MASTER

Hydrogen atom based tin cleaning

Crijns, V.M.C.

Award date:
2014

Link to publication
Hydrogen atom based tin cleaning

V.M.C. Crijns

January 2014

Under supervision of:

dr. ir. M. van Kampen
prof. dr. ir. G. W. M. Kroesen
Abstract

In next-generation lithography machines, tin resulting from the EUV source is regarded as a seriously contaminating element of the EUV optics. Atomic hydrogen appears to be an appropriate candidate for selective in-situ tin cleaning. However, understanding of the hydrogen atom based tin cleaning process is lacking. Therefore, the goal of this thesis is to identify and understand the mechanisms involved in the tin cleaning process. Initially, tin cleaning is compared with hydrogen atom based carbon cleaning – carbon being another contaminating element of EUV optics. The cleaning rates for both carbon and tin are determined as a function of atomic hydrogen flux at various pressures. Atomic hydrogen is generated through hydrogen dissociation at the surface of a hot tungsten filament. In order to quantify the atomic hydrogen flux, an isothermal catalytic probe is successfully employed. Atomic hydrogen was generated within a pressure range of 5 – 100 Pa and with filament temperatures between 1300 °C and 1950 °C. The resulting flux values were determined within a range of $10^{15} - 5 \cdot 10^{17}$ at cm$^{-2}$ s$^{-1}$ with an absolute error of $4.4 \cdot 10^{16}$ at cm$^{-2}$ s$^{-1}$. Both carbon samples and various types of tin containing samples were exposed to quantified atomic hydrogen fluxes. Results of the carbon cleaning rate demonstrate a linear relation with flux, as is expected from literature. When thick layers of tin (~160 nm) on Si substrates are cleaned, the tin cleaning rate appears not to be proportional to the atomic hydrogen flux. The results indicate a cleaning threshold for very low fluxes as well as a decreasing cleaning efficiency at the high end of the studied flux range. Next, the thick layered tin samples are exposed to a fixed atomic hydrogen flux for various exposure times. Studying the tin cleaning rate as a function of exposure time displays a threshold period of approximately 50 minutes, during which the cleaning rate is relatively low. This period corresponds to the time after which the substrate underneath the tin layer becomes partially uncovered as a result of atomic hydrogen exposure. When cleaning thin layers of tin (~30 nm) on ZrN and Mo substrates, the cleaning rate shows a reverse dependency on time. Within the initial minutes of the cleaning experiments, the cleaning rates for both types of samples are relatively high. During this time, the tin structure changes rapidly. After less than 20 minutes, the cleaning rate has declined to a steady value and distinct tin islands have been formed. The islands become more spherical as the cleaning experiments continue, which appears to significantly impede the cleaning process.
# Table of contents

Chapter 1. Introduction..........................................................................................................................4
  1.1 Project goal and description.......................................................................................................6

Chapter 2. Theory..................................................................................................................................7
  2.1 Cleaning carbon using atomic hydrogen..............................................................................7
  2.2 Cleaning Sn using atomic hydrogen......................................................................................8
  2.2 Influencing the cleaning rate..................................................................................................9
  2.3 Hydrogen dissociation..........................................................................................................13

Chapter 3. Experimental setup...........................................................................................................15
  3.1 Hydrogen Radical System....................................................................................................15
  3.2 Samples....................................................................................................................................18
  3.3 Diagnostics..........................................................................................................................19

Chapter 4. Measuring the atomic hydrogen flux.............................................................................25
  4.1 Theory......................................................................................................................................25
  4.2 Design of the catalytic probe...............................................................................................26
  4.3 The experiments..................................................................................................................28
  4.4 Results and Discussion........................................................................................................32

Chapter 5. Results and discussion....................................................................................................36
  5.1 Carbon cleaning results........................................................................................................36
  5.2 Tin cleaning results................................................................................................................39

Chapter 6. Conclusions.....................................................................................................................55

Bibliography.........................................................................................................................................59
Chapter 1
Introduction

Computers, mobile phones and navigation systems are just a few of many electronic devices that we use on daily basis. Nowadays, these devices are considered indispensable and new products are being developed at full speed; we want our devices to be faster, lighter, better. The main elements in an electronic device that determine its performance, are integrated circuits (ICs). An IC – a set of electronic circuits on a semiconductor substrate – can be made increasingly compact as technology advances.

For the production of ICs, the semiconductor industry makes use of a technique known as (photo)lithography. During this process, light is used to project extremely small patterns onto a photoresist layer on a substrate. This photoresist is a light-sensitive material and enables deposition or etching in the exposure pattern. By repeating the lithography process, 3-dimensional structures can be built on nanometer scale. The resolution of these structures is physically limited by wavelength of the light used in the lithography process. In order to further improve the resolution, the next-generation lithography technology makes use of an extreme ultraviolet (EUV) radiation. The selected wavelength of this radiation is 13.5 nm due to an optimal combination of performance of both the mirrors and the EUV source. At this wavelength, no material is transparent; EUV is easily absorbed. This means that the EUV can only be collected and projected by carefully designed multi-layer mirrors (MLMs). The optics are integrated in an entire machine, as depicted in figure 1.1.

Figure 1.1: The EUV lithography machine as developed by ASML.
EUV is preferably generated using a tin (Sn) plasma, since tin converts energy more efficiently into EUV radiation than other EUV fuels such as xenon and lithium [Bak2005, Shi2005, Shi2007]. Light is generated by shooting energetic laser pulses at 35 µm tin droplets, as shown in figure 1.2. The plasma that is created is heated to such temperatures that it emits EUV. The tin plasma is generated at a distance of only 20 cm from the first mirror, called the collector. In the process, particles (ions) may be created that fly towards the collector. High-energy ions are likely to cause damage to the collector surface on impact. Also, the remaining tin vapor may diffuse towards the collector, and stick to its surface. Tin contamination seriously degrades the mirror’s reflectivity – the reflectivity decreases with 18% per nm of deposited tin, affecting the quality and productivity of the entire system.

Mitigation techniques are developed to reduce tin deposition and to avoid harmful ion impact. However, these techniques are insufficient to completely prevent tin build-up on the mirrors to sub-nm levels. In order to achieve an acceptable collector lifetime, an effective and selective method to remove tin contamination, preferably during operation, is indispensable. Hydrogen plasma appears to be a good candidate for the job. In that case, hydrogen will be employed as a buffer gas in the EUV source. It surrounds the tin plasma and slows down energetic tin particles resulting from the plasma. By doing so, the hydrogen gas will become ionized; a hydrogen plasma is automatically generated.

Back when carbon (C) was believed to be the primary contamination degrading EUV optics [Ban2004, Baj2005, Hil2009], using hydrogen plasma was already considered as a suitable cleaning method. Research shows that also tin can be cleaned from different surfaces using hydrogen plasma, at a significant cleaning rate [Bra2012, Soe2012, Her2012, Spo2012]. Braginsky et al. compared tin cleaning with carbon cleaning and reported a great difference in reaction mechanisms. Removing carbon particles using hydrogen plasma appears to be ion-stimulated, while hydrogen atoms dominate the removal of tin. Numerous factors have been indicated to influence the cleaning rate; however, the mechanisms involved in the cleaning
process are far from being understood. In order to be able to use a hydrogen plasma as an in-situ method for the removal of tin contamination on EUV optics, the cleaning process must be optimized for the operation conditions of the lithography machines. Understanding the reaction mechanisms is key to the adaptation of this cleaning method for EUV lithography.

1.1 Project goal and description

The goal of this thesis is to understand the mechanisms involved in the Sn cleaning process using atomic hydrogen. Discussion of these reaction mechanisms is based on cleaning rate measurements. To this end, the cleaning rate is experimentally studied as a function of factors relevant to EUV lithography, including pressure, material of the contaminated substrate, and atomic hydrogen flux to the surface. Previous studies have found strong indications that the cleaning rate largely depends on the atomic hydrogen flux impinging onto the contaminated surface. At present, the atomic hydrogen flux in the EUV source can be theoretically predicted. Knowledge of the relation between the magnitude of the atomic hydrogen flux and the tin cleaning rate allows for predicting this cleaning rate in the source.

In a hydrogen plasma, atomic hydrogen is generated together with a variety of charged particles. In order to investigate the individual role of hydrogen atoms in the cleaning process, atomic hydrogen is generated without the use of a plasma. Instead, molecular hydrogen is dissociated into atoms at a hot surface in the experimental setup. The dissociation process is described in Chapter 2, after the discussion of current conception of the tin cleaning process. In order to extend the knowledge about this process, cleaning experiments have been conducted under various conditions. The experimental setup and the different samples used to conduct the experiments are described in Chapter 3, as well as the used diagnostic methods. Since the cleaning rate appears to be highly influenced by the magnitude of the atomic hydrogen flux used for cleaning, the method and means used to measure this flux are extensively discussed in Chapter 4. In Chapter 5, the results of the cleaning experiments are presented. Implications of both the results and the methods used to obtain them will be discussed in Chapter 6. Based on this, reaction mechanisms will be proposed to explain the Sn cleaning process using atomic hydrogen. Finally, a general conclusion and suggestions for further research are presented in Chapter 7.
Chapter 2
Theory

Tin contamination on the collector mirror is a major challenge in the development of EUV light sources for lithography. Since the contamination cannot be prevented, methods are needed to remove it. Cleaning methods based on the reaction of Sn with both hydrogen [Gra2003, Klu2005] and halogens [Shi2008] demonstrated high cleaning rates. A great advantage of hydrogen over halogens is its selectivity towards Sn. Moreover, hydrogen gas is relatively transparent for EUV [Bru2003, Bru2000]. Because of this, atomic hydrogen-based cleaning is a promising non-disruptive cleaning method for EUV optics.

2.1 Cleaning carbon using atomic hydrogen

The removal of carbon by atomic hydrogen is extensively investigated [Bla1967, Hor1994, Bie1995, Des2013], in particular in the fields of EUV lithography and nuclear fusion. Researchers in both fields show great interest in the cleaning process, although their motives are opposed. Whereas the goal for lithography is to optimize carbon removal, fusion requires a minimal erosion of the carbon reactor wall tiles due to hydrogen plasma exposure.

When amorphous carbon is exposed to atomic hydrogen, the carbon surface will become hydrogenated before being etched. Hydrogenation can occur through two reactions [Wit1996]:

\[
\begin{align*}
\cdot C & \quad + \quad \cdot H \\
\rightarrow & \quad \cdot C \quad - \quad \cdot H
\end{align*}
\]  

Hydrogen atoms bond one by one to hydrocarbon species until a stable gas phase molecule is formed leaving the surface immediately. The etched carbon particles primarily leave the surface as methane molecules [Kra1970]. During methane production, the addition of H to CH2 is the slow step [Bal1975]. Besides methane, acetylene is a frequently detected etching product at high temperatures. Then, CH species at the surface are believed to become sufficiently mobile to permit acetylene production [Bal1975]. The elementary steps of carbon removal through either methane or acetylene production is shown in figure 2.1.
2.2 Cleaning Sn using atomic hydrogen

Atomic hydrogen (H) together with tin (Sn) is known to form a tin hydride called stannane (SnH₄). This reaction occurs spontaneously and is exothermic [Pea1933].

\[
Sn (s) + 4H (g) \rightarrow SnH₄ (g) \quad \Delta H° = -709.2 \text{ kJ mol}^{-1} \quad (2.2)
\]

Here, \( \Delta H° \) is the standard enthalpy of the reaction. At room temperature, this tin hydride is volatile and thermo-dynamically unstable, causing it to decompose. The decomposition may be accelerated when the hydride comes into contact with an active catalytic surface. Metallic surfaces, and Sn in particular, act as catalysts, whereas a tin oxide film is non-catalytic and practically stops the dissociation [Tam1956, Ugu2014].

Tin hydrides decompose spontaneously at a surface, dissociating into two H₂ molecules and a Sn atom [Gun1961]:

\[
SnH₄ (g) \rightarrow Sn (s) + 2H₂ (g) \quad \Delta H° = -162.8 \text{ kJ mol}^{-1} \quad (2.3)
\]

The decomposition proceeds spontaneously also, according to the standard enthalpy of the forward reaction. The Sn atom remains attached to the surface, causing redeposition of Sn. This redeposition is a first indication of the complex mechanisms involved in the cleaning reaction. Redeposition can seriously counteract the removal of Sn from a surface. This affects the net Sn cleaning rate, which represents the amount of Sn that is removed from a surface per unit time.

