METAL DIFFUSION AND CHEMICAL PROCESSES OF MONO AND BI-LAYER THIN FILMS

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Cover: Delta value for the full spectral range obtained from in situ measurement of tin deposition on silicon wafer. Picture shows data obtained at 1 minute intervals during deposition.

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Metaal diffusie en chemische oppervlakte processen van mono en bi-laag dunne films

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PROCESSES OF MONO AND BI-LAYER THIN
FILMS

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Chapter 1

Introduction

1.1. Semiconductor motivated thin film materials research

This thesis deals with two examples of materials research as motivated by modern semiconductor developments. The research concerns physical and chemical studies of thin film systems as used for optics and high-k dielectrics.

In thin-film applications, diffusion, and surface binding play key roles in the longevity of the film. For instance, the interface between the gate material and its surroundings plays a role in determining the capacitance and charge mobility. The stability of that interface, which is influenced by diffusion, will influence the lifetime and performance of an electronic device. Likewise, optical coatings must adhere to substrate surfaces, but, at the same time, the coating should not allow atmospheric contaminants, such as dirt, or oil to bind strongly. If this is not achieved, the coating performance will decay with time because contaminants cannot be cleaned.

In this thesis, surface binding and diffusion has been studied in model systems to investigate how the surface and the underlying thin-film changes surface binding. We show that for metal-metal interactions, surface binding strength can be predicted using a simple electronegativity model. In later work, we show that metal-dielectric binding is strongly influenced by the underlying thin-film with electron diffusion and tunneling playing a role in controlling the surface-binding strength.

The difference between conventional optical lithography (DUV) and EUVL is the use of very short wavelength light, and has required new research across the entire technology spectrum.¹⁻¹⁵ New types of plasma light sources, based on tin,¹⁶ are required to generate the short wavelength EUV light, and wafers must be exposed under vacuum to minimize EUV intensity losses by gaseous absorption, and to avoid contamination or oxidation of the optical elements.

EUV optics are reflective multilayer optics, consisting of artificial Bragg crystals with periodicity of half of the 13.5 nm wavelength. A stack of thin layers of alternating materials (with high and low refractive index) is created and reflected waves from all interfaces add up constructively. In practice 50-70 bilayers of Mo and Si have a reflectance of around 70%, close to the theoretical maximum.^{1, 13, 17-18}

Under EUV exposure, the optics may be subject to recoverable and non-recoverable reflectivity losses due to contamination. Thus, the MLM is terminated with a material that is more resistant to the environment (physical and chemical processes), while, at the same time, maximizing the mirror's reflectivity. Although not the only relevant surface binding process,^{11, 19} the focus of this thesis is mostly on understanding metal-metal and metal-dielectric surface processes, using tin as a model material.

1.1.1. Tin contamination control

Plasma facing mirror surfaces and any surfaces that are within the diffusion range of Sn particles and vapor may be contaminated with Sn.²⁰ Any Sn particles on the mirror surface can also decrease its reflectivity. For instance, the presence of 1 nm Sn on a mirror results in a reflection loss of 10%.^{9,20}

In order to prevent the optics from losing reflectivity and to enhance the mirror's lifetime, in situ mirror cleaning technologies may be used to maintain the optics performance.¹ Carbon can be

removed by atomic hydrogen etching. Oxidation is more problematic. But, for a Ru-terminated mirror, as long as a monolayer or less of oxide is formed, oxidation can be reversed by exposure to atomic hydrogen.²¹ Sn can also be removed from mirror surfaces using hydrogen etching.²⁰ Atomic hydrogen reacts readily with Sn (see equation 1-1), in the +4 oxidation state, to form stannane (SnH₄), which is volatile at room temperature:

Stannane is unstable and decomposes slowly at room temperature to give metallic tin. Moreover, the dissociation of SnH₄ can be accelerated by the presence of catalytically active surfaces (metallic Sn catalyzes the dissociation of SnH₄).²² Transition metals may also catalyze the dissociation of stannane.²³⁻²⁴ On the other hand, the addition of a small amount of oxygen considerably slows the dissociation due to the formation of a non-catalyzing tin oxide film.

Although Sn can be etched rapidly by atomic hydrogen, the etching process was found to be incomplete when Sn was deposited on a Ru surface. Sn etching from a Ru surface can be improved by adding Si₃N₄.²⁰

There have been numerous empirical studies on Sn removal from thin metal layers like Ru, Mo, Si, Pd, Au, Si₃N₄, SiO₂.^{9, 15, 20, 25-26} However, no systematic investigation has been performed, and the previous studies had little predictive power for the materials not directly investigated. To predict lifetime, the physics and chemistry of Sn etching must be understood in order to ensure that etching is complete and that the process does not damage the surface of the optical element.

In this thesis, we propose electronegativity as a factor that can be used to determine if Sn is etchable from a given material. We show that electronegativity is highly predictive in the case of metals.

1.1.2 Hydrogen penetration control

In this thesis, we initiated the study of the application of catalytic surface reactions with carbon species to control hydrogen penetration. In principle carbon monoxide is the ideal species, since it strongly adsorbs to metallic surfaces, and is known to react directly with hydrogen to produce volatile hydrocarbons (via the Fischer-Tropsch reaction).²⁷ However, even though a low partial pressure of CO may be sufficient to protect mirror surfaces, the sheer volume of the EUVL vacuum vessel requires dangerous amounts of CO to be available in a fabrication facility. Thus, it was decided to investigate carbon dioxide (CO₂) as a possible candidate for consuming hydrogen at the surface layer. Carbon dioxide may either directly react with hydrogen in a reverse water gas shift reaction, or indirectly via partial dissociation followed by a Fischer-Tropsch reaction. In both cases, hydrogen would be consumed, thereby preventing hydrogen from penetrating into the mirror. Although the CO₂ absorption has been studied on many materials, such as Ph, Pd, Pt, Fe, Cu, Re, Ni, Al and Mg, CO₂ adsorption on Ru has not been investigated.²⁸ In this thesis we studied CO₂ adsorption and dissociation on single crystalline Ru.

1.2. High-k dielectrics applications

In semiconductor manufacturing processes, silicon dioxide (SiO₂) has been used as a gate oxide material. In order to continue the miniaturization of integrated circuit features, the implementation of high-k gate dielectrics, among several other strategies is required.²⁹⁻³⁰ As transistors have decreased in size, the thickness of the SiO₂ gate dielectric has steadily decreased to increase the gate capacitance and, thereby, drive current. The reduction in current raises device performance and reduces power consumption, both desirable attributes. However, decreasing the thickness of SiO₂ also leads to higher leakage currents due to tunneling, which increases

power consumption, and reduces device reliability. Replacing the silicon dioxide gate dielectric with an alternative material that has a higher k value allows increased gate capacitance without the associated leakage effects.³¹⁻³³ The gate oxide material must satisfy several criteria: in addition to the electronic function of a gate dielectric, the gate oxide material must maintain a high dielectric constant, and serve as a diffusion barrier against diffusion of material from the top electrode. Hence, it is also of importance to know the diffusion-barrier behavior.³⁴ Group III based dielectrics, such as scandium oxide (Sc_2O_3), have been studied as possible candidate for high- k dielectric applications.²⁹ Although the electronic properties of Sc_2O_3 were widely studied, the diffusion-barrier properties have not been investigated.³¹⁻³³ In this thesis, diffusion studies were carried out. We used Sn to test if Sc_2O_3 layers of various thicknesses act as a diffusion barrier. Moreover we estimated electron tunneling rates for layers in the range of 0.7-1.5 nm.

1.3. Surface chemistry - electronegativity

To understand the behavior of Sn at a surface, we use the concept of electronegativity. Electronegativity, χ (chi), is one of the three most important factors (electronegativity, electron affinity, ionization energy) which influence the type of bond between two atoms.³⁵ Electronegativity is a parameter that was introduced by Linus Pauling (in 1932) as a measure of the power of an atom to attract electrons to itself when it is part of a compound.³⁶ In Pauling's relative scale, valence-bond arguments were used to suggest that an appropriate numerical scale of electronegativities could be defined in terms of bond dissociation energies, E_d . Pauling proposed that the difference in electronegativities (equation 1-2) could be calculated based on:

$$E_d(A-B) = \frac{1}{2} [E_d(A-A) + E_d(B-B)] + a(\chi_{(A)} - \chi_{(B)}) \quad (1-2)$$

Where E_d are the dissociation energies of the A–B, A–A and B–B, $\chi_{(A)}$ and $\chi_{(B)}$ are the electronegativities of A and B, respectively, and a is equal to 96.5 when all energies are expressed in kJ mol^{-1} ($1\text{eV}=96.5 \text{ kJ mol}^{-1}$). As only differences in electronegativity are defined, it is necessary to choose an arbitrary reference point in order to construct a scale. Hydrogen was chosen as the reference with an electronegativity of 2.2, as it forms covalent bonds with a large variety of elements.³⁶ The periodic table with the electronegativities values is presented in Figure 1-2. Electronegativity generally increases from left to right on the periodic table and from bottom to top. Metals are the least electronegative of the elements. An important application of electronegativity is in the prediction of the polarity of a chemical bond (Figure 1-1).

It was found that the greater the difference in electronegativities between elements, the greater the polar nature of the bond.³⁵ In this thesis, relative electronegativities are used to successfully predict the success or failure of Sn etching from different surfaces.

Figure 1-1. Percentage of ionic bond in chemical bond as a function of difference in electronegativity between the atoms.

1.4. Surface analysis

Most of the techniques for surface analysis are used in vacuum to reduce scattering of electrons and/or ions by gas phase molecules. Measuring in vacuum also allows the influence of the ambient on the surface to be controlled.³⁸ Many surface analysis techniques are not surface specific, so surface sensitivity plays an important role. The surface sensitivity depends on the escape depth of the detected probe. Moreover, the possibility of surface damage during analysis and influence of the incident electrons, photons or ions on the results must be taken into account.³⁸

Many surface studies have been performed using scanning tunneling microscopy (STM), low energy electron diffraction (LEED), and X-ray photoelectron spectroscopy (XPS). STM can provide an information on the surface morphology, however it can be challenging to resolve some chemical reactions.³⁹⁻⁴¹ LEED is sensitive to ordered overlayer structures and XPS is sensitive to chemical changes at the surface, but, the relatively high energy of the electron and X-Ray irradiation can lead to surface modifications that may be difficult to separate from the changes of interest.⁴²⁻⁴⁷ For surface adhesion and etching, studies, we have used X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and ellipsometry, which, taken together, give a very good overview of the surface chemistry and morphology changes during various experiments.^{25, 42-48} XRF has even higher elemental sensitivity than XPS, but no chemical sensitivity and cannot distinguish between surface and buried elements. Some of the techniques used in this thesis are described in more details below.

1.4.1. Spectroscopic ellipsometry

Spectroscopic ellipsometry was originally used in the work of Paul Drude in the 19th century, when he used a polarized light in a reflection configuration to study the optical properties and

thickness of very thin metallic films.⁴⁹⁻⁵³ In ellipsometry, polarized light is used to characterize the optical properties of materials.^{49, 51, 53} The change in polarization is represented by an amplitude ratio, Ψ , and a phase difference, Δ .⁵⁰ Together, these quantities determine the complex reflectance ratio (equation 1-3), ρ , according to:

$$\rho = \tan(\Psi) e^{i\Delta} \quad (1-3)$$

In general, the measured values for Ψ and Δ cannot be used to directly calculate the dielectric properties of the individual layers that comprise the sample (though the effective dielectric properties can be directly calculated). Instead, Ψ and Δ must be combined with modeling, which can provide layer thicknesses and material properties, making it an excellent tool for contact free determination of thickness and optical constants of films of all kinds.^{50, 53-59} To create a proper model for measured samples, it is usually required that the structure/composition of the sample is already known to a certain extent. Such information may be obtained from a different measurement technique e.g. TEM or XPS, or from knowledge of how the sample was created^{49, 51}

Ellipsometry can yield information about layers with a sensitivity below a single atomic layer⁵⁴, moreover, no reference measurement is necessary. By measuring two independent values at each wavelength, this technique provides more information than other optical techniques, such as conventional reflectometry.⁴⁹ The maximum film thickness that can be measured with ellipsometry is limited to the coherence length of the light source. Thus, transparent or low absorbing thin films, with thickness ranging from less than a nanometer to several micrometers, can be measured with ellipsometry.⁴⁹

Besides high sensitivity, ellipsometry has the advantage of being non-destructive and contactless. Additionally, ellipsometry can be used in an external configuration, which means that vacuum is not

necessary, and with calibration, the instrument can probe the sample via optical ports, rather than being placed in the vacuum chamber.⁴⁹ Ellipsometry measurements are also very fast (in a typical commercial instrument, a full spectrum can be collected every 3 seconds), providing data with high temporal resolution and allowing for the characterization of a sample in “real-time”. A spectroscopic ellipsometer is also relatively easy to use and requires no sample preparation.⁵⁴

1.4.2. Low-energy ion scattering and x-ray photoelectron spectroscopy

During low-energy ion scattering (LEIS) measurement sample surface is exposed with noble gas ions (He⁺, Ne⁺, Ar⁺, or Kr⁺) in the range of 0.5 to 10 keV and an incident angle of <60° with respect to the surface normal.⁶⁰⁻⁶² Energy of the scattered ions depends only on the mass of the surface atoms. Elastic binary collision at the sample surface is characteristic for each element and is shown as a peak in LEIS spectrum, with a characteristic energy for each element. Moreover surface concentration of specific element is proportional to the peak intensity.⁶² Thus, due to high surface sensitivity, surface atomic composition can be determined with this technique. LEIS can also be used for the analysis of much deeper layers by using it in combination with sputter depth profiling. Moreover, the detection limit, for example, for light elements from Li to O can reach $\leq 1\%$.^{60, 62} With LEIS, rough amorphous insulating samples as well as conducting flat single crystals can be analyzed. This flexibility allows LEIS to be used for studying important processes like adhesion, catalysis, diffusion, film growth, and electron emission for a wide variety of materials.⁶² The only restriction for the measurements is that measured samples must be put into vacuum for analysis.⁶²

An alternative to LEIS is X-ray photoelectron spectroscopy (XPS).⁶¹⁻⁶² The sample in XPS is irradiated with monochromatic soft

