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The inhibition of copper surface oxidation by ion beam irradiation

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THE INHIBITION OF COPPER SURFACE OXIDATION BY ION BEAM
IRRADIATION

A Thesis

Presented to

The Faculty of the Department of Materials Engineering
San Jose State University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

By

Norman S. Somcio

August, 1997

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A handwritten signature in cursive script, appearing to read "Emily Allen", written above a horizontal line.

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ABSTRACT

The Inhibition of Copper Surface Oxidation by Ion Beam Irradiation

By

Norman S. Somcio

The oxidation of copper surfaces irradiated with ion beams was investigated. Ion beam irradiation has been known to inhibit oxidation of copper surfaces and the effect was attributed to the formation of a carbonaceous layer partially protecting the surface from oxidation. It was believed that this carbonaceous layer formed when adsorbed contaminants such as pump oil were degraded by the ion beam irradiation.

This thesis determined the role surface hydrocarbons play in inhibiting oxidation by testing whether any differences can be seen on copper samples with and without surface hydrocarbons present during irradiation. It was found that the presence of surface hydrocarbons is necessary during irradiation in order to inhibit oxidation. This protection can be achieved with layers as thin as 10 monolayers. This leads to a model based on a site-blocking mechanism where carbon atoms occupy preferred sites on the surface where oxygen would otherwise be adsorbed.

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1. INTRODUCTION

Previous investigations have reported the passivation of copper surfaces from oxidation following ion beam irradiation. The first published reference comes from a patent by B.L. Crowder [1] in which they described the protection of copper against corrosion after bombarding with high energy ion beams. The phenomenon is familiar to the ion beam analysis community where the analysis beam would leave a protected image of the beam spot.

Various attempts made to document and explain the phenomenon varied widely, but many have focused on bulk effects, i.e. structural or chemical changes due to the presence of implanted ions [2, 3, 4, 5, 6]. However, recent developments have pointed towards surface effects, specifically the formation of a protective carbonaceous layer on the surface of the metal resulting from ion beam irradiation [7]. It was suggested that contaminant hydrocarbons adsorbed on the surface, possibly due to poor vacuum conditions or prior exposure to the atmosphere, are degraded by the ion beam to form a hard carbonaceous surface layer. This layer would serve to protect the metal surface from oxidation. However, prior to the present study no mechanism has been satisfactorily established. Thus this

project was begun in hopes of finding an underlying mechanism that would establish a reproducible processing routine that could be applied to protection of copper, and possibly other metal surfaces in technological applications.

Controlling the oxidation behavior of copper is a consideration that depends heavily on the application. An example where oxidation has some beneficial effect is commonly seen on roof tops of many large commercial structures. The roofs of many of these structures are made out of copper that oxidizes to form an adherent green patina that serves to enhance the aesthetic appeal of the roof. This green patina is responsible for giving the Statue of Liberty a distinctive "greenish" color.

However, oxidation becomes an important issue in applications where it begins to have a harmful effect. A good example is the possible application of copper as metallization in integrated circuits that require, among other considerations, passivation against oxidation. Currently, aluminum forms the backbone of semiconductor metallization and has been the main conductor used since the inception of the integrated circuits. Aluminum has exceptional conductivity, low stress, and high adherence to silicon.

Nevertheless, despite its wide acceptance, aluminum suffers from several inherent flaws. Its susceptibility to corrosive etching solutions like hydrofluoric and sulfuric acid makes it a borderline gate metal. In addition, aluminum suffers from electromigration which results from the "frictional force between metallic ions and the flowing charge carriers, called the 'electric wind' force" leading to mass transport [8] and eventually discontinuities when the interconnect line is narrow. The decreasing size of integrated circuits requires conductors to carry higher current densities making the problem of electromigration even more significant.

Copper as a potential alternative has several advantages over aluminum. It has a resistivity at 22°C of $1.7 \mu\Omega\text{-cm}$ compared to $2.7 \mu\Omega\text{-cm}$ for pure aluminum. In current applications, aluminum interconnects are alloyed with copper to increase resistance to electromigration and stress induced migration, but the resistivity typically increases to between 3.0 and $3.2 \mu\Omega\text{-cm}$. Copper's lower resistivity allows it to carry higher current densities and makes it less susceptible to electromigration. In addition, copper has a higher melting temperature, which makes it more tolerant to subsequent high temperature semiconductor

processing like annealing. However, for copper to become an alternative conductor to aluminum, oxidation along with other process issues must be addressed. This is particularly important because advances in integrated circuits utilize multilevel interconnects that require proper adhesion between layers. Oxidation of copper lines can lead to inadequate adhesion thereby compromising the integrity of the device.

This thesis will describe an investigation of the passivation phenomenon and present a provisional model for its underlying causes. The structure of the thesis will be as follows: Chapter 2 provides a background review covering the physical concepts of ion implantation, oxidation of metals, and a survey of available literature; Chapter 3 includes a detailed description of the experimental procedures; Chapter 4 presents a discussion of the experimental results; and Chapter 5 provides a conclusion discussing possible future work.

2. BACKGROUND

The present study utilized ion beams to modify as well as analyze, using RBS, the surface of copper. Therefore, it is only fitting to discuss the early developments of ion beam technology and current commercial applications. This will be followed by a discussion of ion beam interactions in materials, including the energy loss mechanisms involved. In addition, a general description of the oxidation mechanism of metals will be discussed.

2.1 Ion Implantation

Ion implantation falls within a broad category of ion beam processes using ions as the primary source of energy to initiate structural and/or chemical modifications in a material [9]. The applications vary widely ranging from surface modifications, sputter etching and deposition of thin films to doping of semiconductors. The technique was developed from the early uses of energetic ions (>100 keV) to modify the chemistry or structure of sub-surface layers after it became apparent that low energy (few keV) ion treatments can sufficiently improve the macroscopic properties of thin film layers [10]. The source to produce such low energy ions had evolved rapidly over the years from

research conducted by the U.S. space program on propulsion systems. These were mainly intended as propulsion for space-based systems in the early 1960's. However, it did not take long before ion beams were applied to reactive processes where the intention was to modify the surface characteristics of materials [10].

In the early 1970's, researchers from Britain began to experiment with applications of ion beam processes to metals. The area of research includes friction and wear resistance of metals by ion implantation. An example is the improved wear resistance of metals such as iron following ion implantation [9].