The cleaning rate \( CR \) is a useful measure to investigate the cleaning process and to identify factors influencing this process. It is defined as the amount of material removed during exposure time \( t \). Commonly, the amount of tin is denoted as the thickness of the tin layer \( h \); then, the cleaning rate is expressed in (nm min\(^{-1}\)) or (nm h\(^{-1}\)) using:

\[
CR = \Delta h / t \quad (2.4)
\]
However, expressing the cleaning in these units gives a rather distorted idea of the tin cleaning process. During cleaning, tin is not removed layer by layer, but rather inhomogeneously. Besides that, the morphology of the tin layer tends to transform, as will be discussed shortly. The thickness is merely an easy-going quantity. More appropriate is it to express the amount of tin as the number of tin atoms \( n \) per area \( A \). Now, the cleaning rate

\[
CR = \frac{\Delta n / A}{t}
\]  

(2.5)

is defined in \((\text{at cm}^{-2} \text{s}^{-1})\). The number of removed tin atoms \( \Delta n \) is determined by measuring the number of atoms per cm\(^2\) before and after a cleaning experiment. From these results, the thickness of the tin layer is obtained by assuming the tin is homogeneously spread over the surface. Then, the thickness can be calculated from the number of atoms per cm\(^2\) using the molar mass \( M \) and the density \( \rho \):

\[
h = \frac{\Delta n}{A} \cdot \frac{M}{NA \rho}
\]  

(2.6)

with the Avogadro constant \( N_A = 6.022 \cdot 10^{23} \text{mol}^{-1} \). For tin, the constant factor \( M / \rho = 16.29 \text{cm}^3 \text{mol}^{-1} \), and for carbon \( M / \rho = 6.16 \text{cm}^3 \text{mol}^{-1} \) [Wea1969].

The exposure time, mentioned earlier, is the effective time that atomic hydrogen is generated and interacting with the tin. Cleaning rates discussed in this report are averaged over the duration of the cleaning experiments, since the amount of tin cannot be determined in-situ.

### 2.2 Influencing the cleaning rate

During the last two decades, Sn cleaning experiments have been conducted by different researchers at a broad range of conditions. The results of these experiments provide good insight into the numerous factors that influence the cleaning rate. These factors and their relevance to the current study will be discussed here. Based on their relevance, a series of factors will be investigated using specially designed experiments, which are discussed in the next chapter.

In the case of hydrogen-based Sn cleaning, an atomic hydrogen source is required. In various cleaning studies, a hydrogen plasma has served this purpose [Shi2008, Bra2012]. Besides atomic hydrogen, ions will be created in the hydrogen plasma that might have impact on the cleaning process. Studies on carbon cleaning for EUV optics have demonstrated that the cleaning rate is greatly enhanced by a combined use of hydrogen ions and atoms, compared to cleaning based on solely atoms or ions [Hop2002, Bra2012]. One might bluntly assume a similar effect for Sn cleaning.

However, the presence of ions appears to have little to no effect on the Sn cleaning rate [Bra2012]. Braginsky et al. conducted both Sn and C cleaning experiments using identical conditions. Two sets of experiments were conducted for both contaminations. Firstly, cleaning was performed using a combination of hydrogen
atoms and ions. Secondly, merely atomic hydrogen was used as a cleaning agent. Figure 2.2 shows the obtained cleaning rates as a function of atomic hydrogen flux. The open dots represent the cleaning rates corresponding to combination-based cleaning, whereas the full dots correspond to atomic hydrogen-based cleaning.

Clearly, C cleaning using atomic hydrogen is enhanced by the addition of ions, in contrast to Sn cleaning. The linear relation between the Sn cleaning rate and the atomic hydrogen flux is not at all influenced by the presence of ions, within the studied range of conditions. Knowledge about this relation is lacking, most likely because the magnitude of the atomic hydrogen flux is not easily measured.

Commonly, the Sn cleaning rate is compared with the C cleaning rate, since hydrogen-based C cleaning is an extensively studied process [Hop2002, Gra2003]. The fact that the C cleaning process is ion-enhanced, while the Sn cleaning is dominated by atoms, dictates a certain caution when comparing the two processes. Excluding cleaning experiments involving hydrogen ions enables a fair comparison. Previously obtained results are shown in figure 2.3 and indicate a more than linear relation between the Sn cleaning rate and the C cleaning rate.
Sn cleaning has been studied using various substrate materials that might be present in EUV lithographic systems; the cleaning rate depends strongly on the type of substrate. Cleaning rates over 30 nm/min are obtained for silicon substrates and substrates with Si₃N₄ and B₄C cap layers, while the removal of Sn on molybdenum is significantly slower [Soe2012]. All Sn particles can be removed from these materials. However, substrates of ruthenium are more difficult to clean. For Sn on Ru, cleaning rates as small as 0.3 nm/min have been reported when the Sn layer becomes a few nanometers thin [Her2010]. Another experiment in the same study revealed that enhanced re-deposition of Sn occurs on Ru substrates compared to Si substrates.

Another factor related to the cleaning, may be the morphology of the Sn layer. A rocky island-type morphology is observed on Sn samples prepared for cleaning experiments. Though, the morphology is different depending on substrate material and thickness of the Sn layer [Spo2012, Soe2012], as shown in figure 2.4. With an island-like structure, the surface of the substrate will be exposed, enhancing its effect on the cleaning process for that particular sample. In what way the morphology is linked to the cleaning rate is yet to be determined.
Theoretical studies predict that the tin cleaning rate is strongly influenced by the temperature of the tin contaminated substrate [Spo2012]. As shown in figure 2.5, the cleaning rate is expected to decrease quickly with increasing temperature. Unfortunately, no explanations are suggested for this strong temperature effect and literature is lacking to validate these theoretical findings. Nonetheless, the temperature of the experimental setup will be monitored during the cleaning experiments.

Since oxide films are believed to stop the dissociation of tin hydrides, adding a little oxygen may increase the cleaning rate by eliminating Sn re-deposition. Nevertheless, a study on Sn cleaning using Ar/Cl₂ plasma shows that increasing water vapor pressure decreases the cleaning rate dramatically [Shi2008], as shown in figure 2.6. Two explanations for this result are suggested by the authors. One, water reacts with the etchant, depleting the etchant density, and two, the Sn layer is rapidly passivated by the formation of an oxide layer, as is known in Al etching [Ago1989]. Besides that, Sporre et al. found that long-term oxidized samples could not be etched at all using hydrogen plasma. Important to note here is that many of their Sn
cleaning experiments resulted in no etching as well, supposedly due to wall contamination.

![Figure 2.6: Variation of cleaning rate with water vapor pressure at 5 sccm Ar / 25 sccm Cl2, and 20 mTorr processing pressure. Increasing water vapor pressure decreases the cleaning rate dramatically. Figure 2 from [Shi2008].](image)

Finally, different cleaning rates have been observed when varying pressure or gas flow. These effects can be most likely credited to varying atomic hydrogen fluxes. Quantifying this flux is essential to understand the effect of the H flux on the cleaning rate. The method used for measuring atomic hydrogen, and the corresponding results are described in chapter 4.

### 2.3 Hydrogen dissociation


In gas discharges, H₂ is not merely dissociated into atoms, but also ionized. Ions are an unwanted by-product when studying the role of atomic hydrogen to the cleaning process. A simple method for atomic hydrogen production through thermal cracking makes use of a hot tungsten (W) wire. When the wire has a temperature above 800 ºC, hydrogen molecules start to dissociate at the hot tungsten surface to form atomic hydrogen radicals [Hic1960, Smi1962]. Increasing the temperature of the wire enhances the radical production, as shown in figure 2.7. At temperatures above 2000 ºC, the tungsten wire starts to evaporate, causing contamination in the reactor chamber.
Figure 2.7: Dependence of the rate of formation of atomic hydrogen on tungsten filament temperature and hydrogen pressure. Gas temperature is 298K. Figure 12 from [Hic 1960].
Chapter 3
Experimental setup

To perform the cleaning experiments using atomic hydrogen, the Hydrogen Radical System (HRS) is used. In this setup, hydrogen is dissociated at the surface of a hot filament. The gas flow is directed along the filament straight to the sample holder which will contain the samples during the cleaning experiments. Five types of samples will be exposed to atomic hydrogen under various conditions. Before and after the cleaning experiments, the samples are analyzed using a range of diagnostics which will be discussed in this chapter.

3.1 Hydrogen Radical System

The HRS consists of a double cruciform shaped, stainless steel reaction chamber with eight large ports, as depicted in figure 3.1. At some of these ports, a connector part is placed containing three smaller ports. One of the small ports at the top is used to position the filament right above the sample holder. The filament consists of tungsten (W) wire with a diameter of 0.2 mm and seven windings with a diameter of 1.5 mm. The filament is connected to a power supply (Delta, ES 030-10); by altering the voltage over the filament, its temperature is controlled. The filament is operated at temperatures between 1250 °C and 1950 °C in order to sustain a sufficient H production. As discussed previously, above 2000 °C the evaporation of tungsten becomes important and may affect experiments. Within the selected temperature range, contamination of the system due to tungsten evaporation is avoided.

Figure 3.1: Schematic representation of the experimental setup including (a) a side view and (b) a top view of the Hydrogen Radical System.
During cleaning experiments, the filament is repeatedly on during 30 seconds, then off during 10 seconds. This duty cycle is implemented to avoid excessive heating of the experimental setup. When the filament is turned off, its temperature drops immediately and no more hydrogen is dissociated at filament surface. The duration of cleaning experiments is defined solely by the on-time of the filament, i.e. by the time that samples are exposed to atomic hydrogen.

The filament temperature is measured using a two-color pyrometer (Raytek Marathon series MR1SC) through a glass viewport. The measured temperature is reproducible to ±10 °C during the experiments. Although this statistical error cannot be disregarded, it does not affect the cleaning experiments. Nor does it affect the atomic hydrogen flux measurements that will be discussed in the following chapter. The primary purpose of measuring the filament temperature is to determine the required voltage corresponding to the desired temperature. Secondly, the pyrometer is used to verify that the voltage-temperature relation is preserved during all the experiments.

At the top of the HRS, a H₂ and a He gas lines are connected to the same inlet at one of the small ports. The He gas supply is an essential element in the atomic hydrogen measurements discussed in the next chapter. The gas lines are manually opened using a handle, and the gas flows are controlled by calibrated mass flow controllers (Bronkhorst EL-FLOW). The cleaning experiments are conducted with constant gas flows in the range of $7.07 \cdot 10^{-5}$ mol/s to $7.81 \cdot 10^{-5}$ mol/s (corresponding to 95-105 sccm).

The background pressure of the vacuum chamber (below $1 \cdot 10^{-6}$ mbar) is monitored using a pressure gauge (Granville-Phillips series 356 Micro-Ion Plus) ranging from high vacuum to atmospheric and calibrated for N₂. In addition, a capacitance manometer is employed to measure the pressure when gas flows through the reaction chamber. The latter gauge enables high-accuracy measurements independent of the nature of the gas. And finally, a capsule dial gauge (Edwards, CG16K) indicates the close-to-atmospheric pressure.

The pumping circuit of the HRS consists of a turbopump (Pfeiffer HiPace 80), supported by a scroll pump (Edwards, XDS10). The effective pumping speed for H₂ and He is 48 l/s and 58 l/s, respectively. Although these exact values are only valid for low pressures, helium is pumped more efficiently than hydrogen at any pressure. During the atomic hydrogen flux measurements a fixed pressure and gas flow are required, independent of the type of gas. In order to match the pressure during He inlet to the pressure during H₂ inlet at identical flow rates, the rotation frequency of the turbopump is adjusted. Table 3.A lists the combination of pressure, gas flow and the corresponding pumping frequency applied during the experiments. The combination of settings is selected such that the inlet of particles is varied as little as possible at different pressure. In order to do so, the complete range of pumping frequencies is utilized (without turning off the turbopump).
Table 3.A: Overview of different pressures with corresponding gas flow and pumping frequency used during the experiments.

<table>
<thead>
<tr>
<th>Pressure (Pa)</th>
<th>Gas flow (sccm)</th>
<th>Gas flow (mol/s)</th>
<th>Pump frequency (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>98.8</td>
<td>7.35⋅10⁻⁵</td>
<td>H₂ 1236</td>
</tr>
<tr>
<td></td>
<td>98.8</td>
<td>7.35⋅10⁻⁵</td>
<td>He 1500</td>
</tr>
<tr>
<td>100</td>
<td>104.2</td>
<td>7.75⋅10⁻⁵</td>
<td>H₂ 484.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>He 594.9</td>
</tr>
</tbody>
</table>

Inside the reaction vessel, a sample holder is mounted on a moveable arm, allowing it to move along the chamber’s vertical axis. A thermocouple is connected to the sample holder in order to monitor its temperature. The temperature of the sample holder will be a good indication for the temperature of the entire setup. Although the measurements are easily reproducible, the accuracy of these measurements is highly affected by the poor contact area between the thermocouple and the sample holder. Nonetheless, it is safe to say that the thermocouple and the sample holder are heated by identical mechanisms. Despite the poor contact between the two, their temperatures will be similar during cleaning experiments. A typical result of the temperature measurements during a cleaning experiment of 600 minutes is presented in figure 3.2. The duty cycle of the filament is reflected in the temperature measurements. Based on this graph, it can be concluded that the temperature of the sample holder will most likely not exceed 35 °C, even during long-term cleaning experiments.