X-ray radiation. This energy is absorbed by the sample, which emits photoelectrons. The energy difference between incident radiation and emitted photoelectrons is used to calculate the binding energy of the electrons. XPS allows the sample elements and their atomic concentrations to be determined and the chemical states can, in many cases, be determined from small changes in the measured binding energy.⁶³ In situ XPS has elemental sensitivities in the parts per thousand range, and is often directly sensitive to the average chemical changes in the top ~5-10 nm of the surface layer, limited by the escape depth of the photoelectrons.⁴²⁻⁴⁷ Electrons generated deeper in the solid may escape, but on the way out they collide with other atoms and lose energy, therefore, they are not use for analysis. The surface sensitivity can be significantly increased by irradiating the surface at grazing incidence. However, in a grazing incidence geometry, less X-Ray radiation is absorbed, reducing the electron emission intensity, and increasing the time of XPS scans, which also reduces the temporal resolution of dynamic measurements.³⁸

Similarly to the case of LEIS, XPS measurements require high vacuum (10^{-8} mbar) or ultra-high vacuum, making it inappropriate for in situ measurements of processes when relatively high pressures may be required for a surface process (e.g., deposition or etching processes).⁶³

1.4.3. Reflection-absorption infrared spectroscopy

With reflection-absorption infrared spectroscopy (RAIRS), the infrared spectrum of light, reflected from a (normally metallic) sample surface, covered with a thin layer, is examined. Infrared-frequency dependent absorption by the thin layer is used to characterize the layer. Such absorption bands correspond to the normal ro-vibrational modes of molecules, and can provide detailed information about the geometric structure of the molecules and the force constant of bonds, both within molecules

and between the molecules and the underlying metal surface.⁶⁴ The growth and decay of vibrational modes can be studied in situ. Depending on the species of chemical in the adsorbed layer, the sensitivity of RAIRS can be lower than a monolayer of coverage (down to a few percent of a monolayer). Thus, RAIRS is used for studying reactions, molecular adsorption, surface phase transitions, and/or lateral inter-molecular interactions. Moreover, RAIRS is very suitable for studying catalytic reactions under a wide range of pressure conditions.⁶⁴⁻⁶⁶

RAIRS has excellent energy resolution ($< 2 \text{ cm}^{-1}$) which is useful for separating multiple peaks, phase transitions, lateral interactions and dynamics of coupling. Furthermore, due to the low energy of the radiation in RAIRS, in situ studies are highly unlikely to modify the surface during measurement.⁶⁴ Beside the fact that it is a straightforward instrument to use, RAIRS is not restricted to vacuum conditions, making it highly versatile.

The fact that the signal is weak, owing to the small number of absorbing molecules, is one of the limitations of this technique. Moreover, RAIRS only excites out-of-plane vibrational modes of the dipole moments via constructive interference. While the in-plane surface vibrational modes are suppressed by the metal surface due to destructive interference effects. This limits the technique in quantifying the coverage.^{64-65, 67-68}

1.4.4. Temperature programmed desorption

In temperature programmed desorption (TPD) spectroscopy it is possible to detect elements and components at the surface by measuring the temperature at which molecules desorb from the surface. This is achieved via controlled surface heating at a constant rate and use of a mass spectrometer positioned close to the surface. Depending on the mass spectrometer, TPD allows several masses to be detected at the same time. TPD provides a direct measurement of the surface binding energy, and allows for an

absolute measure of surface coverage. Analyzed species on the surface are desorbed during measurements, thus it a technique that significantly changes the surface chemical composition during the measurement.^{66, 69-71} Residual background gases will prevent the TPD from being measured, thus the measurements require UHV.

By combining TPD and RAIRS, it is often possible to draw more quantitative conclusions from the results than from both techniques separately.

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Chapter 2

Electronegativity-dependent tin etching from thin films

The influence of a thin film substrate material on the etching of a thin layer of deposited tin (Sn) by hydrogen radicals was studied. The amount of remaining Sn was quantified for materials that cover a range of electronegativities. We show that, for metals, the etching depends on the relative electronegativity of the surface material and Sn. Tin is chemically etched from surfaces with an electronegativity smaller than Sn, while incomplete Sn etching is observed for materials with an electronegativity larger than Sn. Furthermore, the amount of remaining Sn increases as the electronegativity of the surface material increases. We speculate, that, due to Fermi level differences in the material's electronic structure, the energy of the two conduction bands shift such that the availability of electrons for binding with hydrogen is significantly reduced.

2.1. Introduction

A hot Sn plasma emitting at a target wavelength of 13.5 nm is used as an EUV (extreme ultraviolet) source for photolithography applications.¹ Tin materials, in the form of debris resulting from the plasma, can be deposited on mirrors and consequently decreases the mirror reflectivity.²⁻⁴

Reactive hydrogen species are able to form the volatile hydride stannane ($\text{Sn} + 4\text{H} \cdot \rightarrow \text{SnH}_4 \uparrow$), which can subsequently be removed from the surface.⁴ Stannane slowly decomposes (at 35°C)

to metallic Sn and hydrogen^{5 6}, which reduces the effective etch-rate due to re-deposition.

Successful Sn etching using hydrogen atoms will depend on the surface material.^{3 7} For example, the cleaning rate of the last few nm of Sn from a Si surface is almost twice as fast as that from a Ru surface.⁷ This disparity in etching rate increases for Sn layers that become thinner than 2 nm. A possible explanation for this disparity is Sn re-deposition on the surface, due to the decomposition of Sn hydride. Metallic surfaces like Ni, Ru, Rh or Au effectively catalyze the decomposition of SnH₄.⁷ During the etching process, the substrate becomes more exposed, which favors Sn decomposition and re-deposition, and may lead to a dynamic equilibrium between SnH₄ formation and decomposition. However, the amount of Sn remaining after hydrogen etching is significantly more than a monolayer, which cannot be fully explained by enhanced re-deposition due to catalytic activity.⁷

Aside from environmental factors, such as hydrogen flow rate and substrate temperature, an additional factor that contributes to the etching of Sn is the surface material's electronic structure, which has remained relatively unstudied as a factor. Experimental studies on the influence of electronic structure are challenging because surface states depend intrinsically on the local geometry of the surface material where the Sn atoms adsorb. As a first step towards quantifying the influence of surface electronic structure, we use a proxy that may allow some general principles to be revealed. Because electronegativity provides a simple empirical model for binding strength (and, indirectly, the changes to electronic structure), we propose here to use electronegativity as a proxy for electronic structure.

The electron distribution in a bond in a diatomic molecule containing different atoms is not symmetrical between the atoms⁸, the degree to which this redistribution occurs can be described by a single parameter, called the electronegativity.⁹ The probability

density of an electron pair, shared between two elements, has a maximum that is located closer to the more electronegative element. The more electronegative element acquires a partial negative charge, and the molecule may also acquire a dipole moment.

When electrons are shared by two metallic atoms in a bulk material, a metallic bond may be formed. The electrons that participate in metallic bonds are delocalized, thus, metallic bonds have no dipole moment. An interface between two metals acquires a potential difference, however, that depends on the difference between their Fermi levels. At thermodynamic equilibrium, the Fermi level is constant across the interface, meaning that the energy of the two conduction bands must smoothly shift to be coincident at the interface.¹⁰ This modifies the electronic structure of the Sn near the interface, and changes the availability of electrons for bond formation with, in our case, hydrogen atoms. Due to this change in charge availability, the relative electronegativities of the surface material and the Sn may be used to predict the degree to which electrons are available for bonding. This allows the success or failure of Sn etching from a thin metallic surface material to be predicted. Specifically, we hypothesize that Sn can be fully chemically etched from surfaces with electronegativity lower than Sn, while incomplete Sn etching is expected for materials with electronegativity higher than Sn.

2.2. Experimental

2.2.1. Material selection

From all chemical elements, 15 were chosen for further study (see Table 2-1). The chosen surface materials belong to different groups and periods in the periodic table.

As stated, electronegativity is a measure of the ability of an atom in a molecule to draw bonding electrons to itself. The most

commonly used electronegativity is a relative scale of electronegativity, developed by Linus Pauling in 1932.¹¹ In this scale, electronegativity differences are defined by differences in bond dissociation energies with hydrogen set to an arbitrary reference point value of 2.1.

Elements with electronegativities, χ , higher and lower than Sn ($\chi=1.8$) were chosen. It should be noted that Sn has a rather high electronegativity, limiting the number of appropriate materials with an electronegativity higher than Sn. Finally, to avoid cases dominated by excessively fast oxidation, elements from the first and second groups were excluded. Furthermore, elements that were known to react strongly with hydrogen, such as Pd and Co, were excluded. Within these restrictions, it was desirable to choose elements that covered as broad a range of the periodic table as possible. The aim was to include a large range of possible electronegativities. Elements from groups 3-14, consisting of transition metals, metalloids, other metals and non-metals were chosen for further investigation.

2.2.2. Methodology

Thin films of chosen materials, with the average thickness of 5 nm, were deposited onto silicon wafers (10 x 10 x 0.5 mm) by magnetron sputtering or electron-beam deposition. The film thickness was monitored during deposition using a quartz microbalance. After deposition, the samples were removed from the chamber and exposed to ambient conditions. Grazing incidence x-ray reflection measurements were performed to extract accurate layer thicknesses. The deposition method, and XRR derived layer thicknesses are shown in Table 2-1. The uncertainty in the film thickness was estimated to be 10%.

X-ray photoelectron spectroscopy (XPS) (Thermo Scientific Theta Probe) analysis showed that for many materials a surface oxide layer forms upon exposure to ambient conditions. For most of the

materials that we chose, the oxide layer is usually self-limiting at atmospheric pressure and room temperature, resulting in a so-called native oxide layer with a thickness of few nanometers at most.¹²

Table 2-1. Electronegativity values, deposition method, thickness of surface material and native oxide thickness on each sample for test materials used in this work.

Element	Sc	Ta	Ti	Nb	V	Cr	Al	W	Mo	Si	Si wafer	Ag	B	Ru	Au	C	Sn	H
Type of metal	TR	TR	TR	TR	TR	TR	OM	TR	TR	ML	ML	TR	ML	TR	TR	NM	OM	NM
Electronegativity (Pauling scale) ¹¹	1.3	1.5	1.5	1.6	1.6	1.6	1.5	1.7	1.8	1.8	1.8	1.9	2	2.2	2.4	2.5	1.8	2.1
Method of deposition on silicon wafer	EB	MS	MS	MS	EB	MS	EB	MS	MS	MS	-	EB	MS	MS	EB	MS	-	-
Thickness [nm]	5.5	6.7	6.6	5.7	5.5	8	5.5	7	5.5	4.7	-	5.5	4.4	17.5	5.6	5.1	-	-
Native oxide [nm] XPS	3.6	3.2	3.2	3.5	4.7	1.5	2.2	2.3	2.5	1.3	1.3	-	~0.9	0.8	-	~0.5	-	-

TR – transition metal, ML – metalloids, OM – other metal, NM – non metal, MS – magnetron sputtering, EB – e-beam, “-” for native oxide means that presence of oxide cannot be determined

Tin deposition and etching experiments were performed in a vacuum chamber (Figure 2-1b) with a base background pressure of 10^{-9} mbar (10^{-7} Pa), which increases to 10^{-8} mbar during Sn deposition. The samples described in Table 2-1 were not subjected to further preparation and were placed directly in the vacuum chamber. The sample was held upside down on a movable sample holder, 4 cm above the exit port of an evaporation source. The temperature of the sample was monitored using a Pt-100 temperature sensor, installed under the sample (Figure 2-1a).

Tin (Umicore) with a bulk density of 7.3 g/cm^3 was evaporated from an Effusion Cell EF 40C1 (PREVAC) evaporator operated at 980°C . The Sn deposition rate was calibrated using a quartz microbalance (INFICON XTM/2 Deposition Monitor). It was found that the evaporation rate as measured using the quartz microbalance (QMB) at 980°C was approximately 0.4 nm/min .

In a typical experiment, 8 nm of Sn was deposited. During deposition, the sample temperature remains lower than 55 °C, and, after deposition the sample is allowed to cool to room temperature. The influence of a surface temperature on mobility of Sn was additionally checked and no mobility of Sn was observed below 150 °C. Tin deposition and etching (see below) on the sample surface was monitored with spectroscopic ellipsometry (J.A. Woollam Co., M-2000, spectral range 245-1689 nm) at an angle of incidence of 76.4 ° (with respect to the surface normal).

Tin was etched with atomic hydrogen ($H^\cdot$), which was generated using a hot (2000 °C) tungsten filament (placed 3 cm from the sample holder). In order to achieve sufficient $H^\cdot$ flux with a stable flow rate, the hydrogen (purity 99.999 %) pressure during exposure was fixed at $8 \cdot 10^{-2}$ mbar. The hydrogen radical flux at the surface was measured to be 10^{17} at/($\text{cm}^2 \cdot \text{s}$).¹³ To prevent the sample from heating excessively, the filament was operated at a duty cycle of 0.5 with a period of 10 min, and a shield was placed between the filament and the sample.

a)

b)

Figure 2-1. Experimental set up inside (a) of vacuum chamber (b), 1-Quartz microbalance, 2-sample holder, 3-pressure gauge, 4-tungsten filament (H radical generator), 5-effusion cell, 6,7-ellipsometer detector and source, respectively.

Selected samples were removed from the deposition chamber before exposure to hydrogen radicals, allowing Sn layer thickness analysis using X-ray fluorescence. X-ray fluorescence (XRF) (PW2400 chemium anode sequential XRF-spectrometer) has a detection limit for Sn of $0.01 \mu\text{g}/\text{cm}^2$ (0.014 nm). Other samples were analyzed after hydrogen etching.

2.3. Results

2.3.1. Tin deposition and etching *in situ* monitored with ellipsometry

Although the absolute thickness of the Sn layer is relevant, the total amount of remaining Sn after etching is the parameter of interest. To avoid uncertainties on the amount of deposited Sn, we use XRF and determine the layer thickness using the bulk density of Sn (7.287 g/cm^3). The average thickness of the Sn layer on the samples before etching was measured to be $7.7 \pm 0.9 \text{ nm}$ (Table 2-2). XPS measurements could not detect the underlying material, indicating that the layers were closed to within a few percent. The Sn etching experiments do not include exposure to ambient, and the etching experiments were performed less than one hour after deposition, thus we do not expect Sn oxidation. Therefore, for the hydrogen etching measurements, the initial etching is dominated by the chemistry of Sn and hydrogen, while further into the etch process, the substrate starts to play a role.

Table 2-2. Deposited Sn thickness (XRF) for all surface materials.

