Tin etching from metallic and oxidized scandium thin films

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ABSTRACT

The role of oxide on Sn adhesion to Sc surfaces was studied with in-situ ellipsometry, X-ray photoelectron spectroscopy and secondary electron microscopy. Sn etching with hydrogen radicals was performed on metallic Sc, metallic Sc with a native oxide, and a fully oxidized Sc layer. The results show that Sn adsorbs rather weakly to a non-oxidized Sc surface, and is etched relatively easily by atomic hydrogen. In contrast, the presence of native oxide on Sc allows Sn to adsorb more strongly to the surface, slowing the etching. Furthermore, thinner layers of scandium oxide result in weaker Sn adsorption, indicating that the layer beneath the oxide plays a significant role in determining the adsorption strength. Unexpectedly, for Sn on Sc₂O₃, and, to a lesser extent, for Sn on Sc, the etch rate shows a variation over time, which is explained by surface restructuring, temperature change, and hydrogen adsorption saturation.

I. INTRODUCTION

In previous work, it was demonstrated that the formation of stannane (SnH₄), and, as a result, the successful etching of tin (Sn) from a metallic surface could be predicted by the electronegativity (χ) difference between the surface material and tin.¹ Sn can be successfully etched from surfaces consisting of metals with electronegativity values lower than or equal to Sn. Incomplete Sn etching was predicted for metals that have electronegativity values higher than that of Sn.¹ However, in that publication, all metals, except gold and silver were strongly oxidized (the presence of oxide on Ag could not be determined). Notably, metals with high electronegativities form weak oxides, while those with low electronegativity form strong oxides (e.g., scandium and aluminium), leaving open the question of the role of oxidation in tin adhesion.
Although in many conditions a metallic surface is oxidized, this is not universally true. In some cases, the native oxide layer can be removed by hydrogen reactive species, changing the surface properties.\textsuperscript{2} Furthermore, in many applications, such as extreme ultraviolet lithography (EUVL), space applications, and ultra-high vacuum (UHV) science, the environmental conditions may be sufficiently reducing, removing, at least temporarily, the surface oxide, and exposing the bare metal to surface processes.\textsuperscript{2,3} It is known that the presence of oxide on EUVL optics causes a reduction of reflectivity \textsuperscript{2,4}, thus optics with oxide-free surfaces would be beneficial in terms of optical performance. Because of the difficulties in preparing oxide-free metallic surfaces, there is limited published data on tin adsorption to non-noble, oxide free metal surfaces. To our knowledge, the role of oxide in tin etching from oxidized metals has only been studied in the context of molybdenum (Mo) and silicon (Si)\textsuperscript{5}, which have the same electronegativity as tin. However, it is unclear if Mo or Si are representative for low electronegativity materials. Furthermore, Mo oxide has a relatively low dissociation temperature \textsuperscript{6}, making it more likely that the etch process (and perhaps even the tin deposition process) will result in the reduction of the top layer of molybdenum oxide.\textsuperscript{7-12} Of the transition metals, scandium (Sc) has the lowest electronegativity, representing a relatively extreme case, and making it an ideal test case. By studying Sn adsorption and etching from Sc, and combining that with already published data on noble metals and Mo, it will be possible to conclude if the electronegativity difference is indeed the main predictor of the energy of adhesion between tin and the surface. Furthermore, by comparing etching from oxidized and metallic surfaces, it will be possible to determine if the oxide layer plays a significant role in Sn adhesion.

Previous surface adhesion and etching studies have used X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and ellipsometry, which, taken together, give a very good overview of the surface chemistry and morphology changes during various experiments.\textsuperscript{13-20} Of these, ellipsometry measurements, combined with modeling, provide layer thickness and material properties, making it an excellent tool for contact free determination of thickness and optical constants of films of all kinds.\textsuperscript{21-26} Ellipsometry can yield information about layers even down to a single atomic layer.\textsuperscript{21}
moreover, no reference measurement is necessary. Ellipsometry measurements are also very fast, providing high resolution temporal data. In situ XPS, on the other hand, has elemental sensitivities in the parts per thousand range, and is often directly sensitive to chemical changes in the top \( \sim 5\text{-}10\) nm of the surface layer \(^{15\text{-}20}\). However, XPS scans take much longer, limiting the temporal resolution of dynamic measurements. Moreover, XPS requires high vacuum \((10^{-8}\) mbar) or ultra-high vacuum, making it inappropriate for in situ measurements due to the relatively high pressure during etching. XRF has even higher elemental sensitivity than XPS, but no chemical sensitivity and cannot distinguish between surface and buried elements. Thus, in our study we use in situ ellipsometry to study Sn deposition and etching. XPS and SEM were used for ex situ analysis. In this paper we study the role of native scandium oxide on the adhesion between Sn and Sc.

