did not involve dissociation, and occurred directly via, $(\text{H}_2\text{O})_{\text{ads}} + 2\text{Cu} \rightleftharpoons \text{Cu}_2\text{O} + 2\text{H}_{\text{ads}}$, and that at 200 C this is a relatively slow process. Another possibility is that dissociation of $(\text{H}_2\text{O})_{\text{ads}}$ occurred, and that the subsequent hydroxide was unstable and quickly converted to Cu_2O or CuO . These data suggest that the dissociation of intercalated water initially proceeds rapidly, and that much of the adsorbed $\text{Cu}(\text{OH})_2$ is stable.

These observations suggest that there are regions of the Cu surface, whereby water dissociation readily occurs, as well as regions where it is inhibited. Shown in Figure 4.22 A is an SEM image acquired from a water intercalated graphene coated Cu foil. A network of dark features is observed throughout the field view, and suggests local dissolution of the Cu substrate, possibly at grain boundaries in the graphene film (c.f. left panel Figure 4.10). A high magnification SEM image of one of these dark features is shown in Figure 4.22 C. Auger spectra shown in Figure 4.22 D were acquired from the same field of view. The black and red curves correspond to spectra acquired from the black and red X shown respectively in the SEM image of Figure 4.22 C. The spectrum acquired from the dark feature (red curve), indicates the presence of S and Cl. If present as an impurity in the Cu substrate, this suggests that localized dissolution of the film is correlated with the presence of substrate impurities