![Figure 3.2: A typical temperature measurement during a cleaning experiment of 600 minutes at 100 Pa. The filament temperature is set to 1950 °C by applying 9.97 V over the filament. The duty cycle of the filament is reflected in the temperature measurements.](image)
3.2 Samples

In order to separately investigate different characteristics of the cleaning process, five types of samples have been prepared for the experiments. All samples consist of a Si wafer on which the materials of interest are deposited by magnetron-sputtering.

Sputter deposition is a physical vapor deposition (PVD) that involves ejecting material from a target onto a substrate. From the solid target material, atoms are ejected due to bombardment of the target by argon ions, as schematically shown in figure 3.3. These particles are generated using an argon plasma. The sputter gas, Ar, also serves as a buffer to slow down highly energetic ions coming off the target, which otherwise might damage the substrate. The argon plasma is confined close to the sputter target by strong electromagnetic fields resulting from a magnetron. The magnetron is operated at radio frequency (RF) in order to prevent charge build-up on the target. This improves the sputtering of low-conductivity materials.

![Figure 3.3: Schematic representation of sputter deposition. Atoms are ejected from a solid target due to the bombardment of the target by energetic ions from the sputter gas (argon).](image)

Using RF sputter deposition, the following samples are prepared to be used in specific cleaning experiments. First, samples with carbon are required to study and verify the linear relation between carbon cleaning rate and atomic hydrogen flux. For these samples, a solid C target is used to deposit approximately 20 nm of C onto 1 inch Si wafers.

Next, the cleaning rate of Sn as a function of atomic hydrogen flux and pressure is studied. To exclude any effects that the material of the substrate might have on the cleaning rate, samples are prepared with a relatively thick layer of Sn. This way, only tin-on-tin cleaning is studied, regardless of the material beneath the tin layer. Using a solid Sn target, approximately 160 nm Sn is deposited onto a Si wafer. Out of efficiency considerations, a large Si wafer with a diameter of 150 mm is covered with Sn and, after deposition, diced into 17 mm square samples.

Then, the effect of the substrate material is studied in-depth. To do so, two materials that are used in EUV lithography machines, have been selected as substrate, namely zirconium nitride (ZrN) and molybdenum (Mo). These materials are components of the multilayer mirrors, including the collector mirror, in the lithography machines. In order to use these materials as proper substrates, 20 nm of ZrN and 100 nm Mo have been sputter deposited on 1 inch Si wafers. Mo does not bond well to Si, so a 2 nm layer of titanium (Ti) was first sputter deposited on Si, followed by the Mo
deposition. On top of the prepared substrates, relatively thin layers of Sn have been
deposition using the described RF sputter technique. This results in samples with
30 nm Sn on ZrN and 20 nm Sn on Mo. The dissimilarity in Sn thickness is a
consequence of using the identical deposition exposures for different substrate
materials.

Lastly, the cleaning rate of tin oxide will be studied as well. A thin layer of SnO is
known to stop the decomposition of SnH\textsubscript{4}, thus preventing Sn redeposition.
Determining the cleaning rate of SnO will indicate whether it is desirable to oxidize
Sn contamination in order to enhance the cleaning process. For these experiments,
the substrate material must not influence the cleaning rate. Therefore, thick layered
samples are prepared, consisting of approximately 160 nm SnO on Si substrates. To
prepare these samples, a solid oxygen target is used in addition to the Sn target,
used also in the Sn depositions.

### 3.3 Diagnostics

All samples are analyzed before and after cleaning experiments to gain insight into
the various aspects of the cleaning process. First, the amount of carbon or tin (oxide)
on the samples is determined using ellipsometry and x-ray fluorescence (XRF)
respectively. The morphology of the tin layers is explored with a scanning electron
microscope (SEM); besides that, cross sections of the tin morphology are obtained
with a focused ion beam scanning electron microscope (FIB-SEM). Finally, a
selection of samples is analyzed using x-ray photoelectron spectroscopy (XPS) in
order to investigate the atomic composition of the upper few nanometers of the
sample.

#### Ellipsometry

Ellipsometry is a non-destructive and contactless technique, employed in the
current study to map the thickness of carbon layers on the samples. This optical
technique uses radiation for the characterization of dielectric properties of material
structure, typically thin films. The obtained dielectric properties can be used to
determine other structure properties, e.g. composition, roughness and thickness of
the thin film. The radiation beam can be focused, enabling the imaging of small
sample sizes. By leading the beam through various positions on the sample, the
desired characteristics can be mapped over a larger area.

With an ellipsometer, a change in polarization is measured as an incident radiation
in a known state interacts with the material of interest. Typically, such interaction is
reflection; besides that, it can include absorption, scattering and transmission of the
radiation. Regardless of the interaction type, the measured signal depends strongly
on the material's properties.

The change in polarization is represented by the amplitude ratio \( \Psi \); and the phase
difference \( \Delta \). Together, these quantities determine the complex reflectance ratio \( \rho \)
according to:
\( \rho = \tan(\Psi) e^{i\Delta} \) \hspace{1cm} (3.1)

In general, the measured values for \( \Psi \) and \( \Delta \) cannot be converted directly into dielectric properties of the sample. For this, a model is required to compare the obtained data to. In the case of analyzing a carbon sample to determine its thickness, this model includes the optical constants known for carbon and the properties of the underlying silicon substrate.

The spectrometric ellipsometer (J.A. Woollam Co. M-2000) used in this study has a spectral range of 210.9 to 999.0 nm. It is schematically depicted in figure 3.4. A light source emits radiation that is linearly polarized by a polarizer. It can pass through an optional compensator and falls onto the sample. After reflection, the radiation passes through another compensator and a second polarizer, which is called an analyzer, before it reaches the detector.

![Figure 3.4: Schematic representation of the spectrometric ellipsometer.](image)

**X-ray fluorescence spectroscopy**

X-ray fluorescence spectroscopy (XRF) is a well-established technique for the determination of the elemental composition of solid materials. X-ray fluorescence arises from a material that has been irradiated by highly energetic x-rays. It is the emission of secondary radiation, which is characteristic of the irradiated material. With this technique, the number of tin atoms per cm\(^2\) is determined on all tin containing samples (tin oxide included), before and after cleaning experiments.

In XRF, a sample is bombarded by an x-ray beam. The energy of the radiation is high enough to ionize the exposed elements; electrons are ejected from the inner orbitals of sample atoms. Now, the electronic structure of the atom is unstable, and electrons from the outer orbitals will fall back to fill the hole, as shown in figure 3.5.

![Figure 3.5: Schematic representation of x-ray fluorescence.](image)
The outer and inner orbitals have different energy levels. When an outer electron fills a hole in an inner orbital, a photon is emitted having the energy $E$ that equals the energy difference of the orbitals involved. The wavelength $\lambda$ of this photon is calculated from Planck's law:

$$\lambda = \frac{hc}{E}$$  \hspace{1cm} (3.2)

Here, $h$ is Planck's constant and $c$ is the speed of light. Since each element has distinct energy levels, an element can be identified by detecting the secondary radiation. The radiation can be analyzed by determining either the energy (energy-dispersive analysis) or the wavelength (wavelength-dispersive analysis) of the detected photons. In both cases, the intensity of the radiation is a measure for the concentration of the elements.

The analysis of the samples used in this study is wavelength-dispersive. The basics of a wavelength-dispersive spectrometer are depicted in figure 3.6. After irradiation, the fluorescent radiation is collimated and subsequently separated according to wavelength by crystal diffraction (Bragg's law).

![Figure 3.6: Schematic representation of the wavelength-dispersive spectrometer used for the XRF analyses of the tin and tin oxide samples. From [Phi2008].](image)

Within the electron orbitals of an atom, different energy levels exist. When a material is irradiated with x-rays, the electron distribution across the different levels within one orbital is altered [Smo2013]. This results in x-ray discoloration; the absorption spectrum, and thereby the reflection spectrum, of the material changes. The degree of discoloration, and with that the perceptibility, depends on the irradiated material. The discoloration is reversible, though it is a slow process at room temperature. The process can be accelerated with a temperature treatment; heating the material up to 350 °C for 20 minutes will suffice. The high temperature enhances the mobility of the electrons, enabling them to re-overcome the energy barrier more easily.
Although x-ray exposure might alter the appearance of the samples, the morphology and chemical properties of solid materials – plastics excluded – will definitely not be altered [Smo2013]. The XRF analysis is a non-destructive technique that has no effect on the cleaning results in any way. Therefore, no temperature treatment is performed on XRF analyzed samples.

**Scanning electron microscopy**

In this study, a scanning electron microscope (SEM) is employed to investigate the tin morphology on the samples, before and after the cleaning experiments. This technique images a sample by scanning its surface with a focused electron beam. The electrons interact with the sample atoms producing a signal that contains information about the sample’s topography and composition.

The SEM used in this study, a Philips XL50 SFEG, generates images by detecting secondary electrons. These electrons are emitted by atoms that are excited by the focused electron beam, similar to the case of x-ray fluorescence. The amount of detected secondary emission depends on the angle between the sample surface and the electron beam, and on the elements present in the sample.

The secondary electrons are ejected from the k-shell of the sample atoms, and have low energies (< 50 eV). Due to their low energy, the detected electrons must have originated from the upper few nanometers of the sample surface [Gol1981]. Secondary emission generated in deeper parts of the sample will be absorbed by other atoms before reaching the surface. Since electron beams are attenuated at atmospheric pressure, imaging by secondary electron detection requires the samples to be placed in vacuum inside the SEM.

The number of secondary electrons reaching the detector determines the intensity of the signal. If the electron beam hits the sample surface perpendicularly, the activated region is uniform across the cross section of the beam. A certain number of electrons will penetrate the sample without causing detectable secondary emission. As the angle of incidence increases, the penetration depth of the beam will decrease, and more secondary electrons will be detected. Hence, edges and non-uniform surfaces will appear brighter than flat surfaces in a SEM image, resulting in well-defined, three-dimensional images. Using the signal of secondary electrons, it is possible to obtain images with a resolution less than 0.5 nm. A typical image generated with SEM is shown in figure 3.7.
Figure 3.7: SEM image of a broken human hair. The image is magnified 1510 times. Image obtained by Frans Holthuysen [Ker2008].

Focused ion beam
A focused ion beam (FIB) system is in many ways similar to a SEM; the primary difference is the use of ions, instead of electrons. While a SEM generates top-view images of a sample surface, FIB enables the imaging of the cross section by milling a highly accurate trench into the sample. This technique is used to obtain a complete three-dimensional view of the tin morphology, especially after cleaning with atomic hydrogen.

Before FIB treatment, the entire sample is coated with a conductive carbon layer (nm range) to avoid charging of the sample due to ion bombardment. Subsequently, a platinum layer of 1 µm is deposited in the FIB at the region of interest to protect the top layers during the milling. Next, a small part of the sample material is removed with a very high spatial resolution. Due to its high precision, the FIB technique is preferred over other cutting methods.

The FIB system makes use of a finely focused beam of gallium ions. The ions have enough energy to remove sample material upon impact; this process is known as sputtering. The system is operated at high beam currents in order to mill a trapezoidal trench at the region of interest. The trench has one steep edge that is perpendicular to the sample surface, as shown in figure 3.8. After the milling, the cross-section of the sample is imaged at a tilted angle of 52° using a SEM.

Figure 3.8: Schematic representation of the FIB-SEM analysis. A trench with one steep edge perpendicular to the sample surface is sputter etched using FIB. Then, the sample is tilted and the cross section is imaged with a SEM. From [Wee2013].
The SEM images are recorded by detecting both secondary electrons and backscattered electrons. The analysis of secondary electrons primarily provides an image of the surface structure, as discussed in the previous subsection, whereas the backscattered electrons primarily contain information about the difference in density of studied materials.

Backscattering occurs when high-energy electrons from the incident electron beam are elastically scattered, i.e. reflected, at the sample surface. The electrons are backscattered more strongly by heavy elements than by light elements. Hence, areas with a high density or a large concentration of heavy elements will appear bright in a SEM image. Materials with low density are displayed darker.

For the entire analysis, a FEI Nova200 NanoLab system is used. This is a Small Dual Beam (SDB) machine equipped with both a FIB and a SEM column. This system has the advantage that a cross section made using the FIB can be imaged directly using the SEM, without exposure to air. A typical image generated with FIB-SEM is shown in figure 3.9.

![Figure 3.9: SEM image of a FIB cross section through a nanostructured photovoltaic architecture. From [Joe2014].](image-url)
Chapter 4
Measuring the atomic hydrogen flux

A controlling factor for the speed of the tin cleaning process is believed to be the number of hydrogen atoms arriving at a tin contaminated surface. Knowledge about this quantity is essential to gaining insight into the kinetics and efficiency of the tin cleaning process.