Element	Sc	Ta	Ti	Nb	V	Cr	Al	W	Mo	Si	Si wafer	Ag	B	Ru	Au	C
Sn thickness [nm]	7.58	7.74	7.95	8.43	7.25	7.62	7.18	7.8	7.88	7.21	8.6	7.25	8	7.95	7.18	7.42

During Sn deposition and hydrogen radical etching, the surface was monitored *in situ* with spectroscopic ellipsometry. These measurements were primarily used to distinguish the end point for Sn etching by monitoring the ellipsometric angles Psi (not shown) and Delta (see Figure 2-2 for Delta). For a sample where complete Sn etching was observed (confirmed afterwards with XRF measurements), e.g., crystalline silicon (Figure 2-3a), it can be seen that, after 120 minutes of hydrogen etching, the Delta value for a wavelength of 530 nm, which shows the largest Delta modulation, nearly returns to the value it had prior to Sn deposition, and is

stable thereafter (end point of etching). This is typical for the entire Delta (Figure 2-2) and Psi (not shown) spectrum for surfaces from which Sn could be etched completely. The similarity of the initial and final Psi and Delta spectra also means that the surface is very close to its original state after etching. It is most likely that the small differences in the Psi and Delta spectra are due to a very slight change in sample alignment during etching.

The Ru surface is an example of incomplete Sn etching, which can be clearly seen from the ellipsometry measurements (Figure 2-3b). After 100 min of etching, the Delta value is stable, but it has not returned to the value it had prior to Sn deposition. It is clear that Sn remains on the sample surface (confirmed with XRF measurements, see below).

Although the ellipsometry measurements can be used to estimate the Sn layer thickness during deposition and etching, this process proved to be unreliable. The as-deposited Sn surface is rather rough³, and the surface roughness is expected to change during etching, which influences the interpretation of the ellipsometry data during etching, but not at the end point of etching. For some samples, the ellipsometry measurements showed evidence that the Sn and hydrogen radicals interacted with the underlying surface, changing its optical properties as well. As a result of these factors, a reliable model fit could not be obtained. Therefore, to quantify the amount of Sn remaining on the surface after etching, XRF measurements were performed.

a)

b)

Figure 2-2. Delta as a function of wavelength during Sn deposition (a) and hydrogen radical etching (b) on a silicon wafer. Delta values for a clean silicon wafer are presented as a dashed line in Figure 2-2b.

a)

b)

Figure 2-3. Delta value for 530 nm during Sn deposition and hydrogen radical etching for a) silicon wafer and b) Ru layer.

2.3.2. Electronegativity dependent Sn etching

Figure 2-4 shows the Sn layer thickness derived from XRF after etching as a function of difference in electronegativity between the surface material and Sn. The surface materials can be divided in two groups in terms of complete and incomplete Sn etching.

The first group includes surface materials that have electronegativity values that are lower or equal to Sn ($\chi_{\text{Sn}} - \chi_{\text{M}} \geq 0$). For these materials, Sn is completely etched (less than 0.08 nm of Sn on the surface) with two exceptions, where 0.4 nm and 0.14 nm of Sn remain on the Mo and W surfaces. For these materials, it is possible that the re-deposition plays a role, especially just after the etch is terminated.³

The second group consists of surface materials that have an electronegativity value higher than that of Sn ($\chi_{\text{Sn}} - \chi_{\text{M}} < 0$). In this group incomplete Sn etching is observed. Moreover, the thickness of the remaining Sn increases for smaller electronegativity values, indicating that Sn is more strongly bound to these surfaces. It is remarkable that we find a simple linear relationship between the Sn thickness and electronegativity for $\chi_{\text{Sn}} - \chi_{\text{M}} < 0$. A possible explanation for this result (see below) is that the surface material modifies the electronegativity of the first few layers of the Sn. For this to occur, the two layers should not be significantly intermixed. To determine if the Sn intermixes with the surface layer, angle resolved XPS analysis was performed on the etched Ru sample. This showed minimal intermixing between Ru and Sn. For Au and Ag, angle resolved XPS was inconclusive.

The XPS spectra, however, show that, for Ag, the Sn 3d_{5/2} spectral line shifts from 484.78 eV (Sn as deposited) to 484.91 eV (after etching with H⁺), while the expected chemical shift (CS) for Sn 3d_{5/2} spectral line upon Ag-Sn alloy formation is 1 eV.^{14, 15} Likewise, the Ag 3d_{5/2} spectral line shifts from 368.22 eV (Ag as deposited) to 368.32 eV (after etching with H⁺), which is also less than the

expected 1 eV shift. These measurements confirm that Ag and Sn do not significantly intermix.

In contrast, the XPS spectra for Sn and Au are suggestive of intermixing. The expected CS for the Au 4f_{7/2} spectral line upon Au-Sn alloy formation is 0.45 - 1.1 eV¹⁶, while for the Sn 3d_{5/2} spectral line the expected CS is 0.1 - 0.4 eV. The Sn 3d_{5/2} spectral line after etching with H⁺ was measured to be 485.29 eV, a CS of 0.34 eV, while the Au 4f_{7/2} spectral line shifts from 84.06 eV to 84.6 eV (0.4 eV). These results are consistent with intermixing.

Two notable exceptions from the second group are carbon and boron. It is known from the literature that carbon can be successfully etched from silicon using hydrogen reactive species.^{17, 18} Thus, because the Sn layer grows in islands³, hydrogen radicals also have access to the underlying carbon surface before the Sn is completely removed. An XPS analysis of a carbon sample before and after Sn deposition and etching confirmed that the carbon layer thickness was reduced by approximately 25 % during Sn etching. As a result, the etching process may remove carbon from around the Sn, allowing the Sn to also be etched. It is also possible that hydrogen radicals may react to create more complex organo-metallic volatiles, which effectively allows Sn to be etched together with carbon.

Boron can be etched by hydrogen radicals, but only at elevated temperatures.¹⁹ XPS analysis confirmed that boron was not etched during hydrogen radical exposure, eliminating both the possibility of boron hydride formation and of volatile metallo-complexes. This illustrates that, although electronegativity is generally predictive (especially for the first group), detailed electronic structure also plays a role.

Our results show that the etch rate, near the interface between two materials, can be suppressed or enhanced, depending on the electronegativity difference. The suppression is sometimes sufficient to prevent the last few nanometers of material from

being etched, as seen in Figure 2-4. It should be noted that, for Ag and Ru this certainly includes Sn that is not in direct contact with the surface material.

Figure 2-4. Remaining Sn after etching with hydrogen radicals as a function of difference in electronegativity between Sn and the surface material.

2.4. Discussion

During etching, an electron must be donated for hydrogen to form a stable bond. However, for Sn, bound to a highly electronegative surface, the valence electrons have probably been donated to surrounding atoms, making it impossible for Sn hydride to form.

Electronegativity also explains why the remaining thickness of Sn increases as the electronegativity difference becomes more negative. Analogous to the case for oxides,²⁰ the effective electronegativity of Sn at the interface is increased when it binds to a strongly electronegative surface (and, likewise, decreased when it binds to a weakly electronegative surface). Thus, the first monolayer of Sn donates its electrons, which are delocalized and are more likely to be found in the surface material. In doing so, the

monolayer of Sn becomes more electronegative because it is now electron poor. However, it is not as electronegative as the original surface. Similarly, the second monolayer of Sn donates electrons to the first Sn layer, becoming slightly more electronegative. This process continues, until, at some layer thickness, the electronegativity of the uppermost Sn returns to its natural value. For Ru and Ag, where XPS confirms that there is minimal intermixing, this screening length is indicated by the thickness of the remaining Sn (4.1 and 2.3 nm), while for Au, it is likely that a similar screening length is present, however, intermixing precludes quantification.

2.5. Conclusions

The remaining amount of Sn after etching with hydrogen radicals depends on the substrate onto which Sn was deposited. Transition metals with electronegativity values that are lower than or equal to Sn ($\chi_{\text{Sn}} - \chi_{\text{M}} \geq 0$) can be fully etched from Sn. The remaining Sn thickness is found to be less than 0.08 nm on Sc, Ta, Ti, Nb, V, Cr, Al, and Si surfaces.

Incomplete Sn etching was observed when Sn was initially deposited onto materials with an electronegativity value higher than that of Sn ($\chi_{\text{Sn}} - \chi_{\text{M}} < 0$). Moreover, the thickness of the remaining Sn increases with more negative electronegativity differences. This indicates that, not only is Sn bound more strongly to the underlying surface material, but, near the interface, the Sn - Sn bonds are stronger than those found in bulk Sn.

It is known that, even though electrons are delocalized in a metal bond, the continuity of the Fermi level requires that the energy levels and occupancy of the electronic states changes within a few nanometers of the interface. These changes make the Sn surface (when it is within a few nanometers of the surface material) less reactive and more difficult to etch, and can even prevent etching

all together. This raises an interesting new approach to surface passivation that warrants further investigation.

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Chapter 3

Tin etching from metallic and oxidized Scandium thin films

The role of oxide on Sn adhesion to Sc surfaces was studied with in-situ ellipsometry, X-ray photoelectron spectroscopy and secondary electron microscopy. Sn etching with hydrogen radicals was performed on metallic Sc, metallic Sc with a native oxide, and a fully oxidized Sc layer. The results show that Sn adsorbs rather weakly to a non-oxidized Sc surface, and is etched relatively easily by atomic hydrogen. In contrast, the presence of native oxide on Sc allows Sn to adsorb more strongly to the surface, slowing the etching. Furthermore, thinner layers of scandium oxide result in weaker Sn adsorption, indicating that the layer beneath the oxide plays a significant role in determining the adsorption strength. Unexpectedly, for Sn on Sc_2O_3 , and, to a lesser extent, for Sn on Sc, the etch rate shows a variation over time, which is explained by surface restructuring, temperature change, and hydrogen adsorption saturation.

3.1. Introduction

In previous work, it was demonstrated that the formation of stannane (SnH_4), and, as a result, the successful etching of tin (Sn) from a metallic surface could be predicted by the electronegativity (χ) difference between the surface material and tin.¹ Sn can be successfully etched from surfaces consisting of metals with electronegativity values lower than or equal to Sn. Incomplete Sn etching was predicted for metals that have electronegativity values

higher than that of Sn.¹ However, in that publication, all metals, except gold and silver were strongly oxidized (the presence of oxide on Ag could not be determined). Notably, metals with high electronegativities form weak oxides, while those with low electronegativity form strong oxides (e.g., scandium and aluminium), leaving open the question of the role of oxidation in tin adhesion.

Although in many conditions a metallic surface is oxidized, this is not universally true. In some cases, the native oxide layer can be removed by hydrogen reactive species, changing the surface properties.² Furthermore, in many applications, such as extreme ultraviolet lithography (EUVL), space applications, and ultra-high vacuum (UHV) science, the environmental conditions may be sufficiently reducing, removing, at least temporarily, the surface oxide, and exposing the bare metal to surface processes.^{2, 3}

It is known that the presence of oxide on EUVL optics causes a reduction of reflectivity^{2, 4}, thus optics with oxide-free surfaces would be beneficial in terms of optical performance. Because of the difficulties in preparing oxide-free metallic surfaces, there is limited published data on tin adsorption to non-noble, oxide free metal surfaces. To our knowledge, the role of oxide in tin etching from oxidized metals has only been studied in the context of molybdenum (Mo) and silicon (Si)⁵, which have the same electronegativity as tin. However, it is unclear if Mo or Si are representative for low electronegativity materials. Furthermore, Mo oxide has a relatively low dissociation temperature⁶, making it more likely that the etch process (and perhaps even the tin deposition process) will result in the reduction of the top layer of molybdenum oxide.⁷⁻¹² Of the transition metals, scandium (Sc) has the lowest electronegativity, representing a relatively extreme case, and making it an ideal test case. By studying Sn adsorption and etching from Sc, and combining that with already published data on noble metals and Mo, it will be possible to conclude if the

electronegativity difference is indeed the main predictor of the energy of adhesion between tin and the surface. Furthermore, by comparing etching from oxidized and metallic surfaces, it will be possible to determine if the oxide layer plays a significant role in Sn adhesion.

Previous surface adhesion and etching studies have used X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and ellipsometry, which, taken together, give a very good overview of the surface chemistry and morphology changes during various experiments.¹³⁻²⁰ Of these, ellipsometry measurements, combined with modeling, provide layer thickness and material properties, making it an excellent tool for contact free determination of thickness and optical constants of films of all kinds.²¹⁻²⁶ Ellipsometry can yield information about layers even down to a single atomic layer²¹, moreover, no reference measurement is necessary. Ellipsometry measurements are also very fast, providing high resolution temporal data. In situ XPS, on the other hand, has elemental sensitivities in the parts per thousand range, and is often directly sensitive to the average chemical changes in the top ~5-10 nm of the surface layer, limited by the escape depth of the photoelectrons¹⁵⁻²⁰. However, XPS scans take much longer, limiting the temporal resolution of dynamic measurements. Moreover, XPS requires high vacuum (10^{-8} mbar) or ultra-high vacuum, making it inappropriate for in situ measurements due to the relatively high pressure during etching. XRF has even higher elemental sensitivity than XPS, but no chemical sensitivity and cannot distinguish between surface and buried elements. Thus, in our study we use in situ ellipsometry to study Sn deposition and etching. XPS and SEM were used for ex situ analysis. In this paper we study the role of native scandium oxide on the adhesion between Sn and Sc.

3.2. Experimental

Three types of samples, each of 1x1 cm size, were prepared: 20 nm Sc, 3 nm and 5 nm $\text{Sc}_2\text{O}_3/\text{Sc}$ Sc_2O_3 (see Figure 3-1(a), (b) and (c) for details). Scandium oxidizes very rapidly in ambient conditions, creating a native oxide layer. To prevent Sc from oxidizing during deposition and sample handling, the Si wafer substrates were covered with 5 nm of amorphous Si to protect the deposited Sc layer from oxidizing via interaction with the native SiO_2 layer on the Si wafer. After the Sc layer was deposited, it was protected from oxidation with a 5 nm thick amorphous carbon (C) layer. It is known that C can be etched from many surfaces with reactive hydrogen species^{21, 27-29}, thus the C layer is removed in-situ before Sn is deposited on top of this sample (see Figure 3-1(a)). For the 5 nm $\text{Sc}_2\text{O}_3/\text{Sc}$ and 3 nm Sc_2O_3 samples, Sc was deposited directly on the Si wafer, which had a native oxide layer of approximately 1.3 nm.¹ To obtain a Sc_2O_3 top surface, these samples were exposed to ambient, letting a native oxide layer to form. After deposition, the samples were characterized with angle resolved (AR) XPS.

Figure 3-1. Composition of the samples used in this work: (a) 20 nm Sc, (b) 3 nm Sc_2O_3 , (c) 5 nm $\text{Sc}_2\text{O}_3/\text{Sc}$.