Perhaps the biggest beneficiary of ion beam processes has been the semiconductor industry. Ion implantation has become the standard method used to dope electronic materials such as silicon to manufacture integrated circuits. Typically, implantation temperatures are in the range where diffusional processes are considered negligible. It offers a technique for introducing a variety of ion species which allows for a more well defined actively doped Si layer than the older method of in-diffusion of dopants. It also allows the implantation of a variety of ion species that would otherwise be restricted by solubility considerations.

2.1.1 Features of Ion Implantation

Ion implantation allows the introduction of impurities into the surface of a material by bombarding it with high energy ions. The ions are extracted from a source which is isolated from ground at the selected accelerator voltage (kilovolts to megavolts). The extracted ions are accelerated by the potential gradient to ground, emerging from the source with corresponding energies (keVs to MeVs). The high energy ions are then focused and selected by bending them through a mass separating magnet. This is necessary in order to select the ion with a specific charge-to-mass ratio from a beam that may contain several different types of ions. The selected ions enter the housing and bombard the surface of the material to be treated. An illustration of a typical ion implanter is shown in Figure 1.

Two considerations must be accounted for in order to properly illustrate implantation systems and ion beams in general. These are range distribution of ions in the bulk material and the amount of defects or lattice disorder created by the ion as it travels through the material. This requires a description of the energy loss mechanisms involved. These considerations, as well as a description of

Figure 1: Schematic of an ion implanter [9].

the energy loss mechanisms, are an important segment of the study since it dictated the ion species selected to irradiate the copper surfaces.

2.1.2 Energy loss mechanisms

Because it is fundamental to the process that will be described later, the following section summarizes several important features of ion-solid interaction. An important quantity that must be considered is the energy loss of ions in solids. As ions travel through a solid they lose energy principally in two ways: (1) through inelastic interactions with bound or free electrons of the lattice atoms, known as the electronic energy loss mechanism and (2) through elastic collisions with the screened or unscreened nuclei of the atom itself known as the nuclear energy loss mechanism. Generally, both processes occur where collisions involving electronic excitation are associated also with large momentum transfer.

However, in many considerations one mechanism dominates such that the other can be neglected depending on the energy and atomic number of the incident ion as well as the target species. Figure 2 shows the relative importance of each energy loss mechanism versus incident particle energy and

Figure 2: Dependence of electronic and nuclear contributions to the stopping cross section ϵ versus energy [11].

how it may be subdivided into nuclear, ϵ_n , and electronic, ϵ_e , components, expressed as stopping cross sections. Stopping cross section, ϵ , is defined as,

$$\epsilon = \frac{1}{N} \frac{dE}{dx} \quad (2.1)$$

where N is the volume density in atoms/cm³ and $\frac{dE}{dx}$ is the energy loss in eV/cm. The total effective stopping cross section may therefore be written as,

$$\epsilon = \epsilon_e + \epsilon_n \quad (2.2)$$

The electronic energy loss mechanism is associated with small energy losses and is responsible for ionization and excitation of atoms in the lattice. The energy loss per unit path length is,

$$-\frac{dE}{dx} = \frac{4\pi Z_1^2 e^4 n}{mv^2} \ln \frac{b_{\max}}{b_{\min}} \quad (2.3)$$

where b is the impact parameter. The energy transferred in a collision, T , is defined as,

$$T = \frac{2Z_1^2 e^4}{b^2 mv^2} \quad (2.4)$$

Solving for b ,

$$b = \frac{\sqrt{2}Z_1e^2}{\sqrt{mv^2T}} \quad (2.5)$$

Electronic energy loss mechanism can be considered as resulting from two types of interactions: (1) close collisions where the incident ions travel within the electron orbits resulting in large momentum transfer and (2) distant collisions where particles travel outside the electron orbits involving small momentum transfer.

Close collision interactions involve setting $b = b_{\min}$. A value for $b_{\min}$ can be obtained by setting $T = T_{\max}$, the maximum kinetic energy transferred. The maximum velocity transferred to a stationary electron by an incident particle is $2v$. Thus, the maximum kinetic energy transferred is,

$$T_{\max} = \frac{1}{2}m(2v)^2 = 2mv^2 \quad (2.6)$$

substituting into equation (2.5) results in,

$$b_{\min} = \frac{Z_1e^2}{mv^2} \quad (2.7)$$

Similarly, distant collision interactions involve setting $b = b_{\max}$ which can be obtained by setting $T = T_{\min}$. The minimum energy transferred to a stationary electron is the

energy required to raise the atom to an allowed excited state defined as,

$$T_{\min} = I \quad (2.8)$$

where I represents the average excitation energy of the electrons in a target atom. Substituting into equation (2.5) results in,

$$b_{\max} = \frac{Z_1 e^2}{\sqrt{2mv^2 I}} \quad (2.9)$$

Substituting $b_{\min}$ and $b_{\max}$ into equation (2.3) results in,

$$-\frac{dE}{dx} = \frac{2\pi Z_1^2 e^4 n}{mv^2} \ln \frac{2mv^2}{I} \quad (2.10)$$

Values for the average excitation energy, I , have been empirically determined as shown in Figure 3.

However, the equation describing the electron energy loss only applies at high velocities (Bethe-Bloch formula). In this regime the incident particles travel at velocities, v_1 , much greater than the mean orbital velocities of electrons in a given atom. Thus, the projectile atoms are stripped of their outer electrons and move through the material as ions colliding elastically with the free or

Figure 3: Calculated and experimental values for the average excitation energy, I , as a function of atomic number Z [12].

bound electrons of the target atom.

As the projectile's velocity decreases the probability of electron capture increases, lowering its effective charge and the influence of the target atom's innermost electrons on the stopping cross section. However, the particle spends more time in the vicinity of the atom. As a result, Figure 2 exhibits a slower increase and eventual decrease in the stopping cross section, ϵ , and thus energy loss, $\frac{dE}{dx}$, as the energy of the incident particle decreases.

A further decrease in the particle's velocity introduces a different component to the total energy loss called nuclear energy loss. This scenario is based on a screened Coulomb interaction between the nuclei of the target atom and the incident particle. Applying equation (2.10) for light incident particles to direct collisions with atomic nuclei, the energy loss equation becomes,

$$-\frac{dE}{dx} = \frac{4\pi Z_1^2 Z_2^2 e^4 N}{M_2 v^2} \ln \frac{b_{\max}}{b_{\min}} \quad (2.11)$$

where the difference lies in the mass of the target nucleus M_2 and charge Z_2 . The above derivation of the electronic and nuclear energy loss was taken from reference [12].