Various methods exist for measuring the number of hydrogen atoms; laser-induced fluorescence [Sch1991, Tse1994], mass spectrometry [Har1988, Hsu1991] and catalytic probes [Fox1959, Har1993 Moz1991, Tsu1995] are most commonly employed. In contrast to other methods, using a catalytic probe does not require significant investments. Its design and the physical principles on which its operation is based, are relatively straightforward. Moreover, this method quantifies the flux of atomic hydrogen on a surface, rather than its concentration. Therefore, a catalytic probe is the diagnostic method of choice for the atomic hydrogen measurements.

4.1 Theory
The operation of a catalytic probe is based on the recombination of hydrogen atoms. This recombination is an exothermic reaction, producing hydrogen molecules:

\[ 2 \text{H} \,(g) \rightarrow \text{H}_2 \, (g) \quad \Delta H^\circ = -435.94 \text{ kJ mol}^{-1} \]  

(4.1)

For this reaction to occur, a third body is required to participate in the process [Sma1929, Amd1933]. This can be either a gaseous hydrogen particle, or a surface [Sma1934, Ste1935, Amd1938]. In case of the catalytic probe, the probe’s surface will function as the third body.

Each recombination reaction will release an amount of energy to the surface that corresponds to the standard enthalpy of the reaction \( \Delta H^\circ \). The total energy released to the surface due to recombination is a measure for the number of recombination reactions at the surface. By determining the recombination heating power \( Q_{\text{rec}} \), the number of hydrogen atoms that reach the probe per second can be calculated. This atomic hydrogen flux \( \phi_H \) is calculated in (at cm\(^{-2}\) s\(^{-1}\)) using:

\[ \phi_H = \frac{2N_A Q_{\text{rec}}}{A_P \gamma \Delta H_{HH}} \]  

(4.2)

Here, \( N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1} \) is the Avogadro constant, \( A_P \) the surface area of the probe, \( \gamma \) the recombination coefficient and \( \Delta H_{HH} = 435.94 \text{ kJ mol}^{-1} \text{H}_2 \) the
recombination heat. The recombination heat equals the absolute value of the standard enthalpy from eq. 4.1.

The recombination coefficient $\gamma$ is defined as the ratio between the number of atoms recombining at the surface and the total number of atoms reaching the surface, per unit time. This coefficient strongly depends on the material of the surface. As a result, the recombination reaction proceeds more efficiently on some materials, such as glass, quartz [Woo1962] and metallic surfaces [Woo1961]. Several metals are known to have recombination coefficient close to 1; they exhibit high catalytic activity for atomic hydrogen recombination [Wis1967]. This is a desirable property for a material to construct a catalytic probe from, and will be elaborated on in the next subsection.

When using a catalytic probe to detect atomic hydrogen, the recombination heating power will not be factor influencing the temperature of the probe. In fact, multiple heat sources and sinks must be taken into account. All heat flows involved in the operation of the catalytic probe can be described in a steady-state heat balance:

$$Q_{in} + Q_{rad}^{in} + Q_{rec} = Q_{cond} + Q_{rad}^{out} + Q_{gas}^{H_2}$$ (4.3)

Here, $Q_{in}$ represents electrical input power which is used in some probe designs to heat the probe. This will be discussed in more detail shortly. The next term is the radiative heat load $Q_{rad}^{in}$ resulting from the presence of the hot filament. On the side of the heat losses, $Q_{cond}$ denotes the conductive heat loss through the leads of the probe, $Q_{rad}^{out}$ the radiative heating of the surroundings by the probe and $Q_{gas}^{H_2}$ the convective heat transfer from the probe to hydrogen gas.

Using the heat balance as a starting point, the recombination heat $Q_{rec}$ can be calculated when all other elements in eq. 4.3 are known. The magnitude of these elements are quantified by a series of measurements that will be described in section 4.3. The measurements are repeated for each set of conditions under which the atomic hydrogen flux is studied.

### 4.2 Design of the catalytic probe

Various designs of catalytic probes for hydrogen detection are proposed in literature [Tsu1995, Moz2006, Ugu2012]. In the basis, a catalytic probe is a piece of metal with a high recombination coefficient, immersed into an atomic hydrogen containing environment. The operation of the probe is characterized either by (A) measuring the temperature of the metal, or by (B) measuring the external power required to keep the metal temperature constant. Both operation methods have advantages and disadvantages.

The first method (A) is sensitive to possible variations of material properties and reaction kinetics with temperature. On the other hand, it allows for a very small probe (1 mm or less) to minimize the disturbance of the probed environment.
The most basic design of this type of probe is a thermocouple; its heat balance equals eq. 4.3 minus the term $Q_{in}$ [Tsu1995]. Another design based on the same method employs two thermocouples of identical materials. The first thermocouple is exposed to hydrogen atoms, whereas the second thermocouple is covered with a material having a recombination coefficient close to 0, as shown in figure 4.1. This way, the covered thermocouple experiences the same heat transfer mechanisms as the exposed thermocouple, except for the heating due to recombination.

![Figure 4.1: A catalytic probe consisting of two identical thermocouples of which one is coated. The recombination heat can be determined from the difference in temperature between the two thermocouples. Figure 2 from [Gru2006].](image)

The second method (B) eliminates temperature variations which enhances the accuracy of the atomic hydrogen flux measurements [Sut1995]. This type of probe is inevitably larger in size than the first type, which might be considered a disadvantage. In the context of the current study however, the size of the probe is of minor importance provided that it does not exceed the dimensions of the tin samples. This way, the probe is allowed to disturb the atomic hydrogen environment to the same extent as the samples do during cleaning experiments.

Due to the superior accuracy of the second method, this type of probe is selected for the current study. The most advanced probe design is described by Ugur et al. (2012). This design serves as a model for the catalytic probe developed in this study which is described directly below.

**The adopted design**

The basis of the catalytic probe is a platinum (Pt) foil on which hydrogen atoms efficiently recombine. Platinum is a commonly selected material for the construction of a catalytic probe. Its recombination coefficient is extensively studied, though the resulting values are contradicting [Woo1961, Mel1971, Gat1993]. A study into the reported values, that range from 0.03 to 1, indicates that these variations result from different levels of cleanliness of the platinum surfaces [Liv1994]. Livshits et al. concluded that the recombination coefficient for a clean platinum surface equals 1.
The 0.025 mm thick platinum foil (99.95% pure, Goodfellow) has a size of 30 x 5 mm². This size is chosen such that the foil is sufficiently large to facilitate a large number of recombination reactions, and small enough to avoid temperature gradients along the probe’s surface.

The foil is connected to three sets of wires, as shown in figure 4.2. To monitor the temperature of the foil, a K-type thermocouple is spot welded to the back of the foil at the center of a long edge. The foil is heated by running a current through it. To this end, two platinum leads (99.99% pure, Goodfellow) with a diameter of 1 mm are spot welded to the back of the foil; one on each side of the foil. A large, but workable diameter is selected for the Pt leads in order to prevent excessive heating through power dissipation. Leads with a smaller diameter reach such high temperatures that they start to glow, when carrying the maximum current required to sustain the probe’s temperature.

Two additional platinum leads are connected to the corners in order to measure the voltage over the foil. The position of the contact points between the foil of the leads is irrelevant for accurate voltage measurements [Pau1958]. Van der Pauw proved that this is true for any position at the boundary of the sample, provided that the sample is approximately two-dimensional. Besides that, the diameter of the leads must be at least one order of magnitude smaller than the dimensions of the sample [Web1999]. These criteria are met in the presented design of the catalytic probe.

![Figure 4.2: Schematic representation of the catalytic probe. The probe consists of a Pt foil to which a thermocouple (center leads) is connected, and four Pt leads; two leads carry the current (outer leads) that heats the foil and two are used to measure the voltage over the foil.](image)

### 4.3 The experiments

To measure the atomic hydrogen flux, the catalytic probe is mounted in the experimental setup described in chapter 3. As depicted in figure 4.3, the probe is placed in the same position as where the samples will be during cleaning experiments. The atomic hydrogen flux is determined for filament temperatures equal to 1300 °C, 1650 °C and 1950 °C using the experimental conditions described in the previous chapter.
During operation, the temperature of the probe is kept at 350 °C. In order to clean the surface of the probe prior to each set of measurements, the foil is degassed at 400 °C. This justifies the recombination coefficient of the platinum foil taken to be equal to 1. The temperature of the probe is actively stabilized by a PI regulated power supply (Delta, ES030-10) controlling the current through the foil. According to the temperature measurements, the current through the foil is adjusted. Meanwhile, the voltage over the foil is monitored using a 6 ½ digit multi-meter (Keithley 2100).

**Elements in the heat balance**

The steady-state heat balance (eq. 4.3) that applies to the catalytic probe in operation is depicted in figure 4.4. The magnitude of the elements in the heat balance are determined by a set of separate measurements discussed directly below. The required conditions per individual measurement are summarized in table 4.A at the end of this subsection.
First, the electrical input power $Q_{in}$ represents the power required to keep the probe's temperature stable throughout the measurements. As discussed, an actively stabilized temperature will enhance the accuracy of the flux measurements [Ugu2012]. This way, temperature dependent material properties and reaction kinetics of the probe remain constant during the experiments [Sut1995]. The magnitude of $Q_{in}$ is simply the product of the current through and the voltage over the platinum foil. This value depends on the operation conditions.

The conductive and radiative heat losses $Q_{cond}$ and $Q_{rad}^{out}$ are determined cumulatively. The sum of these terms equals $Q_{in}$ at high vacuum and with the filament turned off. The magnitude of the sum is assumed constant throughout the measurements due to the constant temperature of the probe.

The term $Q_{rad}^{in}$ denoting radiative heating of the probe, results from the hot filament. In order to dissociate hydrogen at the filament surface, a filament temperature is required exceeding 800 °C as discussed in chapter 2. At these high temperatures, the filament will emit thermal radiation. The magnitude of $Q_{rad}^{in}$ depends only on the temperature of the filament $T_f$. The magnitude of $Q_{rad}^{in}$ is measured also at base pressure; this time, the filament is in operation. Then, the radiative heat input resulting from the hot filament can be calculated from:

$$Q_{rad}^{in} = Q_{in} - (Q_{cond} + Q_{rad}^{out})$$  \hspace{1cm} (4.4)

Next, determining $Q_{gas}^{H_2}$ requires a more elaborate quantification, since the contribution of the convective heat transfer from the probe cannot be isolated like the other terms. The term $Q_{gas}^{H_2}$ represents the heating of the gas by the probe, while the gas is also heated by the hot filament. This produces atomic hydrogen, so the values of both $Q_{gas}^{H_2}$ and $Q_{rec}$ are non-zero and as yet unknown. The recombination heat can be eliminated by replacing the hydrogen gas in the reaction chamber by another, similar gas. Helium gas resembles hydrogen most closely and has shown to be an appropriate replacement in the context of these measurements [Gat1993].
Helium and hydrogen gas have different thermal properties, so a different input power is required to maintain the probe’s temperature. To determine a correction factor for this difference, the convective cooling of the probe by the separate gases is investigated. The convective cooling rate of gas X can be found from a probe measurement with the filament turned off, and by using:

\[ Q_{gas}^X = Q_{in} - (Q_{cond} + Q_{rad}^{out}) \]  

(4.5)

The cooling rate of both gases is determined at identical pressure and gas flow by altering the pumping speed of the turbopump, as discussed in the previous chapter. The correction factor is embodied by \( k \), the ratio between the convective cooling rate of hydrogen and that of helium:

\[ k = \frac{Q_{gas}^{H_2}}{Q_{gas}^{He}} \]  

(for \( T_f = 0 ^\circ C \))  

(4.6)

Next, the convective cooling effect of helium \( Q_{gas}^{He} \) is determined, while the gas is being heated by the hot filament. The heat transfer from the filament depends on its temperature. Therefore, the magnitude of \( Q_{gas}^{He} \) is determined for every filament temperature of interest and by using:

\[ Q_{gas}^{He} = Q_{in} + Q_{rad}^{in} - (Q_{cond} + Q_{rad}^{out}) \]  

(4.7)

Then, the magnitude of \( Q_{gas}^{H_2} \) under atomic hydrogen producing conditions is calculated from:

\[ Q_{gas}^{H_2} = k \cdot Q_{gas}^{He} \]  

(4.8)

The required conditions for the separate quantification of each term described above, are summarized in table 4.A. After this series of measurements, every term in the heat balance for atomic hydrogen production (eq 4.3) is quantified, except for \( Q_{rec} \). Using equation 4.3, the magnitude of the recombination heat is obtained from a measurement with hydrogen flowing and the filament powered up. And with these results, the atomic hydrogen flux is obtained from equation 4.2 for every set of H producing conditions.