Tin deposition and etching takes place in an apparatus that has been described in detail elsewhere.¹ Briefly, experiments are performed in two different manners: for oxidized samples, approximately 8 nm of Sn is evaporated onto the sample at a rate of 0.4 nm/min and, immediately afterwards, etched with hydrogen radicals ($\text{H}^\cdot$). For the metallic Sc sample, the C coating is first

removed (determined by ellipsometry) using $H^{\cdot}$ etching, after which, 8 nm of Sn is deposited, followed by $H^{\cdot}$ etching. In all cases, the $H^{\cdot}$ flux is generated by passing a molecular hydrogen flow (100 sccm) over a tungsten (W) filament that is heated to 2000 °C. The hydrogen radical flux that was measured to be 10^{17} at /s·cm² at the sample surface, which was obtained from the carbon etching rate following the method used in ref. 14. The filament was operated in 5 min cycles to avoid excessively heating of the sample surface. In situ ellipsometry was used to monitor Sn deposition and etching. After Sn deposition and etching experiments, the samples were analyzed ex situ with XPS, as well as SEM with energy selective backscatter detector (SEM-ESB) and high efficiency secondary electron detector (SEM HE-SE2).

3.3. Results

3.3.1. XPS analysis

Keeping the Sc layer of the 20 nm Sc sample type free of native oxide is crucial, thus, directly after deposition, a sample was analyzed by XPS with sputter depth profiling. From the elemental depth profile, presented in Figure 3-2, it can be seen that the Sc layer is not completely oxygen free. However, the ratio of O to Sc in the layer is about 3:20, which is considerably less than the stoichiometric ratio for Sc₂O₃. To verify that the carbon layer prevented oxidation, a sample was kept in ambient for 2 months. Subsequent XPS measurements showed that the ratio of O to Sc did not change in that time.

AR XPS analysis of the as-deposited 5 nm Sc₂O₃/Sc and 3 nm of Sc₂O₃ samples were performed to determine the depth of oxidation of the Sc layers. The fit for the thicknesses of the oxide layers was found to have an uncertainty smaller than 0.1 nm. In the case of 3 nm Sc₂O₃, the deposited Sc was almost fully oxidized, with less than 0.5 nm of metallic Sc remaining. For the 5 nm Sc₂O₃/Sc

sample, the native oxide thickness was found to be 3.6 nm, in agreement with previous work ¹, while the remaining 1.7 nm was elemental Sc. In both cases, the fit to the AR-XPS data indicates that there is some intermixing between Sc and Si. This intermixing may also explain the remaining metallic scandium found in the 3 nm Sc₂O₃ sample, since it was expected that the Sc layer would be fully oxidized in this case. Moreover, the surfaces of both samples were found to have a small amount of carbon and carbonate species due to exposure to ambient.

Figure 3-2. Sputter depth profile of as deposited 20 nm Sc sample.

The protective layer of carbon on 20 nm Sc sample type was removed directly before Sn deposition and etching experiments. After in-situ ellipsometry monitoring of C removal (see details below) the sample was measured ex-situ with XPS (see Figure 3-3).

Figure 3-3. XPS analysis: atomic % of different carbon species on the as-deposited sample and after carbon etching, for a 20 nm Sc sample. As deposited carbon corresponds to magnetron sputtered carbon, while the carbon detected after etching is consistent with carbon that is deposited during sample handling and exposure to ambient.

The carbon layer, which was deposited with magnetron sputtering, is characterized by a high percentage of amorphous C, dominated by sp^2 and sp^3 bonding. In contrast, the C found on the etched sample has mostly sp^3 bonded carbon and a small amount of carbonate, indicating that it is from a different source. The former is typical for magnetron deposited amorphous carbon, while the latter is consistent with atmospheric carbon contamination. From this, and the relative peak intensities of the underlying material, we conclude that the amorphous C was completely etched by H⁺ before the Sn was deposited.

3.3.2. Sn deposition and etching measured with in-situ ellipsometry

The in situ ellipsometry time-series data for Sn deposition and etching from the 20 nm Sc sample are shown in Figure 3-4. The different stages of etching and deposition are indicated by different colors for the delta value, taken at a wavelength of 513 nm. Carbon etching is indicated by a black solid line, Sn deposition by a blue dashed line, and Sn etching by a red solid line. The five minute duty cycle of the H^+ generator is visible during the C etching. After approximately 115 minutes of C etching, the delta value is constant, indicating that C etching is complete. The success of C etching was confirmed by ex situ XPS measurements (see above). Following C etching, 8 nm of Sn was deposited on the surface (see blue dashed line, Figure 3-4). Afterwards, the sample was again exposed to H^+ (in 5 minutes cycles) to etch the Sn (see red solid line in Figure 3-4). After two cycles of 5 min, the value of delta returns to that of metallic Sc, which suggests complete Sn etching. An XPS analysis, performed after Sn etching, failed to detect any Sn, indicating that the amount of remaining Sn is below the sensitivity of our XPS analysis (<0.2 at.%).

The Sc_2O_3 terminated samples were directly covered with approximately 8 nm of Sn and afterwards exposed to H^+ . Similar to the case for 20 nm Sc sample, the ellipsometry time-series data (see Figure 3-5) show that Sn is completely removed. Delta values return to a slightly higher value (indicated on the Figure 3-5 as a dashed lines for each sample) than before Sn deposition due to removal of surface contamination. However, the etch rate of Sc_2O_3 terminated samples is much slower than 20 nm Sc sample, as can be seen by the total etch time. Furthermore, the etch rate for the 5 nm Sc_2O_3 /Sc sample is slower than for 3 nm Sc_2O_3 . The different etch behavior for each of the three sample types is discussed in section 3-4 discussion.

Figure 3-4. Delta value at 513 nm from in situ ellipsometry measurement during carbon etching, Sn deposition and Sn etching on 20 nm Sc sample type.

On closer inspection, it can be seen that the etch rate changes substantially during etching. To highlight this, we use the change in delta with time to estimate the etch rate. In this thickness range, the changes in delta are nearly linear with Sn thickness, thus, the change in slope provides a direct measure of the change in etch rate, which is presented in Figure 3-6. Delta value changes, corresponding to the deposition of 1 nm Sn on the sample, were calculated to be 6.6° , 6.5° and 4.9° for 3 nm Sc_2O_3 , 5 nm $\text{Sc}_2\text{O}_3/\text{Sc}$ and 20 nm Sc, respectively. In Figure 3-6, Delta values corresponding to the moments the filament was off have been removed.

Figure 3-5. Delta value at 513 nm from in-situ ellipsometry measurement during experiments for 20 nm Sc, 3 nm Sc_2O_3 and 5 nm $\text{Sc}/\text{Sc}_2\text{O}_3$ sample types.

The etching rate changes over the whole etching process, as well as over a single 5 min cycle. The 20 nm Sc sample has the highest average Sn etching rate at 0.82 nm/min, while Sc_2O_3 terminated samples have a lower average etching rate, which was calculated to be 0.31 nm/min for 3 nm of Sc_2O_3 , and 0.19 nm/min for 5 nm $\text{Sc}_2\text{O}_3/\text{Sc}$.

We speculate that these findings may be qualitatively explained as follows. Initially, the etch rate increases with time, which may be due to an increase of the Sn surface area. The presence of the Sc under layer (in 5 nm $\text{Sc}_2\text{O}_3/\text{Sc}$ sample) does not influence early etching, but does influence the early stages of Sn deposition. As a result, the three samples may have different initial Sn surface areas and, consequently, different etch rates. For all the samples, the maximum etch rate appears after more than half of the initial Sn thickness has been etched. As expected, at late etch times, the etch rate falls simply because the small amount of Sn remaining on the

surface, and the etch rate is proportional to the surface coverage of Sn.

Figure 3-6. Tin etching rate for Sc, 5 nm Sc/Sc₂O₃, and 3 nm of Sc₂O₃ samples. The dashed lines represents the step between the 5 min etching cycles.

The decay in the etch rate over a single 5 minute period is most likely due to the temperature change of the sample. Sporre *et al.* showed that sample temperature has significant influence on the etch rate for temperatures over 60 °C.³⁰ Likewise, it is expected from the modeling in ref. 31 that the etch rate rapidly decreases with increasing temperature, but that the onset of the decrease begins at a lower temperature.³¹ Higher temperatures decrease the residence time of hydrogen at the surface, thus the surface coverage is lower and, therefore, the etch rate goes down. Apart from the first etch cycle, which begins at room temperature, the temperature of the sample increases over a 5 min period from approximately 30 to 60 °C. The 30 °C temperature change in this temperature range can cause a decrease in the etching rate of up to 30 %³¹, which approximately fits the changes in etch rate that are observed during a single etch cycle. The temperature

dependence does not significantly influence Sn etching from the Sc terminated sample, since the etching process is very rapid and most of the deposited Sn is removed in a single etch cycle.

After Sn deposition and etching experiments, the sample surfaces were analyzed with SEM HE-SE2 and SEM-ESB. For all samples, after Sn deposition and etching, the surface is uniform and free of any features. SEM-ESB analysis shows that there are no traces of Sn, confirming the ellipsometry and XPS analysis.

3.4. Discussion

Even though complete Sn etching is achieved on all three samples, the etch rate is significantly slower for a thin scandium oxide layer, and even slower for a Sc oxide terminated scandium layer. It is postulated here that the differences in etch rate are due to the differences in electron distribution in the different systems.

The fastest etching rate was observed for the 20 nm metallic Sc sample. In this case the top outer-most layers consists of two metals, Sn and Sc, thus there is only a small barrier for electron transfer (contact potential of 0.85 eV³², due to the metal-metal junction). When Sn is deposited, on a metallic Sc surface, electrons will be shared between those two metals. The more electronegative element attracts electrons to itself, which, in our case, is Sn ($\chi_{\text{Sn}}=1.8$, $\chi_{\text{Sc}}=1.3$)¹. When reactive hydrogen species arrive at the surface, the Sn can easily form SnH_4 , and Sn etching proceeds at a rate limited only by the accessibility of Sn to hydrogen radicals.

The situation changes when the Sc layer is oxidized. Due to the manner in which the scandium was oxidized, the oxide layer is likely to have a relatively large number of defect states in the bandgap that can accept electrons.³³⁻³⁵ Electrons from the Sn layer diffuse via tunneling to these defect states, taking into account that the reaction of atomic H at the surface can generate hot electrons with energies in the eV range.³⁶ The defect states effectively trap

electrons in the scandium oxide, slowing their return to the Sn layer, and slowing the Sn etch rate from 3 nm Sc_2O_3 sample in comparison to 20 nm Sc sample.

Although the etch rate of both samples with Sc_2O_3 is slower than the case for metallic Sc, it can be clearly seen that there is also a significant difference between 3 nm Sc_2O_3 and 5 nm $\text{Sc}_2\text{O}_3/\text{Sc}$ samples. In the case of a Sc_2O_3 layer, separating Sn and Sc (5 nm $\text{Sc}_2\text{O}_3/\text{Sc}$), the electrons that diffuse into the defects in the oxide layer may end up in states that are above the equilibrium Fermi level, may decay to a lower energetic state by tunneling into the Sc layer. In this way, the metallic Sc acts as a reservoir for electrons, while tunneling back to the Sn layer must either occur directly, or via defect states. Low lying defect states must first be vacated by Sn etching before they can accept electrons from Sc, while high lying states are energetically unfavorable. Furthermore, the difference in work functions between Sn and Sc creates a driving potential that favors the diffusion of electrons from Sn to Sc, which can be clarified by treating this structure as a metal-insulator-metal tunnel device (MIM) (see Figure 3-7 (b)). MIMs consist of a sandwich with a metal back electrode, an insulating oxide layer and metal top layer. The thin insulator layer (of a few nanometers) acts as high-pass filter for carrier transport.³⁷⁻³⁹ Although the transport is hindered or suppressed through the band gap of an insulator, (hot) electrons and holes may tunnel through the oxide barrier due to its small thickness and presence of local states in the band gap.³⁹ Tunneling from a metal through a thin insulator to metal has been extensively studied for different material compositions.³⁷⁻⁴¹ The difference in schematic band diagrams for 20 nm Sc, 3 nm Sc_2O_3 and 5 nm $\text{Sc}_2\text{O}_3/\text{Sc}$ samples is presented in Figure 3-7 (a), (b) and (c). For drawing those diagrams, we used work function values for Si, Sc and Sn of 4.85 eV, 3.5 eV and 4.35 eV, respectively⁴², while electron affinities were taken to be equal to 0.9 eV for SiO_2 ⁴³, and 0.85 eV for Sc_2O_3 ⁴⁴. Band gaps for Sc_2O_3 , SiO_2 and Si are: 6.3 eV⁴⁵,

9 eV⁴⁶ and 1.11 eV⁴⁷, respectively. The values of work function, electron affinities and band gaps are indicated on a relative scale on the diagrams below.

a)

b)

c)

Figure 3-7. Energy band diagram over the layers for tested samples: (a) 20 nm Sc, (b) 3 nm Sc_2O_3 , (c) 5 nm $\text{Sc}_2\text{O}_3/\text{Sc}$.

The work function difference between Sc and Sn leads to a built-in electric field over the Sc_2O_3 layer that makes tunnelling from Sc to Sn less favourable than the reverse. Electrons that tunnel through the oxide barrier must return when Sn is etched from the surface, thus the existence of the barrier still allows to etch Sn but at the same time significantly slows down the etch rate in comparison to 3 nm Sc_2O_3 and 20 nm Sc samples.

3.5. Conclusions

In conclusion, we have shown that tin can be fully etched from a metallic Sc surface as predicted by Pachecka et al. ¹, as well from Sc thin films with complete and incomplete oxidation. Furthermore, our results show that the presence of Sc_2O_3 on a Sc thin film significantly slows the etch rate. The etch rate was found to change during the whole etch process, as well as over individual five minutes cycles. Changes in the surface area of the Sn layer (in between etch cycles) may account for rate changes between etch cycles, while temperature increases and possible saturation of the surface with hydrogen probably account for changes during an etch cycle. For Sn etching from oxidized Sc, trapping of electrons in defects of the Sc_2O_3 layer lowers the etching rate compared to metallic Sc surface. This effect is strengthened when Sc metal is present below the Sc_2O_3 , due to the built-in electric field over the oxide generated by the difference in work function between Sc and Sn.