For light incident projectiles such as protons, nuclear energy loss is comparatively much smaller in magnitude than electronic energy loss. However, for heavy incident particles, nuclear energy loss mechanism forms the basis for displacement damage, and also for sputtering. The process involves the transfer of energy from the incoming particle to the target atoms producing recoils and corresponding vacancies or lattice phonons. Some of the target atoms recoil backward near the surface where they are ejected as sputtered atoms.

As the ions penetrate into the solid they create lattice disorder and radiation damage as a consequence of ballistic nuclear collision. As discussed earlier, ions lose energy either through collisions with the electrons of the target atoms or with the nucleus of the atoms itself. However, only collisions that displace atomic nuclei can create lattice disorder and radiation damage.

During its travel through the material an ion experiences numerous collisions with lattice atoms. The collisions can cause displacements of atoms which in turn can displace other lattice atoms. This process is generally referred to as a collision cascade. For heavier incident particles the net result is a highly disordered region

surrounding the ion track. A schematic representation of a collision cascade is shown in Figure 4.

Thus lattice damage is small for incident MeV He^+ ions where the interactions with the target mainly involve collisions with atomic electrons. This is very important since it was desirable to avoid or minimize lattice disorder in this investigation in order to isolate the effects of surface carbon by ion irradiation.

An important consequence of the energy loss mechanisms is the distribution of implanted ions with depth. Factors determining the range distribution are the incident ion's energy E and atomic number Z_1 and the substrate's atomic number Z_2 . Since the distance between collisions and the transferred energy are statistically distributed, so also are the depths of the implanted ions below the target surface. Typically, the ion's penetrating depth profile has a broad distribution generally referred to as range distribution or straggling. It can be described to a first approximation by a Gaussian distribution characterized by a mean projected range, R_p , and a standard deviation, ΔR_p .

Figure 4: Illustration of a collision cascade due to a 20 keV P⁺ ion in Si [13].

2.1.3 Rutherford Backscattering Spectrometry

A direct collision between a light incident ion such as He^+ and a target nucleus can cause backscattering of the incident ion. This is the basis for RBS (Rutherford Backscattering Spectrometry), a quantitative technique that is suitable for determining composition and depth profiling in thin film analysis. The technique is non-destructive with absolute accuracy of a few percent or below.

A typical backscattering setup is shown in Figure 5. An accelerator provides a collimated He^+ beam of energy E_0 directed towards the sample to be analyzed. A small fraction of the MeV He^+ ions undergo close impact collisions with the target atoms where they are backscattered. A surface barrier detector collects the backscattered particles with energy E_1 , feeding a charge-sensitive preamplifier whose output voltage pulse amplitudes are proportional to the detected energy of the scattered particles. These are further processed for storage, and subsequent data reduction by simulation, or display as a backscattering spectrum [12].

Figure 5: Typical Rutherford Backscattering Spectrometry setup [14].

Several important factors that determine the form of a backscattering spectrum are: (1) the kinematic factor, (2) the scattering cross sections, (3) the stopping cross sections, and (4) energy straggling.

The kinematic factor allows backscattering spectrometry the ability to determine the mass of the target atom. During an elastic collision, energy is transferred from the incident particle to the target atom. By measuring the energy of the backscattered particles after a collision with an atom at the sample surface, the mass of the target atom can be determined according to the kinematic factor,

$$K = \frac{E_1}{E_0} = \left(\frac{\sqrt{1 - \left(\left(\frac{M_1}{M_2} \right) \sin \theta \right)^2} + \left(\frac{M_1}{M_2} \right) \cos \theta}{1 + \left(\frac{M_1}{M_2} \right)} \right)^2 \quad (2.12)$$

where E_1 and E_0 are the backscattered and incident energies and M_1 and M_2 are the incident and target atom mass.

The probability that such an elastic collision will occur is determined by the scattering cross section. The atomic composition can be quantitatively determined based on the scattering cross section, σ , from the relation,

$$A = \sigma \Omega Q N t \quad (2.13)$$

where A is the number of detected particles, Ω is the solid angle, Q is the number of incident particles, N is the number of target atoms per unit volume and t is the thickness.

The stopping cross section, discussed earlier, describes the energy loss of a projectile. This gives backscattering spectrometry depth resolution, as the incident particle loses energy continuously before and after the collision if the collision occurs below the sample surface.

A typical example of a backscattering spectrum is shown in Figure 6. This spectrum was simulated using known values for σ , Ω , ϵ , etc., as applied for a 4000 Å Cu on a carbon substrate. For elemental layers, higher mass elements appear higher in the spectrum based on the kinematic factor. For this structure the C signal corresponds to a lower energy than if the C were at the free surface of the sample since the He⁺ ion has to travel through the Cu film losing energy before and after encountering a C atom.

Figure 6: A sample RBS spectrum of a 4000 Å Cu on C structure using RUMP.

Simulations such as this can be made by trial-and-error to match an experimental spectrum and thereby obtain information about layer thickness and elemental makeup of the actual sample. Software written for this type of quantitative fitting is called "RUMP" and it was extensively used for such RBS analysis throughout the project described in this thesis.

2.2 Overview of Oxidation of Metals

In order to discuss probable scenarios whereby the oxidation of Cu could be artificially inhibited, an outline of the traditionally understood mechanism of metal oxidation is presented covering the thermodynamics and kinetics which may govern it.

2.2.1 Oxidation Thermodynamics

Different metal surfaces chemically react with oxygen at different rates when exposed to air. For some the reaction is so slow that the metal surface remains intact, however for others the results are disastrous. For gaseous corrosion, the most common reaction is between a metal and adsorbed oxygen. Referred to as oxidation, the driving force for the process can be described in terms of the Gibbs free energy change, ΔG , of the reaction,

where A and B are the reactants, C and D are the products, and a , b , c , and d are the thermodynamic coefficients. The Gibbs free energy, ΔG , is given by

$$\Delta G = \Delta G^0 + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (2.15)$$

where ΔG^0 is the standard Gibbs free energy of formation and a is the chemical activity of the corresponding reactants and products. Based on the value of ΔG , three scenarios are possible; a negative ΔG means the reaction will favor formation of products C and D , a zero ΔG indicates the system is in equilibrium, and a positive ΔG means the forward reaction will not occur.