**Table 4.A: Overview of the operating conditions under which the separate measurements are performed in order to quantify each term in the heat balance (eq. 4.3).**

<table>
<thead>
<tr>
<th>Quantified term</th>
<th>Filament</th>
<th>Hydrogen flow</th>
<th>Helium flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q_{cond} + Q_{out}^{rad} )</td>
<td>off</td>
<td>off</td>
<td>off</td>
</tr>
<tr>
<td>( Q_{rad}^{in} )</td>
<td>on</td>
<td>off</td>
<td>off</td>
</tr>
<tr>
<td>( k )</td>
<td>off</td>
<td>off</td>
<td>on</td>
</tr>
<tr>
<td>( Q_{gas}^{He} )</td>
<td>on</td>
<td>off</td>
<td>on</td>
</tr>
<tr>
<td>( Q_{rec} )</td>
<td>on</td>
<td>on</td>
<td>on</td>
</tr>
</tbody>
</table>
4.4 Results and Discussion

In order to obtain the magnitude of the atomic hydrogen flux impinging on the probe’s surface, the recombination heat in eq. 4.3 is quantified. By conducting the described series of measurements, all elements in the heat balance are determined one by one. The results are presented and discussed next.

First, the radiative and conductive heat losses due to the constant probe temperature, \( T_p = 350 \, ^\circ\text{C} \), are determined at background pressure (< 10^{-6} \, \text{mbar}). The measurements with the catalytic probe at vacuum show that the radiative and conductive cooling together are responsible for a heat loss of \( 0.334 \pm 0.001 \, \text{W} \). The obtained accuracy results from the accuracy of the current and voltage measurements that determine the electrical input power. The radiative cooling of the probe \( Q_{rad}^{out} \) will not change, as the temperature of the probe is constant. The conductive heat loss to the wires \( Q_{cond} \) might slightly vary due to temperature changes in the wires. The input power of the probe varies significantly throughout the different measurements, influencing the temperature of current carrying wires. However, the contact area between the wires and the foil is small enough to neglect temperature changes in those wires. Therefore, the value obtained for \( Q_{cond} + Q_{rad}^{out} \) is assumed to be constant throughout the experiments.

The radiative heating due to the hot filament \( Q_{rad}^{in} \) is also determined at base pressure. Besides directly heating the probe, the filament causes an indirect radiative heat load by heating the walls of the reaction chamber. The term \( Q_{rad}^{in} \) is a combination of these two radiating components of the setup. The magnitude of this heat load is measured as a function of filament temperature, as shown in figure 4.5. The results indicate that the radiative heat load is not proportional to the filament temperature. The values are obtained with an absolute error of 0.002 W based on the stability of the probe and the accuracy of the values obtained for \( Q_{in} \) and \( Q_{cond} + Q_{rad}^{out} \).

![Figure 4.5: The radiative heat load on the catalytic probe caused by the hot filament.](image-url)
Next, the convective heat transfer from the probe to the surrounding gas $Q_{\text{gas}}^{H_2}$ is determined at different pressures. The gas flowing along the probe represents a significant heat sink, especially at higher pressure. Besides the probe, also the hot filament and the heated walls will transfer heat to the gas. In order to determine whether this extra heating affects the convective heat transfer from the probe, the cooling effect of the gas is first determined as a function of filament temperature. Since the hot filament will dissociate hydrogen resulting in recombinative heating of the probe, helium is used for these measurements. The cooling power can be determined with an error of 0.02 W using eq. 4.7 and taking into account the errors of the associated heat terms. The results in figure 4.6 (left) demonstrate that the cooling effect of the gas depends on pressure, but it is unaffected by the temperature of the filament. This suggests that the gas is cold and the probe is cooled by gas conductions to the walls. This can be explained by the fact that the residence time of the gas in the chamber is in the order of a few seconds, based on the gas flow and the volume of the vacuum chamber. The molecules are heated once passing by the filament, after which they lose that energy during several collisions with the cold walls before reaching the probe.

![Figure 4.6: The cooling power of helium on the probe as a function of filament temperature (left), and the cooling power of both helium and hydrogen at different gas pressures (right).](image)

The aforementioned method to determine the cooling power of hydrogen in the presence of a hot filament assumes that hydrogen and helium act in a similar fashion under the studied conditions. This means that it is fair to assume that the cooling power of hydrogen is not affected by filament temperature either. Then, $Q_{\text{gas}}^{H_2}$ can simply be determined when the filament is turned off and no atomic hydrogen is being produced. Calculating $k$ as a means to obtain $Q_{\text{gas}}^{H_2}$ is now unnecessary. The cooling power of both hydrogen and helium is plotted as a function of pressure in figure 4.6 (right). The hydrogen cooling power at 100 Pa represents 86% of the total cooling power acting on the catalytic probe. At 5 Pa, the ratio $k = Q_{\text{gas}}^{H_2}/Q_{\text{gas}}^{He}$ equals 1.95 which corresponds to the ratio $k \approx 2$ determined in a previous study [Ugu2012]. Hydrogen gas exhibits a greater cooling power than helium does.
However, helium cools relatively better at higher pressure. Besides the observed pressure dependence, the cooling power of a gas depends on both the thermal conductivity and the heat capacity of the gas. The values of both the thermal conductivity $\kappa$ and the heat capacity $C_m$ are larger for hydrogen than for helium. The respective ratios at room temperature are $\kappa_{H_2}/\kappa_{He} = 1.19$ (at low pressure) and $C_{m,H_2}/C_{m,He} = 1.38$ [Lid2003]. Based on these ratios, it can be expected that hydrogen cools the probe more actively than helium does.

With the obtained results of the different heat loads, the recombinative power $Q_{rec}$ can be calculated from inserting the heat loads into the steady-state heat balance. The magnitude of the recombinative heat load is presented in figure 4.7 as a function of filament temperature, at different pressures. At 100 Pa and $T_f = 1950$ °C, the heating power due to recombination represents only 7% of total input power heating the probe.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.7.png}
\caption{The recombinative heat load detected by the catalytic probe.}
\end{figure}

In order to determine the accuracy of the obtained values for the recombinative heating, a simple error analysis is conducted using the complete heat balance:

$$Q_{rec} = (Q_{cond} + Q_{rad}^{out}) + Q_{gas}^{H_2} - Q_{rad}^{in} - Q_{in}$$  \hspace{1cm} (4.9)

Then, the absolute error for the obtained recombinative heat load $\Delta Q_{rec}$ simply is the sum of the absolute errors found for all others terms in the heat balance:

$$\Delta Q_{rec} = \Delta Q_{cond + rad\, out} + \Delta Q_{H_2\, gas} + \Delta Q_{rad\, in} + \Delta Q_{in} = 0.024 \text{ W}$$  \hspace{1cm} (4.10)

The error of the electrical input power $\Delta Q_{in}$ is determined to be 0.001 W based on the accuracy of the current and voltage measurements. The values for all elements in the heat balance obtained at 100 Pa and with $T_f = 1950$ °C are listed in table 4.B, together with the corresponding errors.
Table 4.B: The values obtained for all elements in the heat balance, at 100 Pa and with $T_f = 1950$ °C, together with the corresponding errors.

<table>
<thead>
<tr>
<th>Heat balance elements</th>
<th>Magnitude (W)</th>
<th>Error (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{\text{cond}} + Q_{\text{out}}^{\text{rad}}$</td>
<td>0.334</td>
<td>0.001</td>
</tr>
<tr>
<td>$Q_{\text{gas}}^{H_2}$</td>
<td>2.14</td>
<td>0.02</td>
</tr>
<tr>
<td>$Q_{\text{rad}}^{in}$</td>
<td>0.0216</td>
<td>0.002</td>
</tr>
<tr>
<td>$Q_{\text{in}}$</td>
<td>2.29</td>
<td>0.001</td>
</tr>
<tr>
<td>$Q_{\text{rec}}$</td>
<td>0.164</td>
<td>0.024</td>
</tr>
</tbody>
</table>

From the recombinative heat load, the magnitude of the atomic hydrogen flux at the surface of the probe is calculated using eq. 4.2. The obtained flux values are plotted as a function of filament temperature in figure 4.8. The absolute error of these flux values is obtained through

$$\Delta \phi_H = C \Delta Q_{\text{rec}} = 4.4 \cdot 10^{16} \text{ at cm}^{-2} \text{ s}^{-1}$$

(4.11)

with $C = 2N_A/A_P \gamma \Delta H_H = 1.84 \cdot 10^{18} \text{ J} \text{ cm}^{-2}$. The calculated magnitude of the absolute error implies that the atomic hydrogen fluxes generated with $T_f = 1300$ °C are rather inaccurately determined. Therefore, no Sn cleaning experiments will be performed at this low temperature.

Figure 4.8: The atomic hydrogen flux at the surface of the catalytic probe as a function of filament temperature.

The flux generated with $T_f = 1800$ °C at 5 Pa has not been determined, because the catalytic probe was damaged before the measurements corresponding to these conditions could be finished. Therefore, only the fluxes generated with $T_f = 1650$ °C and $T_f = 1950$ °C at 5 Pa, 50 Pa and 100 Pa are selected for the cleaning experiments.
Chapter 5
Results and discussion

Several cleaning experiments have been conducted in order to study the reaction mechanisms involved in the atomic hydrogen-based cleaning process. The main output of these experiments is the cleaning rate, representing the amount of removed material per unit time. As discussed in chapter 2, the exposure time is accurately controlled using a computer, and the amount of removed material is obtained from the difference in material thickness measured before and after cleaning. The accuracy of the thickness measurements dictates the accuracy of the obtained cleaning rates; this will be discussed in detail in the following sections.

The cleaning rate is primarily studied as a function of atomic hydrogen flux and exposure time. The accuracy of the atomic hydrogen flux measurements is intensively discussed in the previous chapter, and is therefore excluded from the following discussion of the cleaning experiments. Exposure time is defined as the time during which the filament is turned on, producing hydrogen atoms, and is accurately controlled. The obtained values of the cleaning rate are time-averaged over the duration of the cleaning experiment, unless mentioned otherwise.

Firstly, the carbon cleaning rate is determined by exposing carbon samples to quantified atomic hydrogen fluxes. The obtained results are compared with results from previous studies. Secondly, a series of experiments is conducted to focus on the tin cleaning process. Initially, ‘thick’ Sn layers are exposed to fixed amounts of atomic hydrogen in order to study the effects of pressure and atomic hydrogen flux. Next, ‘thin’ Sn layers are exposed to a fixed atomic hydrogen flux at 100 Pa to gain insight into the interaction of Sn particles with the substrate material. Before and after the cleaning experiments, the samples have been extensively analyzed, using the previously discussed diagnostics, in order to understand what exactly happens during the cleaning process.

5.1 Carbon cleaning results

The carbon samples are used to conduct cleaning experiments at the same conditions as the atomic hydrogen flux measurements. The accuracy of the obtained cleaning rates is dictated by the accuracy of the carbon thickness measurements. The carbon thickness is determined before and after the cleaning experiments using imaging ellipsometry. The resulting thickness profiles are shown in figure 5.1. Each black dot on the profile represents a data point. The thickness on the unexposed sample (left) displays a small gradient, likely a result of the used carbon deposition method. The large thickness gradient observed on the cleaned sample (right) results from partially covering the sample with aluminium (Al) foil during the cleaning experiments. This enables double checking of the carbon removal; (a) by calculating
the difference in thickness obtained from pre- and post-cleaning measurements, and (b) by studying the thickness distribution of the cleaned sample. The aluminium foil was carefully folded around the sample, as depicted in figure 5.2, to disturb the carbon layer as little as possible. However, this resulted in a narrow opening between the sample and the edge of the foil. Due to the small gap, the thickness profile after cleaning displays a gradient, rather than a sharp transition. From the ellipsometry measurements, the removed amount of carbon can be determined with an error of 2%.

**Figure 5.1:** Thickness profiles of carbon samples obtained with ellipsometry, (left) pre- and (right) post-cleaning measurements. The thickness gradient observed on the cleaned sample is results from partial coverage of the sample during the cleaning experiment.

**Figure 5.2:** The carbon sample (left) is partially covered with aluminum foil (right) during the cleaning experiments. This enables double checking of the carbon removal.

The carbon cleaning rate is determined for various sets of conditions, i.e. at pressures $p$ of 5 Pa, 50 Pa and 100 Pa, and with filament temperatures $T_f$ of 1650 °C and 1950 °C. The results from these cleaning experiments are depicted in figure 5.3. The carbon cleaning rate demonstrates a linear dependence on the atomic hydrogen flux within the studied range of conditions, especially when the origin is included as a data point. This linear relation can be expected based on first-order reaction mechanisms of carbon cleaning discussed in chapter 2. Methane desorption from carbon films is found to be first-order [Kup1995]. Methane is released after a methyl group (CH$_3$) at the surface adsorbs a fourth hydrogen atom. This mechanism is fast and does not limit the cleaning process [Bal1975]. The presented results imply that the rate determining step for carbon removal is bond breaking between methyl molecules and the carbon film. The apparent linear relation supports the idea that
the inaccuracy of the calculated atomic hydrogen flux merely lies in the absolute values, and not so much in the relative values.

Figure 5.3: The cleaning rate of carbon is studied at various pressures (5 Pa, 50 Pa and 100 Pa) using different filament temperatures (1650 °C and 1950 °C).