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Chapter 4

Metal diffusion properties of ultra-thin high-k Sc_2O_3 films

The diffusion barrier properties of Sc_2O_3 against metal diffusion were studied. Tin and ruthenium were used as probe materials to study the barrier properties of Sc_2O_3 in thickness ranges that are of relevance for gate materials. Tin deposition and hydrogen radical etching from Sc_2O_3 layers of 0.5-1.5 nm thickness, deposited on Ru, show that these Sc_2O_3 layers effectively block the diffusion of Sn into Ru. We show that Sn adhesion and etching depends strongly on the thickness of the Sc_2O_3 film. The etch-rate is found to be inversely proportional to the Sc_2O_3 layer thickness, which we attribute to Sc_2O_3 becoming a more effective charge transfer barrier at larger thicknesses.

4.1. Introduction

Group III based dielectrics, such as scandium oxide (Sc_2O_3)¹ and rare earth scandates ² e.g. LaScO_3 have been studied as possible candidates for high-k dielectric applications, due to their possession of a suitably large optical band gap (5-6 eV). Moreover, Sc_2O_3 has a high dielectric constant ($\epsilon = 13$) in comparison to SiO_2 ($\epsilon = 4.5$).³ Scandium oxide, doped with lanthanum, has been investigated as a high-k gate material for silicon-based integrated circuits.⁴ However, much of the interest in Sc_2O_3 has been in applications in AlGaIn/GaN devices. Devices, based on AlGaIn/GaN without passivation, show significant gate lag effects due to the presence of surface states in the region between the gate and drain

contact. Moreover due to large polarization induced field and large conduction band offset, high current density can be achieved with AlGaIn/GaN heterostructures. Scandium oxide has attractive band gap and thermal lattice properties for use on GaN.⁵ A Sc_2O_3 layer was shown to effectively mitigate the collapse in drain current through passivation of the surface traps.⁵⁻⁶ Additionally, it was demonstrated that Sc_2O_3 can be used simultaneously as a gate oxide and as a surface passivation layer for AlGaIn/GaN high electron mobility transistors.⁷

However, the gate oxide material must satisfy several criteria: in addition to the electronic function of a gate dielectric, the gate oxide material must maintain a high dielectric constant, and serve as a diffusion barrier against diffusion of material from the top electrode. Furthermore, the gate dielectric must be as thin as possible, so a high resistance to diffusion is critical. Thus, in addition to the electronic properties of the gate, it is also of importance to understand the Sc_2O_3 diffusion-barrier behavior. The thermal stability of the high-k dielectric material is also of importance, thus, a dielectric material should show good thermal stability, at least at the processing temperatures of the device, and have a low coefficient of thermal expansion.^{4, 8-9}

In order to carry out diffusion studies, we use tin (Sn), a highly mobile metallic probe atom, to test if Sc_2O_3 layers of various thicknesses act as a diffusion barrier. Although Sn is not relevant for high-k dielectric applications we used it due to the fact that Sn has the advantage of forming a volatile hydride, which allows it to be removed from surfaces with hydrogen reactive species.¹⁰ Tin intermixes and/or binds strongly with highly electronegative materials, such as ruthenium (Ru), gold (Au), and silver (Ag). Furthermore, it has been shown that Sn, after it diffuses into the aforementioned materials cannot be etched by atomic hydrogen¹¹⁻¹³, while Sn deposited onto Sc_2O_3 can be completely removed with atomic hydrogen.¹⁴ In this work, we study Sc_2O_3 barriers

deposited on top of highly electronegative Ru surfaces, with in situ ellipsometry. The deposition and etching results are understood in the context of a metal-insulator-metal tunnel device.

4.2. Experimental

Ruthenium and scandium were deposited by direct current (DC) magnetron sputtering from targets with 99.95 % and 99.5 % purity, respectively. First, 4 nm of Ru was deposited onto a silicon wafer. On top of Ru, thin layers of scandium (Sc) with thicknesses of 0.5, 1, and 1.5 nm were deposited (see Table 4-1). An additional sample with 4 nm of Ru, deposited on a silicon wafer, was used as a reference for analysis with low-energy ion scattering spectroscopy (LEIS) measurements (see below). Deposition was performed in a vacuum chamber with a base pressure of $3 \cdot 10^{-8}$ mbar and a temperature of 22 °C inside the chamber. Samples were placed approximately 30 cm from the magnetron. The magnetron current during deposition was 1 A while magnetron voltage was 460 V and 410 V for Ru and Sc deposition, respectively. Argon pressure during sputtering was measured to be $7 \cdot 10^{-4}$ mbar during Ru deposition and $6 \cdot 10^{-4}$ mbar during Sc deposition. The deposition rates for Ru and Sc were 0.169 and 0.166 nm/s, respectively.

Table 4-1. Material and thicknesses composition of the samples. All materials were deposited on silicon wafer substrates.

Material [nm]	Sample name		
	0.5Sc ₂ O ₃ /Ru	1Sc ₂ O ₃ /Ru	1.5Sc ₂ O ₃ /Ru
Sc	0.5	1	1.5
Ru	4	4	4

For many materials, oxidation of the layer is usually self-limiting at atmospheric pressure and room temperature, resulting in a so-called native oxide layer with a thickness of few nanometers at most. It was reported that 5.5 nm Sc, deposited on a silicon wafer, has a native oxide thickness of 3.6 nm, while 3 nm of Sc is fully

oxidized.^{11, 14} Thus, Sc layers with a thickness below 3 nm can be expected to fully oxidize when exposed to ambient. However, to test thinner layers, the oxide layer should be terminated. Hence the Sc was deposited on Ru, a noble metal. Ruthenium does not oxidize easily, thus allowing a sharp interface between Ru and Sc native oxide to be created.

After deposition, all the samples were removed from the chamber and exposed to ambient conditions to form Sc_2O_3 layers. The properties of the deposited layers were then analyzed with LEIS, and x-ray photoelectron spectroscopy (XPS). Tin deposition and etching experiments were performed in an apparatus that has been described in detail elsewhere.¹¹ Tin (Umicore) with a bulk density of 7.3 g/cm^3 and purity of 99.9 % was evaporated from an Effusion Cell EF 40C1 (PREVAC) evaporator operated at 980°C . The Sn deposition rate was calibrated using a quartz microbalance (INFICON XTM/2 Deposition Monitor). It was found that the evaporation rate as measured using the quartz microbalance (QMB) at 980°C was approximately 0.4 nm/min . Approximately 8 nm of tin was evaporated onto the sample and, immediately afterwards, etched with hydrogen radicals ($\text{H}^\cdot$). The $\text{H}^\cdot$ flux is generated by passing a molecular hydrogen flow (100 sccm) over a tungsten (W) filament that is heated to 2000°C . The hydrogen radical flux was calculated to be $10^{17} \text{ /s}\cdot\text{cm}^2$ at the sample surface from the measured carbon etching rate, following the method used in ref. 15. The temperature of the sample was monitored using a Pt-100 temperature sensor, mounted on the backside of the sample. During hydrogen etching, the filament was operated in 5 min cycles to avoid excessive sample heating. As a result, the temperature modulations were less than 25°C , and the maximum sensor temperature was always below 55°C . Thus, the surface temperature is unlikely to be more than $(55+5)^\circ\text{C}$ than the sensor temperature. During Sn deposition and etching, the sample was monitored with in situ ellipsometry. After the Sn deposition

and etching experiments, the samples were analyzed ex situ with XPS.

4.3. Results and discussion

4.3.1. As deposited sample analysis –LEIS

To ensure that the Sc_2O_3 layer forms a closed film, several samples were analyzed with LEIS. To remove surface contaminants, the samples were sputtered with a dose of $4 \cdot 10^{15}$ 3 keV He^+ ions/ cm^2 before analysis. The LEIS spectra after sputtering are presented in Figure 4-1.

It can be seen that, even after mild sputtering of the surface contaminants, the only species present on the surface are Sc and O. No surface Ru was detected for any of the Sc layer thicknesses. This confirms that the prepared Sc native oxide thin layers are uniform and closed layers, thus allowing the oxide layers barrier properties to be studied.

For the different Sc_2O_3 thicknesses, there is a significant difference in the so-called tail signal from sub-surface Ru (especially in the energy range around 2100-2400 eV) . This tail signal results from He ions that penetrate the sample (upon which they are neutralized), backscatter on sub-surface Ru atoms in the direction of the detector and are reionized when leaving the sample, such that they can be detected with the electrostatic analyzer. Due to stopping of ions in the sample, scattering on a Ru atom deeper inside the sample contributes to the tail signal at lower energy relative to the surface peak. The tail signal thus provides a depth profile of Ru in the sample.¹⁶

Figure 4-1. LEIS measurements after mild He sputtering for $0.5\text{Sc}_2\text{O}_3/\text{Ru}$ (blue solid line), $1\text{Sc}_2\text{O}_3/\text{Ru}$ (red solid line) and $1.5\text{Sc}_2\text{O}_3/\text{Ru}$ (black solid line). The dashed line is 4 nm Ru on a silicon wafer, shown as a reference (after the same cleaning step).

For comparison a typical LEIS spectrum for Ru is also presented in Figure 4-1 as a black dashed line. For 0.5 nm Sc, the thinnest oxide studied, the high energy on-set of the tail signal from sub-surface Ru corresponds to the energy of the Ru surface peak (labelled as Ru) of the Ru reference, which indicates that the Sc_2O_3 layer formed is only just closed, and that Ru is present from the 2nd atomic layer. For thicker Sc_2O_3 layers, the tail and its onset shift to lower energies, which indicates that Ru is covered by a Sc_2O_3 layer free of Ru. Hence, we can conclude that the interface between the Ru and Sc_2O_3 is rather sharp.

From the LEIS measurements, the final thickness values of the Sc_2O_3 layers were obtained, following the procedure described in ref. 16, using an effective stopping value for 3 keV He^+ ions in Sc_2O_3 of 151 eV/nm film thickness extracted from SRIM software.¹⁷ The thicknesses of the top layer differ slightly from the target layer thicknesses. The measured thicknesses of the Sc_2O_3 layers of

0.5Sc₂O₃/Ru, 1Sc₂O₃/Ru and 1.5Sc₂O₃ sample were calculated to be 0.71 nm, 1.10 nm and 1.56 nm, respectively, corresponding to a minor swelling of the nominal thicknesses deposited, due to oxidation.

4.3.2. Tin deposition and etching – in situ ellipsometry results

During Sn deposition and etching experiments there is no exposure to ambient, and the etching experiments were performed less than 1 hour after Sn deposition, thus no Sn oxidation is expected. The ellipsometry Delta value at 513 nm is shown for all the samples in Figure 4-2. Tin deposition starts at 5 minutes, and finishes at 25 minutes, corresponding to a Sn layer that is ~8 nm thick. Afterwards, Sn is etched, starting from 25 minutes, using hydrogen radicals. Etching is performed with the filament operated in 5 minutes cycles to maintain the sample below 55°C. After etching is complete, Delta returns to its original value (apart from a small offset due to the removal of carbon contamination), indicating that Sn does not diffuse through the Sc₂O₃ layer. Remarkably, this is also true for the thinnest Sc₂O₃ layer. The deposited Sn is fully removed from all tested samples, which was confirmed with the XPS measurements. This can be compared to Sn etching experiments on Ru, where the remaining thickness of Sn was reported to be 4.1 nm.¹¹

It can be seen that the total etching time increases with increasing Sc₂O₃ thickness. The Sn etching time as a function of Sc₂O₃ thickness is presented in Figure 4-3.

Figure 4-2. Delta value for 513 nm during Sn deposition and Sn etching. Deposition starts at 5 min and finishes at 25 min. H⁺ etching starts at 25 min and proceeds in 5 minutes cycles with the filament ON (solid line) and OFF (dotted line).

The etch-rate is inversely proportional to the Sc₂O₃ layer thickness. Moreover, with increasing Sc₂O₃ thickness, the etching time converges to the value found for bulk Sc₂O₃, which is presented in Figure 4-3 as the point at 3 nm Sc₂O₃ (obtained from ref. 14). It should be noted that, for this point, the Sc was deposited on a silicon wafer and full oxidation of the layer was achieved.¹⁴ For etching to be successful, tin hydride must be formed, and charge transfer from the Ru layer to the Sn layer must occur. Hot electrons are generated when atomic hydrogen reacts with Sn, and these may tunnel through the oxide barrier, or get trapped in defect states in the oxide. The tunneling rate depends on the thickness of the Sc₂O₃ layer, and the potential difference between the work functions. Thus, the contribution of tunnelling to the etch rate may be estimated (see below).

Figure 4-3. Sn etching time (time when filament was OFF is excluded) as a function of Sc₂O₃ thickness on top of Ru. The point with 3 nm Sc₂O₃ is taken from ref. 14. For this point, the Sc is deposited on a silicon wafer.

4.3.3. Binding energy of Sn to Sc₂O₃

The binding between Sn and Sc₂O₃ can be understood in terms of charge transfer between the Ru and Sn layers. In this model, the Ru/Sc₂O₃/Sn structure acts as a metal-insulator-metal tunnel device (MIM) and we can compare the Sn etch rate from the tested samples. MIMs consist of a metal back electrode, an insulating oxide layer and metal top layer. The thin insulator layer acts as high-pass filter for carrier transport.¹⁸⁻²⁰ Charge transport is limited by the band gap of the insulator, but the small thickness of the oxide layer, and the presence of local defect states in the band gap allow (hot) electrons and holes to tunnel through the oxide barrier.²⁰ Tunneling from a metal through a thin insulator to another metal has been extensively studied for different material combinations.¹⁸⁻²² Noting that the Fermi level remains constant across the interfaces, schematic band diagrams for the different

thicknesses of Sc_2O_3 can be constructed (see Figure 4-4 (a), Figure 4-4 (b) and Figure 4-4 (c)). The work function values for Ru and Sn were taken to be 4.71 eV and 4.35 eV, respectively²³, while the electron affinity and band gap for Sc_2O_3 are reported to be 0.9 eV²⁴ and 6.3 eV.²⁵ The values of the work function, electron affinities and band gap are indicated on a relative scale on the diagrams below.

Figure 4-4. Energy band diagram over the layers for $0.5\text{Sc}_2\text{O}_3/\text{Ru}$ (a) $1\text{Sc}_2\text{O}_3/\text{Ru}$ (b), and $1.5\text{Sc}_2\text{O}_3/\text{Ru}$ (c).