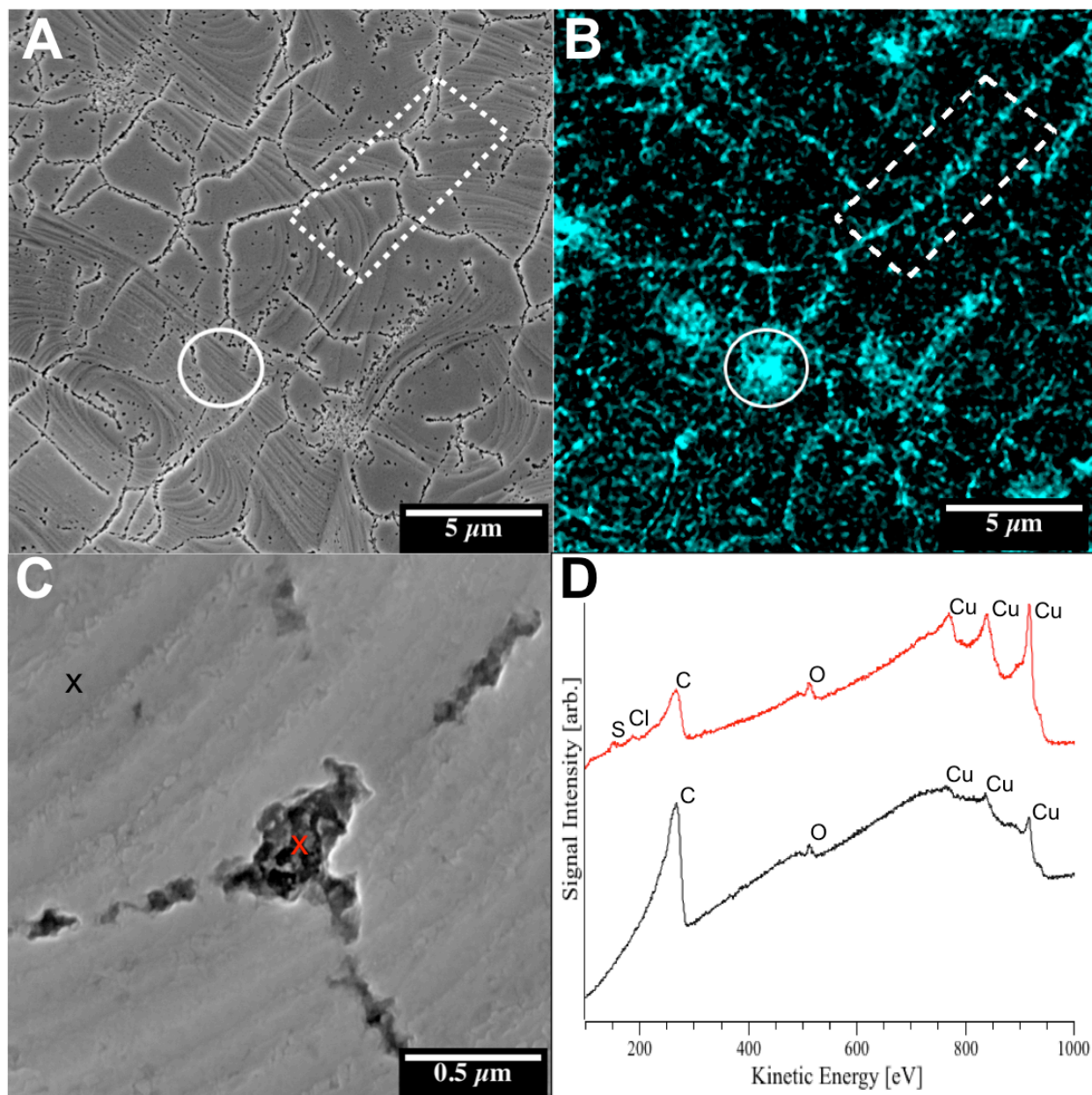


Figure 4.22: A: SEM image of water intercalated graphene on Cu. $E_p = 10\ \text{keV}$. B: Map of intercalated water beneath the graphene surface, same field of view as A. White circle indicates regions of water intercalation not associated with dissolution. White rectangle indicates regions of water intercalation associated with dissolution. $E_p = 10\ \text{keV}$. C: SEM image showing local dissolution of the substrate. $E_p = 25\ \text{keV}$. D: Auger spectra acquired from region of local dissolution (red curve) and a nearby region (black curve). Spectra were acquired from the regions indicated in C. $E_p = 25\ \text{keV}$.

Another hypothesis is that S and Cl are present as trace impurities in the intercalating water, and that their presence enhances dissolution at grain boundaries or other defects in the graphene film. An enhancement in the background is observed in the spectrum acquired from a nearby region (black curve), and is believed to be indicative of intercalated water. S and Cl are not observed in this spectrum. We note that the presence of graphene is confirmed via the presence of the $\sigma+\pi$ loss, which is not observed in the spectrum acquired from the dark region, as expected.

It is thus hypothesized that these dark regions correspond to areas where the graphene film is no longer present, and that electrochemical corrosion of the substrate has begun in these regions. This would correspond to the observed Cu_2O and $\text{Cu}(\text{OH})_2$ in the XPS spectra shown in Figure 4.20.

An attempt was made to map the distribution of intercalated water on a graphene coated Cu surface using Auger spectroscopy. This was accomplished by taking advantage of the relatively high background present on the low kinetic energy side of the Cu *LMM* transition in intercalated samples, as indicated in Figure 4.20. By mapping the intensity variation within the enhanced background, and normalizing to the Cu *LMM* peak intensity, it is hypothesized that the result will be an image of the intercalated water beneath the graphene surface. An example of such an intercalated water map is shown in Figure 4.22 B, which is identical to the field of view shown in Figure 4.22 A. The map is a measure of the variation in the background at 655 eV, normalized to the Cu *LMM* peak intensity. The background energy was selected by comparing the intensity values on the low kinetic energy side of the Cu *LMM* Auger series, and selecting the energy for which the difference was maximum. Bright regions can be observed as indicated by

the white circle in Figure 4.22 B, and are believed to be regions of intercalated water. The same region is shown in the SEM image (Figure 4.22 A), and does not appear to correspond to the regions of localized dissolution. In addition, a network of bright contrast can be observed, as indicated by the white dotted rectangle in Figures 4.22 A and B. Some of these features are correlated with regions of localized dissolution, whilst others are not. This network is believed to be intercalated water, and appears analogous to the network of low surface potential regions shown in Figure 4.13, which was hypothesized to be regions of intercalated oxygen. The observation that this network is spatially correlated with the regions of local dissolution, supports the hypothesis that water is intercalated at grain boundaries in the graphene film. Figure 4.22 B suggests that water does not intercalate homogeneously beneath the graphene surface, and that there are regions where the presence of water does not result in dissolution of the graphene film (i.e. the white circled region in Figure 4.22 A and B). This is in agreement with the XPS data shown in Figure 4.21, which indicated that molecularly adsorbed water was stabilized by the graphene overlayer. The intercalated water near regions exhibiting localized dissolution is believed to be unstable, and thus further dissolution of the graphene film is hypothesized to occur within these regions. It is not clear how the presence of intercalated water effects the reactivity of the graphene surface, and whether it enhances or inhibits interactions with an i.e. aqueous environment.