A more specific description of oxidation between a divalent metal and oxygen is given by the reaction,

where M is the metal species reacting with adsorbed oxygen and MO is the oxide product. This reaction can be further divided into two half-reactions. First, the metal undergoes oxidation by losing two valence electrons,

to produce M^{2+} ions near the metal-oxide interface.

Second, a reduction process occurs near the oxide-gas interface when the excess electrons are absorbed by the oxygen to produce O^{2-} ions,

then,

2.2.2 Oxidation Kinetics

The rate of growth of the oxide film is dependent on the relative speeds of the diffusion through the metal oxide by the metal and oxygen, respectively. A film growing near the metal-oxide interface indicates anionic diffusion characterized by the slow outward diffusion of the M^{2+} ion and dominated by the fast inward diffusion of O^{2-} ions. Cationic diffusion, on the other hand, is dominated by the outward diffusion of M^{2+} ions because of the slow inward diffusion of the O^{2-} ions producing new oxide near the oxide-gas interface.

In general, growth rates are categorized as parabolic, linear or logarithmic in behavior. A parabolic growth rate is observed when the oxidation process is controlled by the diffusion of ions through the film given by,

$$x^2 = \frac{1}{2} k_p t \quad (2.20)$$

where k_p and t are the parabolic rate constant and time, respectively and x is the thickness of the grown oxide. Furthermore, k_p is dependent on temperature according to the Arrhenius equation,

$$k_p = A e^{-\frac{Q}{RT}} \quad (2.21)$$

where A is a constant and Q and T are the activation energy and absolute temperature, respectively.

A second type of growth rate behaves linearly when the oxide thickness varies according to the equation,

$$x = k_l t \quad (2.22)$$

where k_l and t are the linear rate constant and time, respectively. This reaction is observed when the oxidation is constant with time and controlled by the rate of reaction.

A third growth rate follows a logarithmic or inverse logarithmic rate and is observed at low temperatures and for thin films. The rate is given by the equation,

$$\frac{1}{x} = b - k_l \log t \quad (2.23)$$

where k_l is the logarithmic rate constants, b is a constant, and t is time. This behavior results from a transport-limited process driven by an inherent electric field across the film [15].

Oxide films may themselves passivate a metal surface (e.g. the native oxide on Cr or Al). Such layers are categorized based on how well the film adheres to the surface and how well it protects the underlying metal. The Pilling-Bedworth ratio is defined as,

$$Pilling - Bedworth \equiv \frac{A_o \rho_M}{A_M \rho_o} \quad (2.24)$$

where A_o , A_M , and ρ_o , ρ_M are the molecular weights and densities of the oxide and metal, respectively. A $P-B$ ratio between 1 and 2 suggests that the film forms a protective barrier resulting in a parabolic diffusion-controlled growth rate. A ratio above and below that range means the film is insufficient in protecting the metal.

This forces the growth rate to proceed linearly, limited by the reaction or until the metal has been completely oxidized [16].

An example of metal oxidation kinetics is displayed by the oxidation of copper in an oxygen ambient at 140, 170, and 200°C, shown in Figure 7. These are baseline experiments which illustrate copper oxidation following a parabolic growth rate.

2.2.3 Limitations to Oxidation Rate

If the growing oxide has cavities or microcracks due to stresses, it can fail to protect the underlying metal and oxidation can proceed faster than what the parabolic behavior predicts. Other factors affecting the oxidation mechanism include the conduction of electrons and metal ions through the growing oxide. These factors can have a strong influence on the oxidation mechanism. However, are there other variables that can modify the net oxidation rate of metals? If so is it reaction-rate limited or is it diffusion limited? This question is critical in the evaluation of the ion beam experiment that follows.

Figure 7: Oxidation of copper film at 140, 170, and 200°C illustrating the parabolic growth rate of the oxide.

It appears that oxidation is inhibited by irradiation before a continuous layer of CuO_x forms. So we are proposing to inhibit not just the rate of oxide growth but the whole process whereby O_2 is made available as an active adsorbate on the surface in order to begin the oxidation process.

2.3 Passivation of Copper by Ion Beam Irradiation

Work on passivating metal surfaces against oxidation dates back to the early 1960's. Published works on both thermal oxidation and aqueous corrosion of implanted metals have yielded a variety of interesting results. Towler et al. [17] working with Al stressed the importance of impurity valency on the observed passivation. Suffield et al. [18] and Benjamin et al. [19] implanted Ti into Al and reported interesting correlations between electronegativity and ionic radius to the oxidation mechanism. However, other groups such as Dearnaley et al. reported an enhancement in oxidation after implanting Eu in Ti and stainless steel. The first group to investigate Cu was Crowder et al. [1] who in 1971 reported the protection of thin copper strips after implanting B.

Studies that have reported protection of copper surfaces through ion implantation have suggested several possible mechanisms. The majority have mainly focused on changes that occur in the bulk. This refers to any structural or chemical modifications that occur in the bulk of the material due to the implanted ions. Examples are the work by Morris *et al.* [2] and Ratcliffe *et al.* [4] who attributed the passivation to the creation of a pn junction in the oxide inhibiting the further growth of the oxide. Indeed published data substantiate the oxidation inhibiting effect of ion beam irradiation, but it remains unclear that any feasible mechanism has been satisfactorily established. The work described in the following section is the most relevant to this thesis.

2.3.1 Naguib *et al.*

In a study by Naguib *et al.* [5], several ion species were implanted into polycrystalline copper at various doses and energies. Ion species implanted included B, C, N, and Ne at doses ranging from 1×10^{16} ions/cm² to 1×10^{17} ions/cm² and energies between 50 and 390 keV.

Copper sheets 0.8 mm thick were cut into 3 cm diameter disks and polished in a 1 μ m Al₂O₃ aqueous slurry. Implants

were done at room temperature and at pressures less than 1×10^{-7} torr. The implanted energies for each ion species were chosen to give a theoretical mean projected range, R_p , of approximately 700 Å. The samples were then oxidized at 200°C in dry O_2 at 1 atm.

Quantitative analysis was done to measure the amount of oxygen in the oxide using a technique based on $^{16}O(d,p)^{17}O$ nuclear reaction using a Van de Graaf ion accelerator. Oxidation in the implanted and unimplanted regions was compared and the results were expressed in terms of percent effect defined as,

$$\%Effect = \frac{A - B}{B} \times 100 \quad (2.25)$$

where A and B are the amount of oxygen uptake in the implanted and unimplanted area, respectively. A negative value of percent effect indicates a reduction in oxidation in the implanted area.