Assuming that carbon cleaning is in fact linearly proportional with atomic hydrogen flux, the cleaning rate appears not to be influenced by pressure. However, maximum carbon etch rates as a function of pressure have been reported [Gra2003, Ebe2013]. Pressure is known to directly influence the atomic hydrogen flux impinging on a surface [Tsu1995]. In the aforementioned studies, the atomic hydrogen flux impinging on the carbon samples was not quantified. Therefore, those obtained maximum cleaning rates were most likely the result of an optimal atomic hydrogen flux, rather than pressure.

The cleaning rate can be used to calculate the efficiency \( \eta \) of the cleaning process. This quantity is defined as the number of carbon particles removed per hydrogen atom reaching the surface:

\[
\eta = \frac{\phi_C}{\phi_H}
\]  

(5.1)

Here, \( \phi_C \) is the flux of carbon particles leaving the surface primarily in the form of methane molecules, and \( \phi_H \) the atomic hydrogen flux to which the carbon sample is exposed. The results in figure 5.4 imply that the efficiency of the carbon cleaning process is fairly insensitive to both pressure and atomic hydrogen flux. The efficiency for cleaning with an atomic hydrogen flux ranging from \( 3 \times 10^{16} \) to \( 3 \times 10^{17} \) at cm\(^{-2}\) s\(^{-1}\) is found to be \( \eta = (2.05 \pm 0.77) \times 10^{-5} \). For comparison, an efficiency of \( (3.01 \pm 0.51) \times 10^{-6} \) is achieved by Braginsky based on cleaning experiments with fluxes in the range of \( 10^{18} - 10^{19} \) at cm\(^{-2}\) s\(^{-1}\). This value is nearly a factor 10 smaller than the currently obtained efficiency. This might very well be a result of differences in the experimental setup, such as the atomic hydrogen source, the geometry of the reaction chamber and the placing of the samples.
Figure 5.4: The efficiency of the C cleaning process is defined as the number of C particles that is removed per hydrogen atom. The C cleaning efficiency appears to be insensitive to both pressure and H flux.

5.2 Tin cleaning results

Next, the focus is shifted towards the main purpose of this project: the investigation of the atomic hydrogen-based cleaning of tin contamination. Under various conditions, the tin cleaning rate is determined based on the number of tin atoms removed from the sample. The number of tin atoms on the samples is measured using XRF. From these measurements, the removed amount of tin can be determined within an error range of 2%.

The tin cleaning process is studied by conducting a variety of cleaning experiments. Firstly, the tin cleaning rate is obtained from experiments identical to the carbon cleaning experiments using samples with ‘thick’ layers of tin (~160 nm). This way, tin-on-tin cleaning is studied independent of the underlying substrate. Moreover, a large amount of tin can be removed from these samples which enhances the accuracy of determining the cleaning rate. The set of operating conditions ($p = 5; 50; 100 \text{ Pa}$, $T_f = 1650; 1950 \degree \text{C}$) produces previously determined atomic hydrogen fluxes, as a function of which the cleaning rate is depicted in figure 5.5 (left). In contrast to carbon cleaning, the results of the tin cleaning rate do not necessarily demonstrate a linear relation with the flux. Rather, the results may suggest a less than linear relation that does not intersect with the origin. Such a relation does not correspond to conclusions drawn by Braginsky et al. [Bra2012]. However, the currently used atomic hydrogen fluxes only correspond partially to the smallest fluxes employed by Braginsky, as shown in figure 5.5 (right), making a comparison less straightforward. Besides, Braginsky assumes a linear relation based on data forming a straight line in a log-log graph. Such a line represents a relation of the form $y = ax^k$ where $a$ and $k$ are constant. The value of $k$ does not necessarily equal 1, in fact, $k \approx 0.75$ based on the slope of the trend line. Therefore, those results
might very well display a non-linear relation between cleaning rate and atomic hydrogen flux.

The non-linear behavior might be explained by the fact that tin hydrides are fairly unstable [Ugu2012(2)]. In order for tin to be removed from a surface, hydrogen atoms must be absorbed one by one until the volatile tin hydride SnH₄ is formed. Due to the instability of tin hydrides, hydrogen atoms will be occasionally desorbed forming hydrogen molecules. When (too) little hydrogen atoms are provided to a tin surface, the formation of SnH₄ might be too slow to compete with hydrogen desorption. Then, the cleaning rate drops quickly with decreasing atomic hydrogen flux. The cleaning rate might even equal zero in the presence of a non-zero, but small atomic hydrogen flux resulting in an offset. This could explain the lack of cleaning observed by Sporre et al. (2012); the atomic hydrogen flux to the tin surface was not quantified and might have been insufficient for effective tin cleaning.

Figure 5.5: (top) The cleaning rate of tin as a function of atomic hydrogen flux generated at various pressures. (bottom) The tin cleaning rate as a function of atomic hydrogen flux. Figure 4 from [Bra2012].

All data points appear to correspond to a mutual curve independent of pressure – similar to the carbon cleaning process. This insensitivity to pressure has not been reported before in tin cleaning studies. More experiments are required within the studied pressure range, and outside, to validate these findings.

Efficiency

The efficiency \( \eta \) of the tin cleaning process is determined in the same fashion as for the carbon cleaning process. Now,

\[
\eta = \frac{\phi_{Sn}}{\phi_H}
\]

(5.2)

where \( \phi_{Sn} \) is the flux of tin particles leaving the surface in the form of stannane, and \( \phi_H \) the atomic hydrogen flux to which the tin sample is exposed. The efficiencies calculated for the aforementioned experiments are displayed in figure 5.6. These values cover a similar range as the efficiencies obtained from the previous studies [Bra2012, Ugu2014]. In contrast to the current results, Braginsky assumes a constant efficiency and Ugur et al. (2014) observe that the efficiency increases with the atomic hydrogen flux. This difference might result from different operating
conditions, e.g. sample temperature, tin deposition method and exposure time. Additional experiments are needed to understand what factors determine the efficiency of the cleaning process.

Redeposition of tin atoms due to decomposition of tin hydrides on the sample, may seriously affect the observed cleaning efficiency. At higher pressure, volatile tin hydrides are more likely to return to the sample, since there are more particles present to collide with. Once tin hydrides reach a surface, they have a probability close to 1 of dissociating instantly [Ugu2014]. The effect of tin redeposition is most difficult to determine. Experiments may be designed in order to determine the actual rate of SnH₄ formation during cleaning, from which the redeposition rate may be deduced.

![Figure 5.6: Efficiency of tin cleaning experiments conducted under various conditions.](image)

**Tin versus carbon cleaning**

The tin cleaning rate is compared to the carbon cleaning rate in figure 5.7. Optimistically, the results indicate a less than linear relation between the two cleaning rates. This might be explained by assuming that CHₓ groups are more stable than SnHₓ groups. Then, even at low atomic hydrogen exposure volatile methane is being formed, whereas the formation of stannane is precluded by the desorption of atomic hydrogen forming hydrogen molecules. Clearly, more experiments are required to determine whether the observed relation is indeed less than linear.
A non-linear relation between the tin cleaning rate and the carbon cleaning can be expected based on previous results [Ebe2013]. However, the currently observed behavior does not fully correspond to the behavior displayed by previously obtained data shown in figure 2.3. The low end of this data range coincides with the currently obtained range of cleaning rates. A striking difference between the two data sets is the fact that, for previously obtained small cleaning rates, the carbon cleaning rate exceeds the tin cleaning rate. This might be a result of the different carbon samples used in the cleaning experiments. The atomic structure of carbon strongly depends on the deposition method. The type of atomic structure is very likely to influence the cleaning rate, since it determines the strength of the carbon-carbon bonds. It is not possible to correct the data for different atomic structures of carbon, or tin for that matter. Hence, additional experiments are required in which carbon and tin samples originating from only one batch each are exposed to a broad range of atomic hydrogen fluxes, preferably ranging from 10^{16} to 10^{19} at cm^{-2} s^{-1}.

**Circular patterns**

After the tin samples are exposed to atomic hydrogen, a circular pattern appears on the samples, as shown in figure 5.8. Such a pattern is not observed on carbon samples exposed under identical conditions, nor have observations of this pattern been reported in previous studies. The visibility of the circle appears to depend on the exposure time: a more distinct circle is observed after longer cleaning experiments. The fact that the pattern is perfectly circular makes it unlikely that it is merely a result of particle transport across the sample. The diameter of all observed circles is 15 mm. This equals exactly the diameter of the x-ray beam irradiating the samples during XRF measurements. As discussed in chapter 3, the absorption spectrum of a material changes when it is exposed to x-rays. Apparently, this effect becomes visible in tin layers only after sufficient exposure to atomic hydrogen. Moreover, the gradient that is observed within the circle may very well be a result of inhomogeneous deposition or removal of tin. Then, the circular patterns are expected to appear on different types of tin samples as well. This effect will be elaborated on during the discussion of the cleaning results obtained with the other samples.
In order to verify that x-ray exposure does not alter the morphology of the tin layers, the sample surfaces are studied with a SEM. Figure 5.9 displays the tin morphology observed inside and outside the circular pattern; this appears to be identical. The properties of the tin morphology will be extensively discussed later on. The studied sample has been exposed to atomic hydrogen during 60 minutes. Imaging other sample surfaces results in the same finding; the SEM-images do not show any difference between the structure of the tin surface inside and outside the circles. In fact, a marking on the circle's edge, like a scratch, is necessary in order to know where to look, since the morphology shows no indication of the where the edge of the circle is located.

Exposure time
In order to take a closer look at the mechanisms involved in Sn cleaning, samples with thick layers of tin are cleaned during different exposure times. All samples are exposed to a fixed atomic hydrogen flux generated with $T_f = 1950 \, ^\circ\text{C}$, at 100 Pa. The results shown in figure 5.10 indicate that the cleaning process includes a significant threshold period. During this time, the cleaning process is considerably less efficient. The duration of the threshold can be calculated from interpolating the results; it takes approximately 50 minutes to attain a steady (high) cleaning rate.
The observed cleaning threshold as a function of exposure time can be a result of several factors. One cause of the threshold might be the temperature of the sample. The sample is heated due to the exothermic formation of tin hydrides and hydrogen recombination, and due to the presence of the hot filament. With the current experimental setup, it was not possible to monitor the temperature of the samples. However, the temperature of the sample holder was monitored which does not exceed 35 °C, as discussed in chapter 3. The sample holder is primarily heated by the hot filament and reaches its maximum temperature in 60 minutes of cleaning at 100 Pa and with $T_f = 1950$ °C. With increasing temperature, the cleaning rate is expected to decrease [Spo2012]. Instead, the formation of tin hydrides advances after 50 minutes which should result in an increased heat load on the sample. Such temperature effects are not at all demonstrated in the above figure. Therefore, it may be concluded that the temperature of the sample does not cause the observed cleaning behavior.

Another possible cause for the observed offset might be the atomic composition of the top layers of the samples. The offset implies that removing the first mono-layers of the sample is the most difficult. These layers typically consist of native tin oxide and carbon which is spontaneously grown on the sample when exposed to air. This option will be elaborated on in the following paragraphs by investigating the cleaning process of tin oxide firstly, and the presence of carbon atoms (and other elements) secondly.

On all Sn samples, a native oxide layer of approximately 2 nm is present. In order for this oxide layer to induce the observed cleaning offset, the cleaning rate of tin oxide must be significantly smaller than the tin cleaning rate. This proposition is investigated by exposing samples with a thick layer of tin oxide (~170 nm) to atomic hydrogen generated at 100 Pa and with $T_f = 1950$ °C. Opposed to expectations [Spo2012], the results in figure 5.11 indicate that tin atoms are easier removed in tin oxide than metallic tin. In fact, oxidized tin atoms are cleaned nearly twice as fast as metallic tin atoms under the studied conditions; a finding that has not been reported.
before. The rapid cleaning of oxidized tin might be explained by two steps. Firstly, oxygen atoms readily recombine with both hydrogen atoms and molecules to form water. When an oxygen atom is removed from the tin oxide surface, the corresponding tin atom might be left with a dangling bond. Secondly, this dangling bond improves the absorption of hydrogen atoms by the tin atoms resulting in an enhanced cleaning rate for oxidized tin atoms. Regardless of the exact cleaning mechanisms for oxidized tin, the native oxide layers present on all samples cannot have caused the observed offset.

Figure 5.11: Thick layers of both tin and tin oxide are exposed to atomic hydrogen generated at 100 Pa and with \( T_f = 1950 \, ^\circ\text{C} \). Here, the cleaning processes of metallic tin and oxidized tin are compared based on the number of removed tin atoms as a function of exposure time.