4.6 Conclusions and Future Outlook

The results of the above work can be summarized as follows:

1. There exists a feature on the low kinetic energy side of the Cu *LMM* Auger transition, which is unique to the presence of graphene. This feature is a loss, and believed to be due to excitation of the $\sigma+\pi$ plasmon in the graphene overlayer.
2. Upon removal of intercalated oxygen via UHV annealing, complete suppression of the $\sigma+\pi$ plasmon loss is observed to correlate with an upshift in the C 1s binding energy. It is hypothesized that this correlation indicates an interaction which is more akin to chemisorption, and the formation of a bond between the graphene overlayer and Cu substrate. This is in contradiction to previous work reported in the literature, which suggests that graphene is physisorbed to the Cu substrate, and that the electronic structure of the graphene is preserved.
3. The $\sigma+\pi$ plasmon loss can be used to identify the presence of graphene. The intensity of the loss is believed to be inversely related to the degree of coupling of the graphene overlayer to the substrate. Scanning Auger microscopy can be used to map the distribution of a graphene film on a variety of substrates with nanometer spatial resolution.
4. Localized oxidation of graphene coated Cu substrates is broadly categorized as resulting in substrate oxidation along graphene grain boundaries, as well as via growth of CuO filaments exhibiting a preferred growth direction.
5. CuO filaments were observed to nucleate near film defects, e.g. in the vicinity of small SiO₂ spheres believed to be remnants of the CVD growth process.

6. Surface potential measurements were able to predict locations of substrate oxidation. Regions of relatively low surface potential were found to preferentially oxidize. These low surface potential regions were observed to correlate with surface heterogeneities. It is hypothesized that intercalated oxygen may serve as such an inhomogeneity, and is responsible for the observed filament growth. The observed growth direction of the CuO filaments are believed to indicate the diffusion path of intercalated oxygen.
7. Defective graphene films can be generated with Ar^+ ion sputtering, and subsequently restored via UHV annealing to 400 C. The quality of the graphene film can be monitored via an observed down shift in the peak C 1s photoelectron binding energy. Such defective films were found to enhance the susceptibility of the Cu substrate to oxidation.
8. Cl intercalation was achieved by UHV annealing Cl contaminated graphene on Cu foils to ~ 320 C, and was found to inhibit oxidation of the Cu substrate. Direct interaction between Cl and graphene upon intercalation was observed via a downshift in the C 1s binding energy from 284.4 eV to 284-283.6 eV, and is believed to indicate hole doping of the graphene overlayer.
9. Oxidation is believed to occur via formation of C=O on the exposed graphene surface and subsequent etching via desorption as CO. Thus graphene is believed to be etched on the surface exposed to the oxidizing environment, and not via intercalated oxygen. Intercalated Cl was observed to inhibit the formation of C=O, and is believed to explain the resistance of Cl intercalated graphene samples to oxidation.