The results of their experiment are summarized in the following figures. Shown in Figure 8 is the percent effect for B implanted copper as a function of implant energy and dose. As shown in the figure the percent effect in all cases was negative, which indicated less oxygen in the implanted area following oxidation. No clear relation was

found in terms of energy dependence, but percent effect increased on average as dose increased from $1\text{E}16$ to $5\text{E}16$ ions/cm².

Shown in Figure 9 are the data on percent effect of Ne, C, and N₂ implanted Cu. Samples were oxidized in dry O₂ at 200°C for 40 minutes for the C and N₂ implants and 60 minutes for the Ne implants. Neon implantation reduced oxidation, although not as effectively as B. Nitrogen implants exhibited both reduced and enhanced oxidation behavior as ion dose decreased, whereas C exhibited enhanced oxidation for the whole range of ion dose.

Naguib et al. concluded the study by suggesting possible mechanisms that could explain the effects of each implanted species on the oxidation behavior of Cu. They proposed a combination of lattice damage and chemical effects as possible mechanisms responsible for the observed passivation. Accordingly, they suggested that chemical effects are responsible for the reduction whereas the lattice damage is responsible for the enhancement in oxidation.

In the case of N₂ implants they based their suggestion on two premises. On the basis of lattice damage, they cited

Figure 8: Amount of oxidation of B⁺ implanted Cu in terms of percent effect as a function of energy and dose [5].

Figure 9: Effect of ion dose on the oxidation of Ne, C, and N₂ implanted Cu. Oxidation was done in dry O₂ at 200°C for 40 minutes for C and N₂ and 60 minutes for Ne implanted Cu [5].

a previous work that showed damage was greater for molecular implants (M_2^+) than for atomic implants (M^+). The results obtained for N_2^+ implants seem to follow their claim at low doses. However, at high doses a different mechanism takes over. They suggested that at high doses chemical effects predominate over lattice damage. They suggested that the reduction at high doses for N_2^+ as well as B^+ implants was possibly due to formation of metastable chemical compounds such as copper nitride and copper boride, respectively. However no chemical analysis data were given in order to substantiate the proposed formation of such compounds.

The group attributed the oxidation reducing effects of Ne implants to structural effects. They suggested the reduction was possibly due to the formation of gas bubbles after implantation. These gas bubbles act as diffusion barriers that tend to reduce oxidation.

2.3.2 Ding et al.

An investigation by Ding et al. [6] also attributed the ion irradiated passivation of Cu surfaces to chemical effects. The group implanted 50 keV B^+ ions into 6000 Å thick copper at a dose of $2.5E15$ ions/cm² and oxidized in air at 300°C for various periods of time.

RBS data confirmed the passivating effect of B⁺ implants. In addition, the group also made sheet resistivity measurements to augment their RBS data and found that associated with the protection was an increase in sheet resistance. They directly linked the passivating effect to increases in sheet resistance which they attributed to two things: one, to the presence of B as an impurity in Cu; and second, to damage introduced during implantation. However, their data show that the protection remained even after a post implant anneal to remove damage caused by implantation. Figure 10 and Figure 11 shows the oxide thickness as a function of dose before and after anneal, respectively. On this basis they contend that the protection was possibly linked to chemical effects, particularly the presence of B in Cu as an impurity.

2.3.3 Dadu et al.

Investigations conducted by Naguib et al. and Ding et al. both involved implanting reactive ion species such B. Thus, part of their proposal for a mechanism responsible for the protection was based on structural or chemical modifications within the bulk of the material. However, recent experiments by Dadu et al. [7] have suggested that the protective mechanism might possibly be linked to surface

Figure 10: Copper oxide thickness as function of ion dose for samples oxidized in air at 300°C at the indicated time [6].

Figure 11: Copper oxide thickness versus dose for samples oxidized in air at 300°C. Prior to oxidation these samples were annealed in an Ar ambient at 400°C for 20 minutes [6].

effects, specifically the formation of a carbonaceous surface layer.

In this work, the authors explored the possibility that the carbonaceous layer was due to the ion beam dissociating adsorbed hydrocarbons found on the metal surface after exposure to room air or a contaminated vacuum system. Their approach was to attempt to irradiate Cu surfaces free of adsorbed contaminants. However, they concluded that a significant amount of adventitious carbon was collected during the transfer of the Cu sample from the e-beam evaporator to the implant chamber. In addition, it has also been independently demonstrated that metal surfaces exposed to atmospheric or poor vacuum conditions can adsorb a few monolayers of contaminants forming a carbonaceous layer following ion beam irradiation [20]. Regardless of its origin, it remains that in every case where Dadu et al. observed passivation, a few monolayers of carbon were also detected by XPS.

The present investigation attempted to determine whether a clear difference can be seen between ion beam irradiated "carbon" and "carbon-free" Cu surfaces following oxidation. In order to remove other possible sources such as chemical effects and lattice damage, inert, light ions

such as He were used. As discussed earlier in section 2.1.2, lattice damage caused by MeV He is minimal. If the "carbon" and "carbon-free" experiments show the same result, then structural or chemical changes occurring in the bulk as suggested by Naguib *et al.* and Ding *et al.* must be reconsidered. However, if "carbon" and "carbon-free" surfaces show different degree of passivation after irradiation, it would indicate that a carbon surface barrier may be linked to the passivation mechanism. That is the hypothesis of this thesis.

3. EXPERIMENTAL PROCEDURE

The experiments we set out to perform were designed to isolate the effects of surface carbon on the passivation of ion irradiated thin copper films. Our goal was to test whether the observed oxidation inhibiting effect could be reproduced if surface carbon was excluded during irradiation. Initially, however, we wanted to see whether any differences in inhibition could be detected between Cu surfaces exposed to room air and those intentionally treated with different carbon based solvents. In the "intentional carbon" experiment, the process of intentionally treating the surface was intended to leave a layer of adsorbates on the surface prior to irradiation.

3.1 Intentional Carbon Experiment

Copper samples were prepared by depositing 4000 Å on carbon substrates (Ultra Dense Amorphous Carbon) by electron beam evaporation. UDAC was chosen due to its lack of reactivity with Cu and low Z for clear RBS detection of surface C and O on Cu. A 300 Å Cr underlayer was deposited to improve adhesion of the Cu film. The deposition rate was maintained at 12 Å/sec at 0.65 A beam current done at room temperature with a base pressure of 1E-6 torr. Following

deposition, copper samples were surface treated by spin coating the following carbon based coatings: toluene, isopropyl alcohol, and acetone. These coatings were applied using a photoresist spinner at 2000 rpm for 40 seconds. Although these solvents vaporized instantaneously, this procedure was based on the expectation that a residual thin layer of adsorbates may remain bonded by surface chemistry of Cu even in the vacuum used for implantation. Such a layer would be in addition to any adsorbates picked up during the sample's exposure to room air.