In another attempt to understand the observed offset, the atomic surface compositions of two samples with originally thick layers of tin are analyzed using X-ray photoelectron spectroscopy (XPS). One sample, labeled SiO2Sn65, is analyzed in its original state, i.e. unexposed to atomic hydrogen. The average thickness of the tin layer on this sample is 161 nm. The second sample, labeled SiO2Sn51, is exposed to atomic hydrogen generated at 100 Pa and with \( T_f = 1950 \, ^\circ\text{C} \), during 600 minutes. An average thickness of 12 nm tin is left on this sample. The XPS measurements are conducted at two different positions close to the center of both samples, marked A and B as indicated in figure 5.12.

Figure 5.12: Positions A and B of the XPS measurements that are conducted on two Sn samples (SiO2Sn51 and SiO2Sn65).

The atomic concentrations (%) found in the upper 7 nm, i.e. the typical information depth of XPS, of the samples are presented in table 5.A. Within these top layers, approximately 90% of the tin on both samples is oxidized. The detected traces of chlorine (Cl) and argon (Ar) are negligible, since their atomic concentrations are below the detection limit of XPS. The most striking differences between the atomic
surface composition of both samples, are the concentrations of carbon and silicon. The large amount of silicon detected on the cleaned sample implies that the silicon substrate is not completely covered with tin anymore; this presumption will be studied next. The concentration of carbon found on both samples primarily results from spontaneous carbon growth. Upon exposure to air, carbon grows slowly but steadily on tin surfaces. The difference in the detected carbon concentrations is most likely a result of ‘age’ of the carbon layer. Both samples belong to the same batch and they are analyzed with XPS at approximately the same moment. However, one sample is cleaned between creation and XPS analyses, reducing the amount of carbon on this sample back to zero. On the unexposed sample, carbon had been growing for seven months, whereas carbon had only been growing for two months after the second sample was used in a cleaning experiment.

Table 5.1: Apparent atomic surface concentrations (%) detected on two Sn samples; the first is unexposed to atomic hydrogen and the second is exposed to atomic hydrogen for 600 minutes at 100 Pa. On both samples, XPS measurements are conducted at two different locations close to the center of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>Cl</th>
<th>N</th>
<th>O</th>
<th>Si (el.)</th>
<th>Si (ox.)</th>
<th>Sn (el.)</th>
<th>Sn (ox.)</th>
<th>Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2Sn65 (unexposed)</td>
<td>A 40.2</td>
<td>0.1</td>
<td>1.0</td>
<td>41.0</td>
<td>-</td>
<td>0.6</td>
<td>1.9</td>
<td>15.2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>B 40.7</td>
<td>0.1</td>
<td>1.2</td>
<td>40.4</td>
<td>-</td>
<td>0.4</td>
<td>1.9</td>
<td>15.3</td>
<td>-</td>
</tr>
<tr>
<td>SiO2Sn51 (exposed)</td>
<td>A 17.2</td>
<td>-</td>
<td>1.1</td>
<td>53.1</td>
<td>6.6</td>
<td>17.1</td>
<td>0.5</td>
<td>4.3</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>B 16.6</td>
<td>-</td>
<td>1.2</td>
<td>52.7</td>
<td>7.3</td>
<td>18.2</td>
<td>0.4</td>
<td>3.4</td>
<td>0.2</td>
</tr>
</tbody>
</table>

In order to check whether such carbon layers can account for the observed threshold, the threshold cleaning rate will be compared to a calculated cleaning rate. Assuming that the atomic composition of the top layers indeed account for the threshold, the cleaning rate during the threshold period can be described as a combination of cleaning rates for individual elements. By also assuming that this combination is simply the sum of the separate cleaning rates, an effective cleaning rate can be calculated. This effective cleaning rate will be compared to the actual cleaning rate in order to identify the effect of carbon growth on the cleaning process.

In order to perform the calculation, the cleaning rates for tin oxide and carbon cleaning obtained at 100 Pa and with \( T_f = 1950^\circ C \) are considered. The calculation will be based on the atomic concentrations detected on the unexposed tin sample, neglecting the atomic concentration \( \leq 1\% \). For the sake of simplicity, all tin and oxygen atoms in the upper layers are assumed to be cleaned according to the cleaning rate for tin oxide \( CR_{SnO} \) obtained after 50 minutes of cleaning. The carbon cleaning rate \( CR_C \) is taken to be the rate observed after 300 minutes of cleaning. Then, the cleaning rate for the upper mono-layers of the sample \( CR_{tot} \) is represented by a combination of cleaning rates for the detected elements:

\[
CR_{tot} = 0.4CR_C + 0.6CR_{SnO} = 1.73 \cdot 10^{13} \text{ cm}^2 \text{ s}^{-1}
\]  (5.3)
The computed value is compared to the threshold cleaning rate $CR_{Sn,60} = 5.83 \cdot 10^{12}$ at cm$^{-2}$ s$^{-1}$ that is obtained after 60 minutes of tin cleaning. This indicates that the relatively slow carbon cleaning cannot account for the observed threshold of approximately 50 minutes. To extent the calculation, $CR_{Sn,60}$ is replaced by $CR_{Sn,600}$, the tin cleaning rate obtained after 600 minutes of tin cleaning. Even then, the computed cleaning rate $CR_{tot} = 1.34 \cdot 10^{13}$ at cm$^{-2}$ s$^{-1}$ is overestimating the tin cleaning rate during the offset period. Therefore, spontaneous carbon growth may contribute slightly to the observed threshold, though carbon cannot solely be responsible for it.

As mentioned, the presented XPS data imply that the silicon substrate is partially uncovered after cleaning a tin sample. This indication is verified by studying the tin sample surfaces with a scanning electron microscope (SEM). The SEM-images displayed in figure 5.13 show that the tin layer of an unexposed sample covers the silicon substrate (almost) completely. During atomic hydrogen exposure, the tin is removed and the substrate becomes gradually uncovered. The area of uncovered spots on the substrate expands as a function of exposure time. The SEM-images show that the underlying substrate is exposed within 60 minutes of exposure, an amount of time that is fairly similar to the observed offset period. This observation corresponds to a conclusion from Sporre et al.: the growth of uncovered spots on the substrate is the precursor to an increased cleaning rate [Spo2012].

Figure 5.13: SEM-images made before and after the cleaning experiment depict the changing morphology of Sn layers as a function of exposure time. Starting from the left upper image and going clockwise, the imaged samples have been cleaned during 0; 20; 180; and 600 minutes.

On the uncovered substrate, small traces of tin remain which are similar to ‘coffee rings’. When a coffee drop dries on a solid surface, it leaves a ring-like deposit along its perimeter. The contact line of the drop is pinned to the underlying surface causing liquid from the interior of the drop to be transported to the edge where it
evaporates [Dee1997]. Although tin on the samples is not a liquid solution, a similar mechanism might be at work during tin cleaning. In fact, the traces may not be tin, but some minor contamination embedded in the tin layers.

**More circular patterns**
Next, samples with ‘thin’ layers of tin are exposed to a fixed atomic hydrogen flux generated at 100 Pa, and with $T_f = 1950 \, ^\circ$C. These samples consist of either ZrN or Mo containing a tin layer of 20 to 30 nm. After exposing these samples to atomic hydrogen, again circular patterns with a diameter of 15 mm appear on the surface, as shown in figure 5.14. However, the circles on some samples have a larger diameter of 20 mm. After consulting with the XRF analyst, those exact samples turn out to have been irradiated with a 20 mm diameter x-ray beam. This substantiates the proposition that XRF analyses prior atomic hydrogen exposure causes the observed circles.

![Figure 5.14: Photograph of tin containing Mo substrate showing a circular pattern after atomic hydrogen exposure.](image)

**Cleaning thin tin layers**
Using samples with thin layer of tin, the effect of the underlying substrate material on the cleaning rate is investigated. The substrate materials selected for these experiments are relevant to the field of EUV lithography. As described in chapter 3, the samples contain tin layers of 30 nm on ZrN, and tin layers of 20 nm on Mo. These samples are cleaned during varying exposure times, as shown in figure 5.15. In contrast to the cleaning rate of thick tin layers, the cleaning rate for these thinner layers is maximum at the start of the exposures. Even though short exposure times (several minutes) are not studied for thick layer cleaning, the previously observed offset period appears to be completely absent in the cleaning process of thin layers.
Although the cleaning of tin on ZrN starts off at a rate similar to the maximum observed cleaning rate of tin on Si substrates, the former rate has tripled after only one minute. Moreover, the cleaning rate of tin on ZrN is two to four times as high as the maximum observed cleaning rate of tin on Si, in the first two minutes of cleaning. In less than 20 minutes, the cleaning rate for both ZrN and Mo samples is diminished with a factor 10 to a steady value. However, this steady cleaning rate is approximately a factor 3 smaller than the steady cleaning rate obtained for thick layer cleaning.

In order to gain insight into the mechanisms causing this reversed offset, the effect of several factors is reconsidered. Regarding substrate temperature, all samples are exposed to equal heating by the hot filament. Especially for short exposure times, this cannot account for the great differences between the cleaning rates. Heating of the ZrN and Mo samples will be enhanced due to rapid stannane formation in the first two minutes. This effect might offer an explanation for the steep decline of the cleaning rate, since the tin cleaning rate is expected to decrease with increasing temperature [Spo2012]. However, initially elevated temperatures of the ZrN and Mo samples cannot explain the lack of a threshold period for thin layer cleaning.

In the search for an explanation for the observed difference between thick and thin layer cleaning, two additional samples are analyzed using XPS. The samples, one containing tin on ZrN (labeled ZrNSn09) and the other tin on Mo (labeled TiMoSn07), have not been exposed to atomic hydrogen. Once more, the XPS measurements are conducted at two different positions close to the center of both samples, marked as A and B in figure 5.16.
The atomic surface compositions found on these samples are shown in table 5.B, together with XPS results of the unexposed tin containing Si substrate. Approximately 30% of the atoms detected in the top layers of the ZrN and Mo samples consist of C atoms; significantly less than found on the Si substrate sample. Moreover, the thin layers of tin are relatively more oxidized than a thick Sn layer is. Combining those two findings, may explain a faster start of thin layer cleaning process. Besides that, the XPS results provide no further insight that might clarify the great differences between thick and thin layer cleaning.

Table 5.B: Apparent atomic surface concentrations (%) detected on three Sn samples; the first sample contains Sn on a Si substrate, the second on a Mo substrate, and the third on a ZrN substrate. All three samples have not been exposed to atomic hydrogen. The XPS measurements are conducted at two different positions (A and B) close to the center of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>Cl</th>
<th>Mo</th>
<th>N</th>
<th>O</th>
<th>Si</th>
<th>Sn</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2Sn65</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>40.2</td>
<td>0.1</td>
<td>-</td>
<td>1.0</td>
<td>41.0</td>
<td>-</td>
<td>0.6</td>
<td>1.9</td>
</tr>
<tr>
<td>B</td>
<td>40.7</td>
<td>0.1</td>
<td>-</td>
<td>1.2</td>
<td>40.4</td>
<td>-</td>
<td>0.4</td>
<td>1.9</td>
</tr>
<tr>
<td>TiMoSn07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>28.0</td>
<td>-</td>
<td>9.4</td>
<td>-</td>
<td>44.7</td>
<td>-</td>
<td>-</td>
<td>0.6</td>
</tr>
<tr>
<td>B</td>
<td>27.9</td>
<td>-</td>
<td>9.3</td>
<td>-</td>
<td>44.8</td>
<td>-</td>
<td>-</td>
<td>0.6</td>
</tr>
<tr>
<td>ZrNSn09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>31.7</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
<td>43.8</td>
<td>-</td>
<td>0.3</td>
<td>1.8</td>
</tr>
<tr>
<td>B</td>
<td>28.6</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
<td>45.9</td>
<td>-</td>
<td>0.2</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table A shows that traces of the substrate materials are detected on both samples. The substrates of the unexposed Si and ZrN samples are detected to a similar extent, indicating a similar tin coverage for both types of samples. The fact that 10% of the detected atoms consist of Mo atoms implies that the tin layer does not completely cover the Mo substrate. Both deductions are verified with SEM-images of all three sample surfaces, shown in figure 5.17.
Figure 5.17: SEM-images of original tin layers deposited on (a) Si, (b) ZrN, and (c) Mo. The Si and ZrN substrates are almost completely covered with tin, whereas the Mo substrate is partially uncovered.

Up to now, no explanation has been found for the cleaning rates observed for cleaning thin layers of tin. Studying the structure of the tin layers may provide a better understanding of the cleaning process. Therefore, all samples are studied with SEM, before and after atomic hydrogen exposure. Figure 5.18 demonstrates the transformation of the tin morphology on ZrN during cleaning. The SEM-images show that perfectly round tin islands are being formed on the substrate surface. A similar transformation of the tin morphology on Mo is observed. Therefore, figure 5.19 only displays the transformation during the initial 4 minutes of cleaning. Remarkably, the exposure time required to obtain distinct islands corresponds to the time after which a steady cleaning rate is observed.