The difference in work functions between Sn and Ru creates a driving potential that favors the diffusion of electrons from Ru to

Sn. The potential drop induces an electric field that varies from 0.51, 0.33 and 0.23 V/nm, depending on the Sc_2O_3 layer thickness. To estimate the relative tunnelling rates, we consider a plane wave solution to Schrödinger's equation, $\psi_{Ru} = A_1 e^{ik_1 x} + B_1 e^{-ik_1 x}$, for an electron traveling in the x direction in the Ru layer, orthogonal to the Ru/ Sc_2O_3 interface. Setting the potential of the Ru layer to zero leads to: $k_1^2 = K_e m_e / \hbar^2$, where K_e is the kinetic energy of the electron, m_e is the electron's mass, and $\hbar$ the reduced Planck's constant. The positive complex exponential represents the wave traveling towards the Sc_2O_3 barrier, while the negative complex exponential represents the reflected wave. In the Sc_2O_3 layer, the wave function is given by $\psi_{ScO} = A_2 e^{ik_2 x} + B_2 e^{-ik_2 x}$, where the electron's momentum is given by $k_2^2 = (K_e - V_a) m_e / \hbar^2$ and V_a is the height of the potential barrier at the Ru/ Sc_2O_3 interface. The positive complex exponential represents the transmitted wave function, while the negative complex exponential represents a wave traveling from the Sc_2O_3 into the Ru. In considering electron tunneling from Ru to Sn, we set $B_2 = 0$. To satisfy Schrödinger's equation both the wave function, and its first derivative must be continuous across the interface. This leads to the following expression for the transmitted and reflected amplitudes, A_2 and B_1 , respectively.

$$B_1 = A_1 \frac{ik_1 - k_{2r}}{k_{2r} + ik_1} \quad (4-1)$$

and

$$A_2 = A_1 \frac{i2k_1}{k_{2r} + ik_1} \quad (4-2)$$

where we have assumed that $V_a > K_e$ and k_{2r} indicates that the momentum should be evaluated at the Ru/ Sc_2O_3 interface.

Inside the Sc_2O_3 , the electron's momentum becomes complex, leading to an exponentially decaying wave function. As before, the wave function and its derivative should be continuous at the Sc_2O_3 /Sn barrier, giving:

$$B_{2s} = A_2 \frac{ik_1 - k_{2s}}{k_{2s} + ik_1} e^{-\bar{k}_2 t} \quad (4-3)$$

$$A_3 = A_2 \frac{i2k_1}{k_{2s} + ik_1} e^{-\bar{k}_2 t} \quad (4-4)$$

where B_{2s} is the reflection coefficient from the $\text{Sc}_2\text{O}_3/\text{Sn}$ interface, and k_{2s} is the electron momentum, evaluated at the $\text{Sc}_2\text{O}_3/\text{Sn}$ interface. The bar indicates that the average momentum in the Sc_2O_3 layer should be used. Furthermore, we have also assumed that the potential difference between the Sn layer and the Ru layer is the same as the work function difference between the two materials. From Equations 4-2 and 4-4 the amplitude of the electron wave function in the Sn layer can be estimated as:

$$A_3 = -\frac{4k_1^2 e^{-\bar{k}_2 t}}{(k_{2r} + ik_1)(k_{2s} + ik_1)} \quad (4-5)$$

while the transmission probability can be estimated as $1/(|A_3|^2)$, which is shown as a function of the layer thickness (Figure 4-5 (b)) for 1 eV electrons, and as a function of electron energy (Figure 4-5 (a)) for a barrier thickness of 0.7 nm. Note that for thermal electrons ($K_e \sim 0.025$ eV), the transmission probability is orders of magnitude lower than for electrons with an energy of 1 eV. This implies that the electron flux due to tunneling is negligible for thermal electrons.

In deriving equations 4-1 to 4-5, we have assumed that B_2 is negligible. We confirm this by combining equations 4-2 and 4-3 to calculate the probability density of the B_2 term, due to reflection from the $\text{Sc}_2\text{O}_3/\text{Sn}$ interface. For a layer thickness of 0.7 nm, B_2 is two orders of magnitude less than A_2 , indicating that tunneling due to reflected electrons is, indeed, negligible.

To estimate if tunneling is significant, the transmission probabilities in Figure 4-5 (a) and (b) should be compared to the total number of

electrons that need to traverse the barrier and the integrated atomic hydrogen flux. The number of Sn atoms (per unit surface area) is $3 \times 10^{16} \text{ cm}^{-2}$, thus, the total charge transfer per unit area is $9 \times 10^{16} \text{ cm}^{-2}$ (assuming SnH_3 is the dominant etch product). The atomic hydrogen dose is simply the fluence (flux integrated over the etch time), which varies from $7.5 \times 10^{17} \text{ cm}^{-2}$ to $2.1 \times 10^{20} \text{ cm}^{-2}$. Every hydrogen radical may excite a hot electron that tunnels across the barrier. According to ref. 20 these electrons have an energy smaller than 2 eV, thus, we consider the case of electrons with an energy of 1 eV. For the case of 1 eV electrons, the total expected tunneling charge per unit area ranges from $7.8 \times 10^{16} \text{ cm}^{-2}$ to $2.7 \times 10^{13} \text{ cm}^{-2}$, which, for the thinnest layer is comparable to the required charge transfer per unit area. Thus, using this data, tunneling between Sn and Ru predicts an etch time of 860 s compared to the measured 750 s, which is in good agreement. For thermal electrons, the maximum tunneling charge transfer per unit area is only $1.2 \times 10^{14} \text{ cm}^{-2}$ for the thinnest barrier, indicating that only hot electrons can contribute significantly to etching via tunneling.

Reversing the calculation above, we estimate in Figure 4-6 the contribution of charge transfer between the Sn and Ru layers to Sn etching. The tunneling contribution drops off very rapidly, leaving charge diffusion via defects as the dominant mechanism for most layer thicknesses. This explains the sensitivity for the change of the layer thickness in the etching process. Although the model can take the electron's effective mass into account by replacing m_e with the effective mass, there are, to our knowledge, no reported values of the effective mass of electrons in Sc_2O_3 or Ru. The tunneling probability is most sensitive to the effective mass of the Sc_2O_3 layer. For 1 eV electrons with effective masses down to 0.5, tunneling is still restricted to the thinnest layer (0.71 nm). However, for 1 eV electrons with effective masses ~ 0.1 , tunneling is efficient for thicknesses up to 1.5 nm.

a)

b)

Figure 4-5. Transmission probability as a function of energy of electrons tunneling from Ru to Sn for different Sc_2O_3 barrier thicknesses (a) and as a function of Sc_2O_3 layer thickness for 1 and 0.025 eV electrons (b).

Figure 4-6. Number of tunneling electrons per Sn atom as a function of Sc₂O₃ layer thickness.

4.4. Conclusions

Scandium oxide diffusion barrier properties were tested using a MIM structure, consisting of Ru, Sc₂O₃, and Sn. By depositing, and then etching the Sn layer, it was possible to determine if the Sn diffused through the Sc₂O₃ barrier layer. We observed complete Sn etching from 0.71, 1.1 and 1.56 nm of Sc₂O₃. This demonstrates that even 0.71 nm Sc₂O₃ forms a closed oxide layer that prevents the diffusion of Sn through to the Ru layer.

The Sn etching time was observed to depend on the Sc₂O₃ barrier thickness and increased with increasing Sc₂O₃ thickness. This is explained by the formation of a MIM junction between the Ru, Sc₂O₃ and Sn, where the built-in potential enhances diffusion of electrons from the Ru and Sc₂O₃ defect states to the Sn. This diffusion of electrons becomes less efficient for larger barrier thicknesses. We use a simple model to show that for thicker layers of Sc₂O₃, the etch rate is limited by charge diffusion, while electron tunneling may contribute significantly for thin layers of Sc₂O₃.

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Chapter 5

Adsorption and dissociation of CO₂ on Ru(0001)

The adsorption and dissociation of carbon dioxide on a Ru(0001) single crystal surface was investigated by reflection-absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) spectroscopy for CO₂ adsorbed at 85 K. RAIRS spectroscopy shows that the adsorption of CO₂ on a Ru(0001) single crystal is partially dissociative, resulting in CO₂ and CO. The CO vibrational mode was also observed to split into two distinct modes, indicating two general populations of CO present at the surface. Furthermore, a time-dependent blue-shift is observed, which is characteristic of increasing CO surface coverage. TPD showed that coverages of up to 0.3 ML were obtained, and no evidence for chemisorption of oxygen on Ruthenium was found.

5.1. Introduction

The transformation of carbon dioxide (CO₂) into more valuable compounds (carbon monoxide, methanol, oxalate, organic acids, methane, hydrocarbons) requires activation by a catalyst.¹ Among ionic liquids, proteins, organic compounds, semiconductors², transition metals are studied widely as catalysts, due to their relatively high efficiency. Thus, the interaction of CO₂ with metal and metal oxide surfaces is of importance in understanding a number of relevant surface catalytic processes on an atomic scale.^{1, 3-4}

Reaction of CO₂ dissociation products with hydrogen to produce hydrocarbons is attractive as a potential net-zero emissions fuel cycle. However, for such a cycle to be efficient, the catalysis of CO₂ dissociation and the reverse water gas shift reaction is required. While metallic ruthenium is known to catalyze the reverse water gas shift reaction, its interaction with CO₂ has not, to our knowledge been the subject of investigation.⁵⁻⁸ The chemisorption and reaction of CO₂ on metal oxides, including RuO₂, and metallic alloys, including Ru, are well-studied processes.^{1, 3} Moreover, the adsorption of CO₂ on other single-crystal metal surfaces has been extensively studied. For the surfaces like Fe, Ni, Re, Al or Mg, it was observed that the adsorption of CO₂ is partially dissociative, with CO₂ decomposing to CO and O.⁹⁻¹³ The dissociation of CO₂ proceeds via the formation of negatively charged CO₂⁻ on Ni, Fe, Cu, Re, which may then dissociate into CO and O.¹

These experiments are often complicated by the low desorption temperature of CO₂. In many cases (Rh, Pd, Pt, Fe, Cu, Re) CO₂ does not stably adsorb to the surface for temperatures above 100 K, and desorbs from the surface for temperatures that are relatively low: 130 K (Re), and 135 K (Pd), with Ni being an exception at 220 K.¹ Additionally, surface purity is a very important factor in CO₂ adsorption and reaction on metals. Alkali adatoms, for example, increase the binding energy of adsorbed CO₂, and promote the partial dissociation of CO₂ into CO + O.

Many surface studies have been performed using scanning tunneling microscopy (STM), low energy electron diffraction (LEED), and X-ray photoelectron spectroscopy (XPS). STM provides valuable insight into the morphology and short-range order of surface adsorbed species¹⁴⁻¹⁶, however, it can be challenging to resolve some chemical reactions, such as partial dissociation (CO₂ → CO + O). LEED is sensitive to ordered overlayer structures and XPS is sensitive to chemical changes at the surface, but, the relatively high energy of the electron and X-Ray irradiation can lead

to surface modifications that may be difficult to separate from the changes of interest.¹⁷⁻²²

TPD studies, on the other hand, provide a direct measurement of the surface binding energy, and allow the surface coverage to be absolutely calibrated. RAIRS measurements allow the growth and decay of vibrational modes to be studied in situ. These changes provide evidence for changes in molecular population density, molecular orientation, and the environment in which molecules are adsorbed to the surface. By combining TPD and RAIRS, it is often possible to draw quantitative conclusions that would be otherwise elusive. Moreover, due to the low energy of the radiation in RAIRS, in situ studies are highly unlikely to modify the surface during measurement.

In this article, we present the results of TPD and RAIRS studies of CO₂ adsorption and dissociation on a Ru(0001) single crystal surface at 85 K. Additionally behavior of absorbed species after increasing surface temperature to 120 K was studied.

5.2. Methods

A ruthenium (0001) single crystal with a diameter of 11 mm and thickness of ~3 mm (Surface Preparation Laboratories, The Netherlands) was used for CO₂ adsorption and dissociation studies. The sample was mounted on a 3-axis positioning manipulator in an ultra-high vacuum (UHV) chamber with a base pressure of 10⁻¹⁰ mbar. The temperature of the sample was controlled by a Eurotherm temperature controller with active heating and liquid nitrogen cooling. A K-type thermocouple was spot-welded to the side of the crystal and used to monitor the sample temperature. The system was equipped with facilities for TPD and RAIRS measurements. A Hiden Analytical 3F/PIC quadrupole mass spectrometer (QMS) was used for thermal desorption measurements. To ensure that the signal was dominated by desorption from the crystal surface, the QMS was mounted inside

a differentially pumped housing which was placed approximately 1 mm from the crystal surface during measurements. TPD measurements were performed by heating the crystal surface at a constant rate of 2 K/s in the range 85-600 K and at a rate of 10 K/s from 600 to 1580 K. For RAIRS measurements, a Bruker Vertex 70v Fourier transform infrared (FTIR) spectrometer, employing a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector was used. Background and sample scans were recorded by co-adding 256 scans with a resolution of 4 cm^{-1} .

The crystal surface was subjected to a cleaning process, consisting of oxygen cleaning, annealing, and Ar ion sputtering. In the first step, carbon was removed by sample oxidation at 1300 K with an O_2 background pressure of 1×10^{-7} mbar. Afterwards, Ar ion sputtering (2 keV), with an argon pressure of 2×10^{-6} mbar was performed. Finally the sample was annealed at 1300 K and flashed to 1580 K. Sputtering and annealing were repeated until no carbon monoxide peak was observed on the TPD spectrum, and until a repeatable water TPD spectrum was achieved.²³

Carbon dioxide, with a purity of 99.998 % (residual gasses: O_2 2 ppm, N_2 8 ppm, hydrocarbons 3 ppm, H_2O 1 ppm, CO 1 ppm) was used for the experiments. Carbon dioxide was dosed on the Ru(0001) surface, held at a temperature of 85 K, using a retractable quartz dosing tube, placed 1 cm from the crystal to minimize the increase in the background pressure. A pinhole was mounted between the gas supply and the tube doser, such that a pressure in the mbar range in the dosing system results in effective pressures in the 10^{-8} mbar range in front of the crystal surface. The relatively high pressure in the dosing system minimizes possible contaminations from walls of the gas lines. Since CO_2 does not stably adsorb at the lowest achievable temperature of 85 K, calibration of the dose is not straightforward. Therefore, gas doses are specified as pressure used in the dosing system times exposure time. The surface coverage, which is the more important

parameter, is determined by calibrating the total amount of CO₂ detected via TPD against reference water TPD spectra (see Section 3.3 for details).

It is known that CO₂ adsorption on metal surfaces strongly depends on dosing time, pressure, surface temperature, as well as presence of contaminants on the surface.¹ This results in some additional uncertainty in the initial coverage for identical dosing conditions. To avoid incorporating this uncertainty into our study, we draw quantitative results from time-series data taken from the same experiment, rather than comparing between experiments.