Following surface treatment, one set of samples was implanted with either He⁺ at 2.0 MeV or Ar⁺ at 1.5 MeV, both at a dose of 2×10^{16} ions/cm². In order to allow for direct comparison only half of each sample was implanted. Cooling during implantation was done by flowing liquid nitrogen on a copper tube attached to the sample holder. Following ion implantation, the samples were immediately transferred to the furnace for oxidation in air at 170 °C for 18 hours.

The temperature chosen to oxidize the samples was selected based on the temperature used by Dadu et al. and from our baseline experiments and initial intention to oxidize clean Cu samples in dry O₂ rather than air. Virgin Cu samples were oxidized in dry O₂ at three different

temperatures; 140°C, 170°C, and 200°C at 0.25, 1, 2, 4 hours. From the rates obtained, 170°C was selected. We decided to oxidize in air at 170°C when we encountered problems with O₂ flow and temperature variations with the oxidation furnace.

A summary of sample treatments is shown in Figure 12. The furnace for the oxidation in air was an Al block with the sides open to the atmosphere and heated by a hot plate. Samples were placed on a holder and inserted into the furnace. A photograph and illustration of the furnace are shown in Figure 13 and Figure 14.

The extent of oxidation of each sample was determined using Rutherford Backscattering Spectrometry (RBS) (described earlier in Section 2.1.3). Analysis was done at a backscattering angle of 170° in a 1E-7 torr vacuum, and beam conditions were 30 µC at 30 nA. The spectra were collected and simulated using RUMP.

4000 Å Cu on C substrates

Figure 12: Summary of sample treatments for the intentional carbon layer experiment.

Figure 13: Photograph of oxidation furnace with hot plate temperature set at 170°C.

Figure 14: Front view of oxidation furnace.

3.2 Carbon-Free Experiment

This experiment involved a UHV system and was designed to deposit and implant copper in-situ, avoiding exposure of the copper surface to room air. This allowed irradiation of the copper surface free of adsorbed hydrocarbons. The purpose was to isolate the influence, if any, of surface carbon on the observed inhibition of copper oxidation following ion irradiation. This became necessary when it was realized by Dadu *et al.* that it would be very difficult to deposit and implant copper without adsorbing contaminants during the transfer of samples from one vacuum system to another (from e-beam to implant chamber).

The design incorporated both deposition and implantation of copper in-situ at ultra high vacuum ($<10^{-11}$ torr). A layout of the UHV setup is shown in Figure 15. A copper substrate and pellet were mounted on the holder and Mo boat thermal evaporator, respectively, and installed in the chamber. The chamber was then purged with N_2 followed by a twenty-four hour bakeout. An ion gauge and a residual gas analyzer (RGA) were used to track the total pressure during pumpdown to approximately 10^{-11} torr. The carbon partial pressure recorded by the RGA was less than 10^{-12}

Figure 15: Schematic of UHV illustrating both the deposition and implantation setup.

torr. The actual pumpdown took at least two days before reaching pressures less than 10^{-11} torr.

The 4000 Å thick copper films were thermally evaporated on polished copper substrates. Unlike the intentional carbon experiment, copper substrates were used to avoid problems associated with film delamination during oxidation heating and cooling cycles. We suspected that the difference in thermal expansion coefficients between C and Cu led to the film delaminating during several oxidation cycles. In addition, we wanted to use copper substrates to avoid the possibility of carbon contaminants from carbon substrates. A 6 mm diameter copper bar supported both the sample holder and the Mo boat thermal evaporator which was connected to a cooling source to maintain the deposition at room temperature.

A differential pumping line connected the UHV chamber to the ion beam accelerator. A 1.25 µm thick Ni foil 7 mm in diameter was installed along the beam path to filter out contaminants from the differential pumping line where the pressure was less than 10^{-8} torr. Helium ions were accelerated at 2.3 MeV which was reduced to 1.5 MeV after entering the chamber through the Ni foil. Half of the copper sample was irradiated at a dose of 2×10^{16} ions/cm².

The ion dose was calibrated using an electron suppressed Faraday cup.

An XPS line scan analysis was conducted on the samples following implantation to compare the amount of surface carbon on both the implanted and non-implanted sides. XPS spectra were also examined in detail to gain information on the bonding states of the surface layers. Following analysis the samples were oxidized in air at 170°C for 18 hours using the furnace. The oxide thickness and composition were determined using RBS. For comparison, the above procedure was repeated but with an intermediate isopropyl alcohol rinse. A summary of sample treatments for the carbon-free experiment is shown in Figure 16.

Figure 16: Summary of sample treatments for the carbon-free UHV experiment.

4. RESULTS AND DISCUSSION

4.1 Intentional Carbon Experiment

The results of the experiments using intentionally treated Cu surfaces are summarized in the following figures. In each case, the RBS spectra for both the implanted and unimplanted halves are shown on the same figure. Figure 17 shows the RBS spectra of both halves of an untreated (no intentional carbon layer), as deposited Cu surface following an 18 hour oxidation at 170°C. The spectra show the Cu signal for both implanted and unimplanted halves of the sample. It can be seen from the figure that a considerable amount of Cu has oxidized in the unimplanted half as indicated by the Cu oxide plateau. The unimplanted half shows a much smaller Cu signal indicating that a compound, copper oxide, has formed compared to the higher signal of pure Cu in the implanted half. The extent of oxidation between the two halves is also evident in the photograph shown in Figure 18. The difference between the two can be seen in the oxide's greenish color in the unimplanted region compared to the metallic Cu color retained in the implanted region.

Figure 17: RBS spectrum of untreated as deposited Cu surface following oxidation in air at 170°C for 18 hours. The implanted region was implanted with 1.5 MeV He⁺ at 2E16 ions/cm². Note the protection on the implanted region of the sample as indicated by the pure Cu signal.

Figure 1: Photograph of a 4000 Å Cu film following an 18 hour oxidation in air at 170°C. Prior to oxidation the left side was implanted with 1.5 MeV He⁺ ions at a dose of 2E16 ions/cm².