II. EXPERIMENTAL

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

Tin deposition and etching takes place in an apparatus that has been described in detail elsewhere.\textsuperscript{1} Briefly, experiments are performed in two different manners: for oxidized samples, approximately 8 nm of Sn is evaporated onto the sample at a rate of 0.4 nm/min and, immediately afterwards, etched with hydrogen radicals (H\textsuperscript{˙}). For the metallic Sc sample, the C coating is first removed (determined by ellipsometry) using H\textsuperscript{˙} etching, after which, 8 nm of Sn is deposited, followed by H\textsuperscript{˙} etching. In all cases, the H\textsuperscript{˙} flux is generated by passing a molecular hydrogen flow (100 sccm) over a tungsten (W) filament that is heated to 2000 °C, which results in a hydrogen radical flux that was measured to be 10\textsuperscript{17} at/s·cm\textsuperscript{2} at the sample surface. The filament was operated in 5 min cycles to avoid excessively heating of the sample surface. In situ ellipsometry was used to monitor Sn deposition and etching. After Sn deposition and etching experiments, the samples were analyzed ex situ with XPS, as well as SEM with energy selective backscatter detector (SEM-ESB) and high efficiency secondary electron detector (SEM HE-SE2).

III. RESULTS

A. XPS analysis

Keeping the Sc layer of the 20 nm Sc sample type free of native oxide is crucial, thus, directly after deposition, a sample was analyzed by XPS with sputter depth profiling. From the elemental depth profile, presented in FIG. 2, it can be seen that the Sc layer is not completely oxygen free. However, the ratio of O to Sc in the layer is about 3:20, which is considerably less than the stoichiometric ratio for Sc$_2$O$_3$. To verify that the carbon layer prevented oxidation, a sample was kept in ambient for 2 months. Subsequent XPS measurements showed that the ratio of O to Sc did not change in that time.
XPS analysis of the as-deposited 5 nm Sc$_2$O$_3$/Sc and 3 nm of Sc$_2$O$_3$ samples were performed to determine the depth of oxidation of the Sc layers. In the case of 3 nm Sc$_2$O$_3$, the deposited Sc was almost fully oxidized, with less than 0.5 nm of metallic Sc remaining. For the 5 nm Sc$_2$O$_3$/Sc sample, the native oxide thickness was found to be 3.6 nm, in agreement with previous work, while the remaining 1.7 nm was elemental Sc. In both cases, the fit to the AR-XPS data indicates that there is some intermixing between Sc and Si. This intermixing may also explain the remaining metallic scandium found in the 3 nm Sc$_2$O$_3$ sample, since it was expected that the Sc layer would be fully oxidized in this case. Moreover, the surfaces of both samples were found to have a small amount of carbon and carbonate species due to exposure to ambient.

The protective layer of carbon on 20 nm Sc sample type was removed directly before Sn deposition and etching experiments. After in-situ ellipsometry monitoring of C removal (see details below) the sample was measured ex-situ with XPS (see FIG. 3).
The carbon layer, which was deposited with magnetron sputtering, is characterized by a high percentage of amorphous C, dominated by sp\textsuperscript{2} and sp\textsuperscript{3} bonding. In contrast, the C found on the etched sample has mostly sp\textsuperscript{3} bonded carbon and a small amount of carbonate, indicating that it is from a different source. The former is typical for magnetron deposited amorphous carbon, while the latter is consistent with atmospheric carbon contamination. From this, and the relative peak intensities of the underlying material, we conclude that the amorphous C was completely etched by H\textsuperscript{+} before the Sn was deposited.