5.3. Results and discussion

5.3.1. CO₂ adsorption on Ru(0001)

To ensure that all vibrational features were clearly identified, RAIRS spectra were first obtained from a Ru(0001) surface that was dosed with a large amount (dosing pressure approximately 5 mbar for less than 1 minute) of CO₂ (see Figure 5-1). Five dominant vibrational modes were detected at frequencies that correspond closely to those reported in literature and their attributions are summarized in Table 5-1.²⁴⁻²⁵ The only exception is the feature at 675 cm⁻¹, which we attribute to the (ν_2) O=C=O bend mode, but we note that this is more commonly reported to be at 660 cm⁻¹.^{24, 26-27} As shown in Figure 5-1, the peak at 2343 cm⁻¹ is broadened and several separate peaks between 2283 and 2455 cm⁻¹, are observed. Such broadening is common for thick layers, and, especially for layers that are interacting with a substrate.²⁵ In the following experiments, much less than a monolayer of CO₂ was dosed (1, 2 and 3 mbar) and only the ν_3 stretch (2343 cm⁻¹) and (ν_2) O=C=O bend mode (675 cm⁻¹) were observed. These vibrational modes consist of a single peak each, in line with previous literature reports. The center frequency of the two modes did not change for different CO₂ coverages. Taken together with the consistent shape

of the TPD spectra for different coverages (see below), we conclude that the structure of the adsorbed CO₂ does not change significantly in this coverage range.

Figure 5-1. Reflection-absorption infrared spectrum of CO₂ adsorbed on Ru(0001) at 85 K.

CO₂ adsorption on Ru(0001) surface was additionally studied with TPD. Carbon dioxide already starts desorbing from the Ru(0001) surface at 85 K, moreover, the desorption peak is rather broad and extends beyond 120 K (see Figure 5-2), thus we expect some of the CO₂ to desorb from the surface during dosing.

Table 5-1. Assignment of RAIRS peaks of CO₂/Ru(0001) after Ref.²⁴: ν indicates a stretch vibration, with ν_1 for symmetric and ν_3 for asymmetric stretch.

Peak [cm ⁻¹]	Assignment
3708	($\nu_1 + \nu_3$) combination
3599	($2\nu_2 + \nu_3$) combination
2343	(ν_3) ¹² C=O stretch
675	(ν_2) O=C=O bend

Figure 5-2. Desorbed peaks of CO_2 from TPD measurement after CO_2 dosed at 85 K onto the surface for 10 minutes with different pressures in the dosing system (1, 2 and 3 mbar).

Figure 5-3. Surface coverage of CO as a function of CO_2 dosed onto the Ru(0001) surface in the pressure of 1, 2 and 3 mbar.

To exclude the influence of the instability of CO_2 on our measurements, we dose CO_2 for 10 min with different pressures (1,

2 and 3 mbar) in the dosing system, which corresponds to different surface coverage (0.05, 0.2 and 0.3 of a ML, respectively) of CO_2 . The surface coverage was estimated using a reference water TPD spectrum for calibration purposes. Based on the water TPD ²⁸, we can estimate water coverage, and then taking into account the sensitivity of the mass spectrometer we calculated amount of CO, CO_2 and H_2 (section 5.3.3) on the surface. After dosing, the two main contributions to the TPD spectrum are CO_2 (at 105 K) and CO (at 480 K). Figure 5-3 shows the relation between the CO observed at the surface and the CO_2 dosed onto the surface. Carbon dioxide and CO surface coverages are below 1 ML, thus we expect dose dependence coverage. As we will show later, the surface coverage of CO is clearly above the measured background (see Figure 5-9 for comparison), and depends on the CO_2 dose.

5.3.2. CO_2 dissociation on Ru(0001)

To study that rate at which CO_2 partially dissociates on the Ru(0001) surface, CO_2 was dosed onto the surface for 10 minutes at a pressure of 1 mbar, after which the surface was monitored with RAIRS for 50 minutes (including dosing time). Directly after that, the sample surface was heated to 120 K and RAIRS measurements were obtained after cooling to 85 K. The change in the CO and the CO_2 (ν_3 stretch and ν_2 O=C=O bend modes) over time is presented in Figure 5-4a and b.

To quantify the changes in CO_2 and CO coverage, the intensity of the asymmetric stretching modes of CO_2 and CO were used, although it should be noted that RAIRS spectra are generally not quantitative. Figure 5-4 shows that the CO_2 ν_3 mode slowly decreases with time, moreover, it is also red-shifted from 2343 to 2341 cm^{-1} . For low coverages of CO, like those used in this work, it is known that intensity of the asymmetric stretch mode scales approximately with coverage ²⁹, thus, we assume that all the changes in the spectra are due to changes in coverage. Our analysis

shows that the intensity changes correspond to a reduction in CO₂ coverage from 0.05 to 0.03 ML, as shown in Figure 5-5. Moreover, it can be seen that approximately half of the CO₂ loss is due to desorption from the surface, and the remaining loss is due to dissociation into CO. Similar behavior was observed in CO₂ adsorption on Ni(100) studies^{10-11, 30}, where it was shown that adsorption of CO₂ (100L) on Ni(100) results in CO₂ and CO desorption from the surface. Based on evidence from EELS experiments, the existence of a “bent” CO₂ configuration was proposed as a precursor to dissociative adsorption. A vibrational mode at 1620 cm⁻¹ was assigned to an asymmetric stretching mode of a bent CO₂ species, while peaks at 670 and 2350 cm⁻¹ originate from the vibrational modes of linear, undistorted CO₂.

Although the presence of peaks at 660 and 2343 cm⁻¹ was observed after adsorption of CO₂ on Ru(0001), no evidence for a vibrational mode at 1620 cm⁻¹ was found. Only after increasing the dose and flux of CO₂, by using a higher dosing pressure, a mode at 1580 cm⁻¹ was detected. We speculate that this mode may be due to the asymmetric stretch of distorted CO₂, but we cannot definitively assign it. Due to the low amounts of CO formed on Ru(0001) and the reported instability of bent CO₂, the coverage of this species might be too low to be reliably detected. Transition metals with full d-band are known to be less active than metals with unpaired d-electrons, thus dissociative adsorption is more likely on Ru, as evidenced by the reported behavior of CO₂ on Fe, Ni, and Re.^{1, 31} In contrast, CO₂ does not partially dissociate on evaporated Cu films at 195 and 273 K, as well as on Cu(110) and Cu(111) surfaces, which was attributed to the full d-bands.¹

Figure 5-4. Reflection-absorption infrared spectrum of CO₂ stretch mode (a) and CO (b) for different delay times, after dosing CO₂ onto a Ru(0001) surface at 85 K. Dashed lines indicate the peak positions for “10 min” measurement at 85 K.

The CO vibrational mode, on the other hand, shows a more complicated behavior. The single vibrational mode splits into two. The higher energy mode consistently increases with time, and blue-shifts from 1996 to 2002 cm⁻¹ as the amount of CO increases.²⁹ At the same time, the lower energy mode (at 1983 cm⁻¹) does not grow consistently, but first increases and then decreases. The peak is first blue-shifted to 1986 cm⁻¹, then red-shifts to 1985 cm⁻¹ (see Figure 5-4 for a comparison). To distinguish the changes in intensity of these modes, the peaks (including CO₂ stretch mode) were fit with Gaussians and the changes in areas of the peaks are presented in Figure 5-6.

Figure 5-5. Integrated area of the CO and CO₂ (ν_3 stretch mode) peaks converted into ML coverage after dosing onto Ru(0001) surface. Numbers are just indicative.

Figure 5-6. Peak areas after fit with Gaussians for CO₂ stretch mode and two CO modes, after 10 min CO₂ dose at 1 mbar.

It can be seen in Figure 5-6 that the area of the lower energy CO mode first increases and afterwards saturates, or even slowly decreases. On the other hand, the higher energy CO mode increases as the CO₂ mode decreases. These spectral changes suggest that there are two CO populations. There are a number of possible explanations for the splitting of the vibrational mode: there may be two different binding energies, due to CO binding at two different sites. One site could be associated with nearby CO₂, while the other is associated with CO that is not associated with CO₂. Another possible explanation is that the dissociation of CO₂ results in chemisorbed oxygen with the CO vibrational frequency shifted due to its proximity. A final possibility is that the CO binds to CO₂ or CO rather than the Ru surface.

In our case, the surface coverage is rather low, making the latter case rather unlikely. Furthermore, as can be seen below, there is no evidence that the oxygen dissociation product chemisorbs stably to ruthenium. Therefore, we propose that the CO adsorbs at two different sites with two different binding energies, possibly due to the proximity of CO₂. Only the higher energy vibrational mode is strongly dependent on the concentration of CO₂, which might be associated to the strengthening of the C-O bond (peak at 1996 cm⁻¹) and a weakening of the bond between the surface and CO (peak at 1983 cm⁻¹).³²

5.3.3. CO adsorption from the residual background gasses on Ru(0001)

To avoid mistaking CO₂ partial dissociation for CO adsorption from background, the adsorption of CO from the background was measured. After cleaning the Ru(0001) surface, the surface was flashed to 600 K to remove any residual CO. The sample was then cooled to 85 K and RAIRS measurements were performed after delays of 25 and 50 min (see Figure 5-7). A peak at 1990 cm⁻¹, corresponding to CO adsorbed to the surface is observed.²⁸ It can

be seen that the peak increases with time. Moreover, a slight blue-shift from 1990 to 1988 cm^{-1} is observed.

Figure 5-7. Background CO adsorption on Ru(0001) surface after 25 and 50 minutes of delay at a temperature of 85 K.

To estimate the amount of CO adsorbing on the surface, TPD measurements were performed under the same conditions. TPD was performed immediately after the surface was cooled to 85 K and after delays of 25 and 50 minutes after heating to 600 K and cooling to 85 K. As shown in Figure 5-8, the TPD spectrum showed that the surface coverage of H_2 , H_2O , and CO (Figure 5-8a, b and c, respectively) increases with time.

The surface coverage of CO, H_2 and H_2O due to background gases are presented on Figure 5-9. There is no significant amount of water on the clean sample, but after exposing to ambient for 50 min, the amount of water increased to approximately 0.004 of a monolayer. A small amount of CO (0.001 ML) deposits onto the surface very quickly (faster than water), but only grows slowly (8 times slower than water) after that. Hydrogen grows fastest, from 0.003 ML to 0.017 ML. A comparison between the growth of

the CO peak after CO₂ dosing with the growth of CO from background is presented on Figure 5-10 and in Table 5-2.

Figure 5-8. TPD of species adsorbed from residual background at a sample temperature of 85 K. No other masses detected.

Figure 5-9. Surface coverage of CO, H₂O and H₂ on Ru(0001) due to background gases.

Table 5-2. CO surface coverage in ML from the background residual gases and after CO₂ dose onto the surface.

Time [min]	CO surface coverage in ML	
	Background	With CO ₂ dose
25	0.0016	0.005
50	0.002	0.008

Figure 5-10. Comparison of the reflection-absorption infrared spectrum of CO peak, from the residual background gases and CO peak after CO₂ dosing, after 25 and 50 min delay.

It is clear that the CO peak grows four times more on a surface that is dosed with CO₂ compared to the natural adsorption from background gases. Furthermore, it can be seen from Figure 5-5 that the growth of the CO peak corresponds very well to the decay of the CO₂ peak. This suggests that desorption of CO₂ at 85 K is rather slow and that the changes in the infrared spectra are dominated by partial dissociation. After CO₂ dosing onto the surface two CO peaks at different position are observed, what is indicative of a low and high energy binding site. To determine the stability of those peaks, the surface was annealed above the temperature of the

main desorption peak of CO_2 . As stated earlier, the Ru(0001) surface was dosed with CO_2 (1 mbar, 10 minutes), and after 50 minutes, was heated to 120 K. After cooling to 85 K, a RAIRS spectrum was obtained (see Figure 5-11).

Figure 5-11. Reflection-absorption infrared spectrum after 10 min CO_2 (1mbar) dosing onto the Ru (0001) and 50 minutes delay time on Ru(0001) single crystal at 85 K and after sample annealing to 120 K.

Table 5-3. Surface coverage of CO and CO_2 (after CO_2 dose onto the Ru(0001) surface 50 min delay) at 85 K and after annealing to 120 K.

Temperature [K]	Indicative surface coverage in ML	
	CO	CO_2
85	0.01	0.028
120	0.016	0.014

Table 5-3 shows that the CO_2 coverage is reduced by a factor of two. Complete desorption is not achieved because, as can be seen in Figure 5-2, the CO_2 desorption spectrum has a peak at 105 K, followed by a broad feature that extends beyond 120 K. The surface coverage of CO increases from 0.01 to 0.016 of a ML. Interestingly, the overall increase is accompanied by a 23% reduction in the lower

energy peak and a 65% increase in the higher energy peak. In addition to changes in peak intensity, after annealing, the peak positions also change slightly. The higher energy peak blue-shifts from 2002 to 2010 cm^{-1} and the lower energy peak red-shifts from 1984 to 1980 cm^{-1} . Both shifts are likely to be due to coverage dependent effects.²⁹

5.4. Oxygen TPD

A remaining question relates to the oxygen radical. Since the generated amount of CO is very low, it is possible that the oxygen atoms are consumed for forming CO with residual carbon in the crystal. This should then give a small CO desorption at high temperature, which may be difficult to detect in such small doses. Another option is that oxygen can form water with background H_2 . Formation of such small amounts of water is not detectable due to presence of background water in the TPD spectrum. Our RAIRS measurements were unable to reliably detect an increase in the OH stretch mode, but it should be noted that RAIRS is generally not able to detect sub-monolayer amounts of water, since the first monolayer of water on Ru does not have a significant dipole moment perpendicular to the surface.³³ A third possibility is that the oxygen chemisorbs with the ruthenium surface. To find the role of oxygen chemisorption, the oxygen signal was always recorded in TPD after CO_2 adsorption. However, no significant signal at 1580 K was detected, indicating that ruthenium oxide is not formed during CO_2 dissociation, or that the oxygen is consumed for forming CO from residual carbon that diffuses out of the bulk of the crystal at high temperature.

Furthermore, we also exclude re-association due to

with $k_1 \approx k_2$. If this were the case, then, after annealing the ruthenium and removing the majority of CO_2 , the surface

concentrations would be out of equilibrium and favor the reverse reaction. However, neither an increase in CO_2 , nor a decrease in the CO vibrational mode intensity is observed. This implies that $k_1 \gg k_2$. Finally, the re-association during TPD can also be excluded because there is no evidence for a significant CO_2 desorption peak at the CO desorption temperature.