The same conclusion can be obtained in the RBS spectra in Figure 19 where the O and surface C peaks of both regions of the same sample are shown. The extent of oxidation as indicated by the larger O peak in the unimplanted compared to the implanted region indicates that oxidation inhibition has occurred in the implanted half. The calculated ratio of Cu to O of the oxide in the unimplanted half is approximately 2:1 giving a composition of Cu_2O . In addition, the spectrum shows a noticeable C peak in the implanted region. The amount of surface C was calculated to be around 5×10^{16} atoms/cm² which is approximately 20 monolayers thick. It is suggested that during the transfer of the sample from the e-beam evaporator to the implant chamber, a sufficient amount of organic contaminants were adsorbed on the Cu surface for the ion beam to degrade and thereby form a protective carbonaceous layer.

Several carbon based solvents were used to treat the surface of Cu prior to implantation and oxidation, with the results summarized in the following RBS spectra. Shown in Figure 20 and Figure 22 are the Cu peaks for toluene and acetone rinsed samples where the unimplanted half has formed a significant amount of oxide compared to the implanted region. Figure 21 and Figure 23 shows the O and

Figure 19: RBS spectra of the same sample showing the O and C peaks of the implanted and unimplanted regions following oxidation at 170°C for 18 hours in air.

Figure 20: RBS spectra of toluene coated Cu surface showing the Cu signals from the implanted and unimplanted regions following oxidation at 170°C for 18 hours.

Figure 21: RBS spectra showing the O and C peaks of toluene coated Cu after oxidation. Note the small C peak on the implanted half of the sample.

Figure 22: RBS spectra of acetone coated Cu surface showing the Cu signals from the implanted and unimplanted regions following oxidation at 170°C for 18 hours.

Figure 23: RBS spectra of the same sample showing the O and C peaks of acetone coated Cu after oxidation. Note the small C peaks on both spectra for the implanted half.

C peaks present in both regions of the toluene and acetone rinsed samples. Comparison of the difference in the amount of oxide that have formed in both regions clearly indicate that oxidation inhibition has occurred in the implanted half of the sample. Shown in Table 1 is a summary of the O content in the implanted and unimplanted regions of the treated samples. The different types of coatings led to approximately the same degree of protection as indicated by the amount of oxide formed in the implanted and unimplanted regions of the samples.

Similar to the untreated sample, deliberately treating the Cu surface with various carbon based coatings also produced a thin carbonaceous layer after implantation. The presence of a small C signal on the implanted halves of the samples strongly supports the suggestion that surface C may play an important role in the observed passivation of Cu. The calculated surface C peaks for the various treatments are shown in Table 2. The calculation amounts to approximately 15 to 20 monolayers, similar to the amount calculated in the as deposited sample. It appears that regardless of whether or not the treatment is intentional, the amount of C detected on the surface following implantation is constant and very thin. In fact,

Table 1: Oxygen content of implanted and unimplanted Cu samples treated with different carbon-based coatings after oxidation in air at 170°C for 18 hours. Samples were implanted with He⁺ at 1.5 MeV prior to oxidation.

Surface Treatments	O content Implanted (1E16 atoms/cm ²)	O content Unimplanted (1E16 atoms/cm ²)
As deposited	13.98 ± 0.50	59.93 ± 1.88
Toluene	11.99 ± 0.44	66.17 ± 2.09
Acetone	16.08 ± 0.44	72.51 ± 2.26
Isopropyl	11.94 ± 0.55	53.65 ± 1.73

Table 2: Carbon contents of irradiated Cu surfaces following oxidation in air at 170°C for 18 hours.

Surface Treatments	C content (10^{16} atoms/cm ²)
As deposited	5.91 ± 0.07
Toluene	6.68 ± 0.37
Acetone	7.46 ± 0.26
Isopropyl	6.24 ± 0.29

this is consistent with the idea that the solvents vaporize upon application, and the adventitious hydrocarbon layer from room air exposure is the source of C in all these experiments. It is interesting to note that the carbonaceous layer is not thick enough to form a functional diffusion barrier. This implies that the carbon related protection is by means of control over the surface oxide reaction.

4.2 Carbon Free Experiment

Following the intentional carbon layer experiment, several efforts were made in the UHV experiment to determine the effects of ion implantation on carbon-free Cu surfaces. The purpose of the experiment was to test whether oxidation inhibition is possible when carbon is absent during implantation. In two initial attempts to oxidize Cu deposited and implanted in-situ using the ultra high vacuum system, the RBS spectra of the implanted and unimplanted regions of a sample did not exhibit any difference. No significant amounts of oxidation were found in either area after 18 hours in the furnace at 170°C. Only when oxidized for 72 hours did a noticeable amount of oxide appear.

It was suspected the reason behind the slow oxidation of these UHV samples compared to earlier samples handled externally was that the deposition in the original UHV arrangement took place with the substrate raised to a high temperature (the evaporator boat being close to the sample). The temperature was measured during a typical deposition cycle with a thermocouple and it was found that the substrate temperature reached 250°C. Studies have shown that copper deposited at substrate temperatures above 100°C is compressively stressed [21, 22]. Although unconfirmed, it is possible that compressive stresses in the film could have contributed to the abnormally slow oxidation of our samples. As a result, we redesigned the sample holder for the UHV to avoid heating the Cu substrate during deposition.

The redesigned setup incorporated a separate sample holder and evaporator to eliminate conductive heating of the sample. Figure 24 shows the result of a second UHV deposited and 1.5 MeV He⁺ MeV irradiated Cu sample after 16 hours in the oxidation furnace. The spectra show both regions of the sample oxidizing approximately the same amount.

Figure 24: RBS spectrum of C free UHV Cu deposited and implanted in-situ with 1.5 MeV He⁺ at 2E16 ions/cm² using the new sample holder oxidized at 170°C for 18 hours. Note the small difference between the implanted and unimplanted regions.

The RBS data following oxidation as well as XPS analyses of samples immediately following implantation gave strong support to the importance of surface C and ion implantation in protecting Cu against oxidation. As evident in the RBS spectra shown in Figure 24 little difference can be seen between the implanted and unimplanted regions of the carbon-free Cu sample. After oxidizing for 18 hours, a comparison of the two regions indicates that no inhibition has occurred on the implanted side. This strongly supports the argument that C is necessary during implantation in order to protect the Cu surface from oxidation.