**B. Sn deposition and etching measured with in-situ ellipsometry**

The in situ ellipsometry time-series data for Sn deposition and etching from the 20 nm Sc sample are shown in FIG. 4. The different stages of etching and deposition are indicated by different colors for the delta value, taken at a wavelength of 513 nm. Carbon etching is indicated by a black solid line, Sn deposition by a blue dashed line, and Sn etching by a red solid line. The five minute duty cycle of the H\textsuperscript{+} generator is visible during the C etching. After approximately 115 minutes of C etching, the delta value is constant, indicating that C etching is complete. The success of C etching was confirmed by ex situ XPS measurements (see above).
FIG. 4. Delta value at 513 nm from in situ ellipsometry measurement during carbon etching, Sn deposition and Sn etching on 20 nm Sc sample type.

Following C etching, 8 nm of Sn was deposited on the surface (see blue dashed line, FIG. 4). Afterwards, the sample was again exposed to H⁺ (in 5 minutes cycles) to etch the Sn (see red solid line FIG. 4). After two cycles of 5 min, the value of delta returns to that of metallic Sc, which suggests complete Sn etching. An XPS analysis, performed after Sn etching, failed to detect any Sn, indicating that the amount of remaining Sn is below the sensitivity of our XPS analysis (<0.2 at.%).

The Sc₂O₃ terminated samples were directly covered with approximately 8 nm of Sn and afterwards exposed to H⁺. Similar to the case for 20 nm Sc sample, the ellipsometry time-series data (see FIG. 5) show that Sn is completely removed. Delta values return to a slightly higher value (indicated on the FIG. 5 as a dashed lines for each sample) than before Sn deposition due to removal of surface contamination. However, the etch rate of Sc₂O₃ terminated samples is much slower than 20 nm Sc sample, as can be seen by the total etch time. Furthermore, the etch rate for the 5 nm Sc₂O₃/Sc sample is slower than for 3 nm Sc₂O₃. The different etch behavior for each of the three sample types is discussed in section IV Discussion.
FIG. 5. Delta value at 513 nm from in-situ ellipsometry measurement during experiments for 20 nm Sc, 3 nm Sc$_2$O$_3$ and 5 nm Sc$_2$O$_3$/Sc sample types.

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

FIG. 6. Tin etching rate for Sc, 5 nm Sc$_2$O$_3$/Sc, and 3 nm of Sc$_2$O$_3$ samples. The dashed lines represent the step between the 5 min etching cycles.
The etching rate changes over the whole etching process, as well as over a single 5 min cycle. The 20 nm Sc sample has the highest average Sn etching rate at 0.82 nm/min, while Sc$_2$O$_3$ terminated samples have a lower average etching rate, which was calculated to be 0.31 nm/min for 3 nm of Sc$_2$O$_3$, and 0.19 nm/min for 5 nm Sc$_2$O$_3$/Sc.

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

The decay in the etch rate over a single 5 minutes period is due to the temperature change of the sample. Sporre et al. showed that sample temperature has significant influence on the etch rate.\textsuperscript{30} It is expected from the modeling in ref. 30, that the etch rate rapidly decreases with increasing temperature. Higher temperature decreases the residence time of hydrogen at the surface, thus surface coverage is lower and, therefore, the etch rate goes down. Apart from the first etch cycle, which begins at room temperature, the temperature of the sample increases over a 5 min period from approximately 30 to 60 °C. The 30° temperature change in this temperature range can cause a decrease in the etching rate of up to 30% \textsuperscript{30}, which approximately fits the changes in etch rate that are observed during a single etch cycle. The temperature dependence does not significantly influence Sn etching from the Sc terminated sample, since the etching process is very rapid and most of the deposited Sn is removed in a single etch cycle.

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

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

The fastest etching rate was observed for the 20 nm metallic Sc sample. In this case the top outer-most layers consists of two metals, Sn and Sc, thus there is only a small barrier for electron transfer (contact potential of 0.85 eV, due to the metal-metal junction). When Sn is deposited, on a metallic Sc surface, electrons will be shared between those two metals. The more electronegative element attracts electrons to itself, which, in our case, is Sn ($\chi_{Sn}=1.8$, $\chi_{Sc}=1.3$). When reactive hydrogen species arrive at the surface, the Sn can easily form SnH₄, and Sn etching proceeds at a rate limited only by the accessibility of Sn to hydrogen radicals.