10. Water is capable of intercalating graphene coated Cu surfaces at room temperature, and is stable under UHV conditions allowing for study with conventional electron spectroscopies: i.e. AES and XPS.
11. There are regions of the graphene/Cu interface where the intercalated water is adsorbed to the Cu surface and stable, and regions where it readily dissociates. Stability of the adsorbed water layer is believed to be provided by the graphene film.
12. Stability of the adsorbed water layer was observed up to temperatures of 200 C. At 200 C, oxidation of the substrate is believed to occur either without dissociation via, $(H_2O)_{ads} + 2Cu \rightleftharpoons Cu_2O + 2H_{ads}$, or via the formation of highly unstable $Cu(OH)_2$ which quickly oxidizes the substrate.
13. Some of the $Cu(OH)_2$ formed upon dissociation is converted to Cu_2O via, $Cu(OH)_2 + 3Cu \rightleftharpoons 2(Cu_2O) + 2H_{ads}$ beginning at temperatures of 100 C. A portion of the adsorbed hydroxide remains intact at temperatures of 200 C, and is believed to be stabilized by the graphene overlayer.
14. Dissolution of the substrate is believed to readily occur at grain boundaries in the graphene film. This was associated with the presence of S and Cl. It is hypothesized that the defective regions of the graphene grain boundary are those where water dissociation readily occurs, resulting in localized oxidation of the substrate.
15. Distribution of intercalated water was imaged with AES, and supports the hypothesis that water adsorption is not homogeneously distributed across the graphene/Cu interface. A network of intercalated water was observed to spatially correlate with regions of local dissolution. Intercalated water was also observed in regions not associated with

substrate dissolution, and is believed to correspond to regions of the graphene/Cu interface where the adsorption of molecular water is stable.

When considering the efficacy of graphene as a protective film against corrosion, the above work suggests that several challenges exist. The first is that oxidizing species, i.e. oxygen and water are easily able to infiltrate the graphene/substrate interface. The interaction of these species with the substrate surface appears to be significantly altered by the presence of the graphene film. For example, in the case of water intercalation, the presence of the graphene overlayer appears to stabilize molecularly adsorbed water and hydroxide to the Cu surface, and limit the amount of hydroxide available for substrate oxidation. It is hypothesized that the presence of intercalants alters the reactivity of the graphene overlayer, and in the case of oxygen, is believed to severely compromise the protective efficacy of the graphene. This is also hypothesized to be the case for any given heterogeneity present on the substrate surface. When considering a graphene coated commercial steel, heterogeneities such as MnS inclusions will be ubiquitous, and so it is expected that the reactivity of a graphene overlayer will vary considerably across the surface. Preventing intercalation of oxidizing species is suggested as a method of improving the ability of graphene to act as a protective film. This can be achieved in numerous ways. If intercalation occurs via defects (grain boundaries) in the graphene film, optimizing CVD growth conditions for production of single crystalline or nearly single crystalline films would be advantageous. In this regard, progress in synthesizing single crystalline graphene films on polycrystalline substrates has been made some progress [162]. Another strategy is to increase the substrate/surface bonding by use of an intermediary film which exhibits strong cohesion to

graphene i.e. Ti, Ni, or Co [130]. However, given the strong interaction of graphene with these surfaces, it is not clear if and how the reactivity of the graphene is altered when grown on these substrates. An alternative method suggested by the present work, is chemical doping of the graphene film. It was shown that intercalated Cl protects Cu surfaces against oxidation. In this case, protection is provided by both preventing intercalation of harmful species, and also inhibiting the reactivity of the exposed graphene surface.

The above results also provide motivation for basic surface science research concerning graphene/metal interfaces. For example, it was found that the interaction of intercalated oxygen and chlorine with a graphene coated Cu surface was very different. In the case of oxygen intercalation, graphene behaves as a “freestanding film,” and the interaction is believed to primarily occur between the Cu substrate and intercalated oxygen. Despite this weak interaction, the presence of intercalated oxygen is believed to significantly alter the reactivity of the graphene surface. This is not the case for chlorine, which appears to primarily interact with the graphene overlayer. It would be expected that both Cl and O would strongly interact with the metal substrate. Moreover, it is hypothesized that intercalated O enhances the reactivity of the graphene overlayer, and that intercalated Cl inhibits it. It has been suggested that intercalated O results in n-doping [132] and that intercalated Cl results in p-doping [151] of the graphene overlayer. In both cases, the doping simply results in a shift in the Fermi level relative to the Dirac point. Given the symmetry of graphene’s electronic structure about the Dirac point, it would be of interest to determine if the reactivity of the graphene surface changes when n or p-doped by the same amount.

Another point of interest concerns the nature of intercalated water, and why the graphene overlayer acts to stabilize the molecular adsorption of water to the metal surface. Information regarding the detailed structure and arrangement of intercalated water molecules might provide some insight. Ambient pressure XPS instrumentation would allow for the study of intercalated water on well-defined (oxygen free) Cu surfaces.

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