Figure 25 and Figure 26 show the XPS line scans of two samples with two different histories. The XPS scans were done after implantation and before oxidation. Figure 25 shows the line scan of a sample deposited and implanted in-situ (i.e. without carbon). These data are consistent with the RBS data in Figure 24 showing no significant difference between the implanted and unimplanted regions. The figure shows the same percentages of C, O, and Cu signals across the two regions of the sample. The typical UHV implantation time was less than 2 hours and the residual gas analyzer (RGA) indicated carbon partial pressures less than $1\text{E-}12$ torr. This amounts to less than $1\text{E}15$ atoms/cm² or less than

Figure 25: XPS line scan of unimplanted and implanted regions of a Cu deposited and 1.5 MeV and 2×10^{16} ions/cm² He⁺ irradiated sample. Carbon signal possibly accumulated during the transfer of the sample from UHV to XPS chamber.

Figure 26: XPS line scan of unimplanted and implanted regions of a Cu deposited, isopropyl rinsed, and 1.5 MeV at 2×10^{16} ions/cm² He⁺ irradiated sample. Notice the amount of carbon on the implanted side following irradiation.

a monolayer of carbon related contaminants striking the Cu surface. The scan also indicate C on both halves which is likely the result of the sample's exposure to atmospheric air during the transfer from the UHV to the XPS chamber after implantation. However, the adsorbate hydrocarbon layer alone does not offer any protection. Only after it has been implanted with ions does it protect against oxidation.

These XPS results suggest that there is no C present during the in-situ UHV implantation which we believe is necessary for protecting the Cu surface from oxidation. In comparison, Figure 26 shows the XPS line scan of a sample rinsed with isopropyl alcohol after deposition, but before implantation in the UHV chamber. In contrast to the previous sample there is a considerable amount of C present on the implanted region. This is in addition to the C accumulated during the transfer. The C signal on the implanted half is possibly the result of the degradation of adsorbates and the isopropyl alcohol.

The XPS line scan can also be used to determine the bonding states of Cu in each sample. Using Auger LMM lines the bonding states of Cu on the surface can be identified as Cu^0 (metallic) and Cu^+ (bonded). For the UHV sample, both

the implanted and nonimplanted sides of the sample show both Cu^0 and Cu^+ components. The visible Cu^+ signal was possibly due to the formation of a thin layer of oxide. For the isopropyl rinsed sample, the line scan also show Cu^+ and a smaller Cu^0 signal possibly weakened by the layer of adsorbate C. The implanted side also show a smaller percentage of Cu^+ .

5. PASSIVATION MECHANISM

It has been shown by this work that passivation of Cu surfaces requires the presence of surface C during ion irradiation. Experimental data shows that the protective carbonaceous layer formed after ion irradiation is only ~50 Å thick - too thin to function as a diffusion barrier against oxidation. Therefore, how does that layer of C protect the Cu surface from oxidation? One probable model for the passivation is based on a site blocking mechanism.

Prior to ion irradiation the surface of the metal is exposed to atmospheric contaminants, presumably during the transfer of the sample from one vacuum system to another. The layer of adsorbates are degraded due to secondary electronic interaction with the ion beam irradiation forming a layer approximately 20 monolayers thick consisting mainly of carbon atoms. These carbon atoms may prefer to occupy strategic locations on the surface of the metal that reduce the probability of the underlying metal from bonding with adsorbed oxygen. The study by Van Kooten *et al.* [23] has shown that C atoms in the graphitic state are adsorbed and occupy the threefold hollow sites on the Cu (111) surface. The strategically located C prevents O₂ from chemisorbing and dissociating. The threefold hollow sites are shown in

Figure 27 along with the basic units of C atoms that can be deposited on the surface of a Cu (111) surface. According to Van Kooten et al. the basis for inhibition of Cu oxidation is due to C atoms adsorbing on these threefold sites instead of O, thus preventing the latter from adsorbing onto the surface of Cu. In addition, Van Kooten et al. asserted that the surface does not require complete coverage of C atoms in order to block O from adsorbing.

Before exploring the assumptions that form the basis for the site blocking mechanism, several notations must be introduced. Figure 28 shows how Van Kooten et al. described each site as having three Nearest Neighbor (NN) sites and six Next Nearest Neighbor (NNN) sites. Van Kooten's simulations imply that following C coverage of the Cu (111) surface, O site blocking is possible when only one Nearest Neighbor (NN) site is occupied by C. Therefore, O will not adsorb onto a site which has a C Nearest Neighbor (NN). As a result, O can not react with the underlying Cu metal to form an oxide.

The non-zero oxidation of Cu that we have found following irradiation probably shows that the C coverage is not complete. Also, although the Cu film has a preferred (111) texture (as seen by XRD), it is not monocrystalline;

other grain orientations may populate the surface with facets having a less favorable lattice match to the blocking C.

Previous experiments have used both reactive and inert ions to produce protection of Cu. In cases where heavy ions were used, some resputtering of C may have occurred thus spoiling the protective effect. Other experiments can probably be assumed to have produced the same result, but chemical effects must be the reason for their different behavior.

Figure 27: Schematic representation of C atoms located at threefold hollow sites on the Cu (111) surface [23].

Figure 28: Definition of a site's Nearest Neighbor (NN) and Next Nearest Neighbor (NNN) [23].

6. CONCLUSION AND SUGGESTION FOR FUTURE WORK

Two experiments were conducted to determine the effects of surface C and ion irradiation in producing the observed passivation of Cu surfaces. RBS data show that Cu surfaces exposed to room air and irradiated with 1.5 MeV He⁺ ions at 2E16 ions/cm² are passivated against oxidation. In addition, as deposited Cu surfaces produce the same amount of protection after irradiation as those that were treated with various carbon-based coatings. In contrast, Cu surfaces deposited and irradiated in-situ (C free surface) in the UHV chamber did not exhibit any protection after oxidation. This strongly supports the theory that the observed oxidation inhibition of Cu surfaces is due to the interaction between surface C and ion beam irradiation. In addition to RBS, XPS line scans also show that the protection can be attributed to a carbonaceous layer that is approximately 15 to 20 monolayers. This implies that the passivation is not based on a diffusion barrier mechanism. It is suggested that instead, passivation is due to an O₂ site-blocking mechanism.

It would be interesting to see if the implanted sample can be subsequently implanted more than once or to implant at higher doses to see if the detected surface carbon and

the oxidation inhibition increases. This would reinforce the premise that surface contaminants and ion beam irradiation creates a thin layer of carbon that inhibits the oxidation of copper.

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