The situation changes when the Sc layer is oxidized. Due to the manner in which the scandium was oxidized, the oxide layer is likely to have a relatively large number of defect states in the bandgap that can accept electrons. Electrons from the Sn layer diffuse via tunneling to these defect states, taking into account that the reaction of atomic H at the surface can generate hot electrons with energies in the eV range. The defect states effectively trap electrons in the scandium oxide, slowing their return to the Sn layer, and slowing the Sn etch rate from 3 nm Sc₂O₃ sample in comparison to 20 nm Sc sample.

Although the etch rate of both samples with Sc₂O₃ is slower than the case for metallic Sc, it can be clearly seen that there is also a significant difference between 3 nm Sc₂O₃ and 5 nm Sc₂O₃/Sc samples. In the case of a Sc₂O₃ layer, separating Sn and Sc (5 nm Sc₂O₃/Sc), the electrons that diffuse into the defects in the oxide layer may end up in states that are above the equilibrium Fermi level, may decay to a lower energetic state by tunneling into the Sc layer. In this way, the metallic Sc acts as a reservoir for electrons, while tunneling back to the Sn layer must either occur directly, or via defect states. Low lying defect states must first be vacated by Sn etching before they can accept electrons from Sc, while high lying states are energetically unfavorable. Furthermore, the difference in work functions between Sn and Sc creates a driving potential that favors the diffusion of electrons from Sn to Sc, which can be clarified by treating this
structure as a metal-insulator-metal tunnel device (MIM) (see FIG. 7b). MIMs consist of a sandwich with a metal back electrode, an insulating oxide layer and metal top layer. The thin insulator layer (of a few nanometers) acts as high-pass filter for carrier transport.\textsuperscript{36-38} Although the transport is hindered or suppressed through the band gap of an insulator, (hot) electrons and holes may tunnel through the oxide barrier due to its small thickness and presence of local states in the band gap.\textsuperscript{38} Tunneling from a metal through a thin insulator to metal has been extensively studied for different material compositions.\textsuperscript{36-40} The difference in schematic band diagrams for 20 nm Sc, 3 nm Sc$_2$O$_3$ and 5 nm Sc$_2$O$_3$/Sc samples is presented in FIG. 7a, 7b and 7c. For drawing those diagrams, we used work function values for Si, Sc and Sn of 4.85 eV, 3.5 eV and 4.35 eV, respectively, while electron affinities were taken to be equal to 0.9 eV for SiO$_2$,\textsuperscript{41} and 0.85 eV for Sc$_2$O$_3$.\textsuperscript{43} Band gaps for Sc$_2$O$_3$, SiO$_2$ and Si are: 6.3 eV,\textsuperscript{44} 9 eV\textsuperscript{45} and 1.11 eV\textsuperscript{46}, respectively. The values of work function, electron affinities and band gaps are indicated on a relative scale on the diagrams below.

a) \hspace{2cm} b) \hspace{2cm} c)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{band_diagram.png}
\caption{Energy band diagram over the layers for 20 nm Sc a) 3 nm Sc$_2$O$_3$ b) and 5 nm Sc$_2$O$_3$/Sc c).}
\end{figure}

The work function difference between Sc and Sn leads to a built-in electric field over the Sc$_2$O$_3$ layer that makes tunnelling from Sc to Sn less favourable than the reverse. Electrons that tunnel through the oxide barrier must return when Sn is etched from the surface, thus the existence of the barrier still allows to etch Sn but at the same time significantly slows down the etch rate in comparison to 3 nm Sc$_2$O$_3$ and 20 nm Sc samples.
V. CONCLUSIONS

In conclusion, we have shown that tin can be fully etched from a metallic Sc surface as predicted by Pachecka et al. 1, as well from Sc thin films with complete and incomplete oxidation. Furthermore, our results show that the presence of Sc₂O₃ on a Sc thin film significantly slows the etch rate. The etch rate was found to change during the whole etch process, as well as over individual five minutes cycles. Changes in the surface area of the Sn layer (in between etch cycles) may account for rate changes between etch cycles, while temperature increases and possible saturation of the surface with hydrogen probably account for changes during an etch cycle. For Sn etching from oxidized Sc, trapping of electrons in defects of the Sc₂O₃ layer lowers the etching rate compared to metallic Sc surface. This effect is strengthened when Sc metal is present below the Sc₂O₃, due to the built-in electric field over the oxide generated by the difference in work function between Sc and Sn.

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