5.5. Conclusions

Our results show that CO_2 adsorption on a Ru(0001) surface results in partial dissociation, with CO_2 and CO present on the surface. RAIRS measurements show that CO_2 dissociates into CO over time. For a CO_2 coverage of 0.05 ML, dissociation proceeds to a CO_2 coverage of 0.03 ML, and appears to saturate. Furthermore, the dissociation of CO_2 appears to be irreversible. In comparison with previous results reported for Ni(110)^{18,30}, and Fe(111)^{9,19,34-35}, we note that the dissociation of CO_2 is qualitatively similar, but has some significant differences. For both Ni and Fe, partial dissociation is only observed for elevated temperatures, while for Ru(0001), dissociation is already observed at 85 K. Furthermore, in the case of Ni and Fe, the oxygen is observed to be adsorbed to the surface, while for Ru, there is no evidence of O adsorption. Finally, on further heating, CO decomposes into carbon and oxygen on Fe, while on Ru, CO desorbs intact. Observed vibrational modes at 660 and 2343 cm^{-1} correspond to stretch modes of linear, undisturbed CO_2 , while a vibrational feature that is visible only for higher CO_2 coverages at 1580 cm^{-1} , is tentatively assigned to an asymmetric stretching mode of a bent CO_2 species.

The adsorption (CO_2 does not adsorb for temperatures higher than 100 K) and desorption temperatures of CO_2 on Ru are relatively low in comparison to those reported for other transition metals.¹ By annealing the surface at 120 K—just above the peak desorption temperature of CO_2 —it was observed that the rate of CO_2 dissociation was increased and that the CO restructures to a

weaker bond between the surface and CO. TPD spectra confirm that the changes in the RAIRS spectrum are due to changes in CO and CO₂ coverage. Furthermore, TPD does not show chemisorbed oxygen on the Ru surface, which may be due to H₂O or CO formation from residual H₂ or C on the sample.

5.6. References

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Valorization

Our systematic investigation on Sn etching from different surface materials has very good predictive power and facilitates the choice of materials for EUV and di-electric materials applications.

Knowledge of the Sn etching process provides information on the influence of oxidized capping material in comparison to metallic surfaces. Also, the influence of the underlayer on surface binding can be qualitatively estimated via the electronegativity model, and checked by Sn etching studies. That information allows rational choices to be made for, not only the layer material, but also for its thickness and composition.

The use of CO may reduce the concentration of hydrogen at the optical surface. CO binds stronger than H to the Ru surface, so it can displace H from the metal surface. Moreover, CO reacts with H to form hydrocarbons which further reduces the surface H concentration. However, achieving a constant CO coverage of all the optical surfaces in an EUVL tool will require a significant amount of CO to be delivered to the system. Knowing that CO is highly toxic makes usage of large quantities of it unsafe and uneconomic. That is why CO should be introduced/ delivered to the surface in a different way. Our hypothesis was that CO₂, irradiated with EUV will produce CO and, consequently lead to high CO surface coverage. However, this proved to be inaccurate. Instead, the adsorption of CO₂ on a Ru surface results in partial dissociation, with CO₂ and CO present on the surface. Thus, no EUV is needed to activate CO₂ dissociation into CO, and CO can be delivered to the Ru surface via a small partial pressure of CO₂. This process is not aggressive, thus, the total concentration of CO in the vacuum system will remain very low. Knowledge of CO₂ absorption and dissociation on Ru surface is the first step towards using a good understanding of the

surface chemistry to control surface reactions on EUV optical surfaces via the partial pressure of background gasses.

Summary

The physics and chemistry of Sn etching from optical and dielectrical surfaces must be understood in order to ensure that cleaning is complete and that the process does not damage the surface of the elements. We proposed the use of the relative electronegativities of the surface material and Sn to predict the degree to which electrons are available for bonding. This allows the success or failure of Sn etching from a thin metallic surface material to be predicted. It was found that Sn can be completely etched from transition metals with electronegativity values that are lower than or equal to Sn ($\chi_{\text{Sn}} - \chi_{\text{M}} \geq 0$). We observed incomplete Sn etching when Sn was initially deposited onto materials with an electronegativity value higher than that of Sn ($\chi_{\text{Sn}} - \chi_{\text{M}} < 0$). This shows that electronegativity is a useful predictor for hydrogen etching of Sn from metal surfaces. Furthermore, for high electronegativity surfaces, which we predict to prevent complete etching, the remaining amount of Sn after etching depends on the electronegativity of the surface onto which Sn was deposited. This indicates that even Sn that is separated from the surface by several atomic layers is still influenced by the surface.

Metals with high electronegativities form weak oxides, such as ruthenium, while those with low electronegativity form strong oxides (e.g., scandium and aluminium). This leaves open the question of the role of surface oxidation in tin adhesion. To investigate the influence of oxidation, the removal of Sn from metallic and oxidized Sc thin films was studied. We have shown that tin can be fully etched from a metallic Sc surface as well from Sc thin films with complete and incomplete oxidation. Furthermore, our results show that the presence of Sc_2O_3 on a Sc thin film significantly slows the etch rate. For Sn etching from oxidized Sc,

we propose that etching is slowed by electrons being trapped at defect sites in the Sc_2O_3 layer. This effect is strengthened when Sc metal is present below the Sc_2O_3 , due to the built-in electric field spanning the oxide, generated by the difference in work function between Sc and Sn.

In this thesis, catalytic dissociation of CO_2 was studied as a precursor for hydrogen control studies. Carbon dioxide adsorption and dissociation on a Ru single crystal surface was studied. Our results show that CO_2 adsorption on a Ru(0001) surface results in partial dissociation, with CO_2 and CO present on the surface. Furthermore, the dissociation of CO_2 appears to be irreversible and is already observed at 85 K. The observed vibrational modes at 660 and 2343 cm^{-1} correspond to stretch modes of linear, undisturbed CO_2 , while a vibrational feature, which is visible only for higher CO_2 coverages, at 1580 cm^{-1} is tentatively assigned to an asymmetric stretching mode of a bent CO_2 species. The adsorption and desorption temperatures of CO_2 on Ru are relatively low. By annealing the surface at 120 K—just above the peak desorption temperature of CO_2 —it was observed that the rate of CO_2 dissociation was increased and that the CO restructures to a weaker bond between the surface and CO. The partial dissociation of CO_2 is an important first step, since CO and H may react to form water and volatile hydrocarbons. This may then reduce the hydrogen concentration at the surface, which slows hydrogen penetration into the mirror.

Scandium oxide (Sc_2O_3) is a possible candidate for high-k dielectric applications. However, the stability of the dielectric layer is also very important: metal atoms from the gate electrode should not penetrate into or through the oxide layer. In this thesis, metal diffusion studies were carried out to test if Sc_2O_3 layers of various thicknesses act as a diffusion barrier. Scandium oxide diffusion barrier properties were tested using a MIM structure, consisting of Ru, Sc_2O_3 , and Sn. We observed complete Sn etching from 0.71, 1.1

and 1.56 nm of Sc_2O_3 . It was demonstrated that even 0.5 nm Sc_2O_3 forms a closed oxide layer that prevents the diffusion of Sn through to the Ru layer. The Sn etching time was observed to depend on the Sc_2O_3 barrier thickness and increased with increasing Sc_2O_3 thickness. This is explained by the formation of a MIM junction between the Ru, Sc_2O_3 and Sn, where the built-in potential enhances diffusion of electrons from the Ru and Sc_2O_3 defect states to the Sn. This diffusion of electrons becomes less efficient for larger barrier thicknesses. We use a simple model to show that, for thicker layers of Sc_2O_3 , the etch rate is limited by charge diffusion, while electron tunneling may contribute significantly for thin layers of Sc_2O_3 .

Samenvatting

De fysische en chemische eigenschappen van het etsen van kleine hoeveelheden tin (Sn) is van belang voor diverse optische en diëlektrische oppervlakken. Het etsproces dient in detail te worden gekarakteriseerd, zodat volledig etsen kan worden bereikt zonder dat schade wordt toegebracht aan het oppervlak.

Op basis van de elektronegativiteit van het oppervlaktemateriaal en het Sn hebben we een schatting gemaakt van de sterkte van de Sn-binding. Dit geeft een directe indicatie van het etsen van Sn van een dun metaaloppervlak. Dit promotie-onderzoek laat zien dat volledig etsen mogelijk is wanneer de elektronegativiteit van het transitiemetaal kleiner is dan of gelijk aan Sn ($\chi_{\text{Sn}} - \chi_{\text{M}} \geq 0$). Wanneer de elektronegativiteit groter is dan die van Sn ($\chi_{\text{Sn}} - \chi_{\text{M}} < 0$), is volledig etsen niet mogelijk. Het onderzoek toont aan dat de elektronegativiteit een goede indicator is voor het Sn-etsgedrag van waterstofradicalen aan een metaaloppervlak. Daarnaast verwachten we voor sterk elektronegatieve oppervlakken dat de overgebleven hoeveelheid Sn na het etsen afhangt van de elektronegativiteit van het oppervlak waarop het Sn is aangebracht. Daarbij wordt de elektronegativiteit beïnvloed door meerdere atoomlagen.

Metalen met een hoge elektronegativiteit vormen zwakke oxides, bijvoorbeeld ruthenium, terwijl metalen met een lage elektronegativiteit sterke oxides vormen (zoals scandium en aluminium). Hierbij is de vraag welke rol oppervlakte-oxidatie speelt bij de binding van tin. Om deze processen te onderzoeken is de invloed onderzocht van het tin-etsen van metallische en geoxideerde Sc-samples. We laten zien dat tin volledig geëtsd kan worden van het Sc-oppervlak, onafhankelijk van de oxidatiegraad. Daarbij laten de resultaten zien dat de aanwezigheid van Sc_2O_3 op

het Sc-oppervlak de etssnelheid vertraagt. We verwachten dat het etsen vertraagd wordt doordat elektronen binden met defectlocaties in de Sc_2O_3 -laag. Dit effect wordt nog versterkt wanneer Sc-metaal onder de Sc_2O_3 -laag aanwezig is, vanwege het elektrische veld over het oxide als gevolg van het verschil in de werkfunctie tussen Sc en Sn.

In dit proefschrift werd verder katalytische dissociatie van CO_2 bestudeerd als een voorloper voor waterstofstudies aan oppervlakken. Koolstofdioxide-adsorptie en -dissociatie zijn onderzocht op een Ru monokristallijn oppervlak. Onze resultaten laten zien dat CO_2 -adsorptie op een Ru(0001) oppervlak leidt tot partiële dissociatie, waarbij zowel CO_2 als CO op het oppervlak aanwezig zijn. Daarnaast is de dissociatie van CO_2 irreversibel en al zichtbaar bij 85 K. De geobserveerde vibrationele modes van 660 en 2343 cm^{-1} corresponderen met lineaire strek modes CO_2 , terwijl een vibrationele mode van 1580 cm^{-1} geassocieerd kon worden met een asymmetrische gekromde CO_2 -configuratie. De adsorptie- en desorptietemperaturen van CO_2 op Ru zijn relatief laag. Door het oppervlak te verhitten tot 120 K, net boven de piekwaarde van de desorptietemperatuur, wordt de dissociatiesnelheid van CO_2 verhoogd en de CO vormt een zwakkere binding met het oppervlak. De partiële dissociatie van CO_2 vormt een belangrijke eerste stap in het proces, omdat CO en H kunnen reageren tot water en gasvormige koolwaterstoffen. Dit kan de waterstofconcentratie op het oppervlak verlagen en zo de waterstofpenetratie in de spiegel vertragen.

Scandiumoxide (Sc_2O_3) is een mogelijke kandidaat voor hoge-k diëlektrische toepassingen. De stabiliteit van de diëlektrische laag is echter ook erg belangrijk: metaalatomen van de gate-elektrode mogen niet in of door de oxidelaag dringen. In het kader van dit proefschrift werd onderzoek gedaan naar metaaldiffusie om te testen of Sc_2O_3 -lagen kunnen werken als diffusiebarrière. De diffusiebarrière-eigenschappen van verschillende diktes

scandiumoxide werden getest met behulp van een MIM-structuur, bestaande uit Ru, Sc_2O_3 en Sn. We observeerden volledige Sn-ets van 0,71, 1,1 en 1,56 nm Sc_2O_3 . Er werd aangetoond dat zelfs 0,5 nm Sc_2O_3 een gesloten oxidelaag vormt die de diffusie van Sn naar de Ru-laag voorkomt. Er werd waargenomen dat de Sn-etstijd afhing van de Sc_2O_3 -barrièredikte en toenam met toenemende Sc_2O_3 -dikte. Dit kan worden verklaard door de vorming van een MIM-junctie tussen de Ru, Sc_2O_3 en Sn lagen, waar de ingebouwde potentiaal de diffusie van elektronen van de defecten in de Ru en Sc_2O_3 lagen naar het Sn verbetert. Deze diffusie van elektronen wordt minder efficiënt bij grotere barrièrediktes. We gebruiken een eenvoudig model om aan te tonen dat de etssnelheid voor dikkere lagen Sc_2O_3 wordt beperkt door ladingsdiffusie, terwijl elektronentunneling significant kan bijdragen bij dunne lagen Sc_2O_3 .

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Małgorzata Pachecka was born on 22nd of April 1987 in Siedlce, Poland. In 2006 she started her studies at Warsaw University of Life Sciences and in 2010 she received a B.Sc. degree in Food Technology and Human Nutrition with a major in Food Engineering and Process Management. Two years later she pursued an M.Sc. degree at the same faculty and same major. In parallel (from 2007) she studied Chemical and Process Engineering at Warsaw University of Technology with a major in Chemical Engineering and pursued a B.Sc. degree in 2011 and M.Sc. degree in 2012. During her studies she carried out several internships at different companies, including Silliker Polska Sp. (Warsaw, Poland) and Wetsus, Centre of Excellence for Sustainable Water Technology (Leeuwarden, The Netherlands). In December 2012 she started her PhD research in Chemistry and Physics of EUV optics at the Nanolayer Surfaces and Interfaces (nSI) Group of the FOM Institute Differ. In 2013 the Group relocated and became part of the later founded Industrial Focus Group XUV Optics, within the MESA+ Institute for Nanotechnology. During her PhD period she worked closely with the ASML Research Department, and carried out most of her research in the ASML Research Laboratory. The PhD research was part of the NanoNextNL Program and it was supervised by Prof.dr. F. Bijkerk, with daily supervision of Dr. C.J. Lee. A selection of the results are presented in this thesis.