Figure 5.18: SEM-images showing the transformation of the tin morphology of ZrN as a function of exposure time; tin islands are being formed almost instantly. From left to right and top to bottom, the samples are cleaned during 1; 2; 4; 20; 100; and 200 minutes.
Figure 5.19: SEM-images showing the structural transformation of tin on Mo. The transformation occurs in a similar fashion as for ZrN samples, resulting in circular islands. Therefore, only the transformation after 1; 2; and 4 minutes is depicted here from left to right.

Based on these SEM-images, the particle area coverage (PAC) can be determined for all samples. PAC denotes the percentage of the substrate area that is covered with tin particles. These values can be obtained from the SEM-images which show distinct tin islands, with a statistic error of 3%. In order to study the impact of PAC on the cleaning process, the cleaning rate is plotted as a function of PAC in figure 5.20. In this graph, the values of both PAC and cleaning rate are averaged over a period of (exposure) time. The time intervals are determined from the difference between the subsequent exposure times. The PAC during this time interval is simply defined as the average of the PAC values obtained at the beginning and the end of the interval. The cleaning rate during a time interval is determined by number of tin atoms removed within this interval, divided by the length of the interval. Then, the cleaning rate appears to increase rapidly with increasing PAC. In order to verify this result, cleaning samples with initially different PAC values is required. Then, no averaging is needed and conclusions can be based on more direct results. The data point sticking out at the right side of the graph corresponds to the cleaning rate obtained after one minute of cleaning. The ZrN substrate is covered by tin to a larger extent than the Mo substrate. After one minute of cleaning, the tin structure just starts to transform and island formation on ZrN is not observed yet.

Figure 5.20: Tin cleaning rate as a function of particle area coverage (PAC), for both ZrN and Mo substrates.
The average thickness of the islands can easily be calculated from PAC values and the amount of tin detected on the surface, assuming the islands are flat cylinders. These calculations are executed for ZrN samples and the island thickness is plotted as a function of exposure time in figure 5.21. In the same figure, the tin layer thickness determined with XRF is plotted. After island formation, the average thickness of the islands is fairly constant, while the total amount of tin on the sample is decreasing. The accuracy of the calculated island thickness is dictated by the statistic errors in the obtained PAC values and the systematic errors in the XRF analyses.

Figure 5.21: The average thickness of the observed tin islands, and of the tin layer according to XRF on ZrN substrates are plotted as a function of exposure time.

The tin islands are more closely inspected by imaging the cross section of the tin structures. The cross section is revealed by milling a trench into the sample using a focused ion beam (FIB), and images are generated using a SEM. In order to see the transformation of the islands during atomic hydrogen exposure, two tin containing ZrN substrates are selected for the FIB-SEM analysis. The first sample is cleaned for only 4 minutes, labeled ZrNsn06. The second sample is exposed to atomic hydrogen during 120 minutes, and labeled ZrNsn01. The images in figure 5.22 indicate that the islands are becoming more spherical during the cleaning process. This observation verifies that the tin islands maintain a fairly constant average thickness, while the area covered by the islands shrinks during cleaning.
The formation of spherical tin islands suggests that the tin particles become more mobile while exposed to atomic hydrogen. This chemical transport may be resulting from redeposition of tin. As discussed in chapter 2, tin itself acts as a catalyst for redeposition. Moreover, the contact angle of the tin islands decreases during the cleaning experiments. This suggests that tin is more easily removed from the substrate than from tin islands. The striking island formation of tin was not observed during cleaning experiments with thick layers of tin. Even though the amounts of tin left on the Si substrates after some experiments were comparable to the amounts of tin on either ZrN or Mo, the Si substrates never contained circular tin structures. This indicates that the mobility of tin particles on Si is very different from the tin mobility on ZrN and Mo. On the other hand, the different tin morphologies may be caused by the initial amounts of tin on the samples. Regardless of the cause of island formation, the removal of tin particles grouped in spherical islands appears to be the most difficult cleaning process.

In order to investigate the above propositions, more cleaning experiments are required. On one hand, an uncovered substrate appears to indicate an increasing cleaning rate for thick layer cleaning. However, the cleaning rate for thin layers significantly decreases with reducing PAC. These contradicting observations are far from being understood. Additional cleaning experiments may be conducted in order to study the proposed chemical transport and the mobility of tin during atomic hydrogen exposure. Cleaning tin samples with various particle area coverage may enhance the understanding of the effect of the uncovered substrate on the cleaning rate.
Chapter 6
Conclusions

The goal of this thesis was to understand the mechanisms that determine the tin cleaning process based on atomic hydrogen. In order to gain insight into the reaction process, the cleaning rate was studied as a function of pressure, exposure time and atomic hydrogen flux. The atomic hydrogen was generated at the surface of a hot filament and detected using a catalytic probe, prior to the cleaning experiments. The cleaning experiments were conducted in the Hydrogen Radical System (HRS); both carbon samples and various types of tin containing samples were exposed to quantified atomic hydrogen fluxes.

Catalytic probe
A catalytic probe at constant temperature is successfully employed to determine the atomic hydrogen flux impinging on its surface. The probe was placed at the same location as where the samples would be during cleaning experiments. The atomic hydrogen flux was obtained by determining the heating power due to atomic hydrogen recombination on the platinum foil, the basis of the probe. The recombination heat load was found by measuring all other heat sources and sinks influencing the probe's temperature. The atomic hydrogen flux was determined as a function of pressure and filament temperature, with an absolute error of $4.4 \cdot 10^{16}$ at cm$^{-2} \cdot s^{-1}$. For the planned cleaning experiments within a pressure range of 5 – 100 Pa, the quantified fluxes generated with $T_f = 1650 \, ^\circ\!C$ and $T_f = 1950 \, ^\circ\!C$ were selected. The magnitude of these atomic hydrogen fluxes have been determined with acceptable accuracy.

Carbon cleaning
First, the carbon cleaning process was briefly studied as a function of the atomic hydrogen flux. The carbon samples were cleaned under various conditions in order to compare the results to literature and to the upcoming tin cleaning results. The carbon cleaning rate demonstrated a linear dependence on the atomic hydrogen flux, especially when the origin was included as a data point. The apparent linear relation can be expected from literature. Therefore, the observed linearity supports the idea that the errors of the calculated atomic hydrogen fluxes lie in the absolute values, and not so much in the relative values.

The efficiency of the carbon cleaning process is fairly insensitive to both pressure and atomic hydrogen flux. This may be expected based on the displayed linear relation between cleaning rate and atomic hydrogen flux. The obtained efficiency lies well within the range of carbon cleaning efficiencies found in literature. Any
deviations may be the result of differences in the experimental setup, or in the atomic structure of the cleaned carbon layers.

**Tin cleaning**

The tin cleaning process is investigated by conducting several cleaning experiments, and by employing various diagnostics to analyze the samples. Prior to all experiments, XRF measurements were conducted to determine the amount of tin present on the samples. After exposure to atomic hydrogen, the cleaning rate was calculated from second XRF measurements indicating the amount of removed tin particles.

First, the tin cleaning rate was determined as a function of atomic hydrogen flux. Samples with ‘thick’ layers of tin were exposed to atomic hydrogen under conditions identical to the carbon cleaning conditions. In contrast to carbon cleaning, the tin cleaning rate is not proportional to the atomic hydrogen flux. When the tin and carbon cleaning rates are compared, the observed relation does not fully correspond to the behavior demonstrated by previously obtained results. Additional experiments are required in which samples with identical carbon or tin structures are exposed to a broad range of atomic hydrogen fluxes generated in one particular setup. Such a series of experiments can eliminate any deviations originating from differences in the experimental approach.

When studying the tin cleaning rate as a function of exposure time, a threshold period of approximately 50 minutes is observed. Several factors are investigated in order to find the cause of this threshold. During the initial 60 minutes of a cleaning experiment, the temperature of the entire system increases steadily up to a maximum of 35 °C. Based on literature, the cleaning rate is expected to decrease with increasing temperature. Therefore, heating of the system cannot account for the observed threshold period. The atomic composition of the first mono-layers of the samples is also considered as a factor affecting the cleaning rate. Significant amounts of carbon as well as native tin oxide layers have been detected with XPS analysis. Although the obtained carbon cleaning rate is much smaller than the tin cleaning rate, the measured amounts of carbon cannot have resulted in the observed threshold. Moreover, cleaning results demonstrated that tin oxide is even more easily removed than metallic tin. Then, the detected layers of native tin oxide enhance the cleaning rate rather than diminish it, and cannot have caused a cleaning threshold. The XPS results indicated that the silicon substrate underneath the tin becomes uncovered while the sample is being cleaned. Therefore, the surface of all samples was imaged with a SEM after atomic hydrogen exposure. The SEM-images showed that during long-term cleaning experiments, the silicon substrate becomes partially uncovered indeed. The time after which the substrate is clearly uncovered corresponds to the threshold period. The growth of uncovered spots on the substrate appears to be a precursor to enhanced cleaning. Additional short-duration cleaning experiments are required to understand the cleaning behavior during the
threshold period. Moreover, the effect of the uncovered substrate on the cleaning rate can be identified.

After atomic hydrogen exposure, sharp circular patterns were observed on the tin samples. This was a side-effect of the XRF measurements, during which the samples were irradiated with x-rays. The x-rays alter the absorption spectrum of the irradiated material without changing the material’s structure; an effect that apparently becomes visible after sufficient exposure to atomic hydrogen. The circular patterns were observed on all types of tin containing samples, and it was verified using SEM-images that the morphology of tin within the circle was identical to the tin morphology outside the circle.

Finally, the cleaning process of ‘thin’ layers of tin was studied as a function of exposure time. This cleaning process appeared to evolve completely different from thick layer cleaning. Instead of a long threshold period after which the cleaning rate steadily increases, the maximum cleaning rate for thin layers was observed within the first minutes of cleaning. In less than 20 minutes, the cleaning rate had dropped to a steady value which corresponded to only one third of the steady cleaning rate for thick layers. According to XPS analysis, the thin layers are relatively less contaminated with carbon and more oxidized. However, this does not explain the observed behavior of the cleaning rate. SEM-images indicate that circular tin islands are being formed on these samples, quickly after the start of the cleaning experiments. The time after which distinct islands have been formed corresponds to the time after which the cleaning rate has reached its steady value. The islands are becoming more spherical during the cleaning process. The formation of tin islands with a negative contact angle suggests that tin atoms rather stick to other tin atoms than to the substrate. Moreover, the tin atoms appear to become more mobile while exposed to atomic hydrogen. Removal of tin particles grouped in these spherical islands appears to be the most difficult cleaning process.

**Outlook**

The results discussed in this thesis contribute to the characterization of the tin cleaning process based on atomic hydrogen. The measurements of the atomic hydrogen flux can be improved by optimizing the operation of the catalytic probe. Optimization may be realized by simultaneously employing two isothermal probes as described in this thesis, one of which is covered with a material with a recombination coefficient close to 0. The recombination heat is simply determined by the difference in electrical input power of the two probes. This way, the need for quantifying each term in the heat balance individually, and the corresponding errors, can be eliminated.

Additional experiments are required in order to validate the recent observations regarding the tin cleaning process. This process is considered to be used as a non-destructive method of cleaning tin from EUV optics during lithographic operation. In order to optimize the cleaning process for this purpose, understanding of the
involved reaction mechanisms is required. Cleaning experiments in which tin is exposed to a broader range of atomic hydrogen fluxes in one particular setup will clarify the apparent non-linear relation between flux and the tin cleaning rate. Based on this relation, the tin cleaning rate in the EUV source may be predicted from theoretically modeling the present atomic hydrogen flux. Furthermore, the relevant mechanisms involved in the threshold period may be identified by studying the tin cleaning rate as a function of exposure time ranging up to 60 minutes. The role of the uncovered substrate as a precursor to an accelerated cleaning process must be verified. The extent to which the tin containing substrate is uncovered is strongly related to the transformation of tin islands. However, island formation appears to diminish the cleaning rate. This is an unfortunate and potentially game changing observation regarding the development of hydrogen atom based tin cleaning for EUV optics. Tin deposition on the collector mirror is typically observed as minuscule islands. Removal of these tin islands may be significantly less efficient than the cleaning of a relatively homogeneous tin layer. Further research is required into the causes of island formation and the effect of particle area coverage. Cleaning tin samples with various particle area coverage may enhance the understanding of the impact of tin morphology on the cleaning rate.
Bibliography

<table>
<thead>
<tr>
<th>Reference</th>
<th>Authors</th>
</tr>
</thead>
</table>


<table>
<thead>
<tr>
<th>Reference</th>
<th>Authors</th>
<th>Journal/Academic Work</th>
<th>Volume/Issue/Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sma1934</td>
<td>H. M. Smallwood</td>
<td>J. Am. Chem. Soc.</td>
<td>56, 1542 (1934)</td>
</tr>
<tr>
<td>Smo2013</td>
<td>Private conversation with Sjaak Smolders, XRF analysis expert at MiPlaza Materials Analysis, Philips</td>
<td>(2013)</td>
<td></td>
</tr>
</tbody>
</table>


