Depth Profiling of Tantalum Oxide Layers by Laser SNMS

A. Wucher, W. Berthold, M. Wahl

Fachbereich Physik, Universität Kaiserslautern, Erwin-Schrödinger-Strasse, D 67663 Kaiserslautern / Germany

1. Introduction

Secondary Neutral Mass Spectrometry (SNMS) has evolved as a widely used tool for quantitative surface and depth profile analysis. Among the different experimental realizations employed, non resonant multiphoton ionization represents a relatively new and promising method for non selective post-ionization of the sputtered neutral particles. In combination with time-of-flight mass spectrometry, the corresponding Laser-SNMS technique has also been named SALI /1/. The present study is devoted to the quantitation of measured SALI data for depth profiling of thin amorphous Ta$_2$O$_5$ layers anodically grown on Ta metal substrates. This sample system was chosen, because from similar measurements on ultrathin passivation layers on tantalum /2/ it is expected that for this particular sample the measured SALI signals will be strongly influenced by fragmentation of sputtered neutral molecules. It is known that sputtering of metal oxides produces - besides atoms - significant amounts of metal-monoxide molecules within the flux of sputtered particles /3/. It is therefore interesting to investigate depth profiles of such samples measured with the Laser-SNMS technique in order to gain some insight into the role of photofragmentation in the quantitation of Laser-SNMS data.

2. Experimental

The experiments were performed with an ultrahigh vacuum time-of-flight (ToF) Laser-SNMS system which has been described in detail elsewhere /4, 5/. The setup is based on a home made reflectron ToF mass spectrometer and equipped with a plasmatron microfocus ion gun (Atomika WF 421) which delivers rare gas ions of energies up to 15 keV. In the present work, mass selected 15 keV $^{40}$Ar$^+$ and 8 keV $^{133}$Xe$^+$ ion beams were used with beam currents of 500 nA ($Ar^+$) or 63 nA ($Xe^+$) and spot sizes (FWHM) of about 70 $\mu$m ($Ar^+$) or 150 $\mu$m ($Xe^+$), respectively. During the acquisition of mass spectra, the ion beam was operated in a pulsed mode with a typical pulse duration of 1 $\mu$s and spectra of 100 shots were accumulated in order to reduce statistical noise.

The sputtered neutral particles were postionized by means of a KrF excimer laser (Lambda Physik LPX 120i emitting UV pulses of about 20 ns length at a wavelength of 248 nm ($hv = 5$ eV). The beam was tightly focused to a spot size of approximately $10^{-2}$ mm$^2$ and directed parallel to the sample surface into a region located about 0.5 mm above the surface.

Sputter depth profiling was achieved by means of a sequence of two alternating cycles: First, the measurement of a ToF spectrum (data acquisition cycle) was performed using a fixed ion beam operated in the spot mode. Second, the sample surface was eroded in a sputtering cycle, during which the primary ion beam was raster
scanned across an area of about 0.25 mm² in order to produce a flat crater bottom. For this purpose, a digital scanning method was employed where the pixel frequency was synchronized with the ion beam repetition rate. Two complete scans were performed during each sputtering cycle. In the first scan, the primary ion pulse length was adjusted to the sum of all pulses fired during the acquisition of the preceding mass spectrum and the central point (where the data acquisition took place) was skipped. The purpose of this scan was to compensate for the sample removal during data acquisition, which was found necessary although the depth removed by a single ion pulse is less than 10⁻² nm. During the acquisition of a mass spectrum (100 shots), this already leads to the removal of up to about 1 nm, which in the course of a complete depth profile consisting of many subsequent mass spectra would accumulate to a deep hole in the center of the crater bottom. In the second scan, the primary ion pulse duration was lengthened according to the desired sample erosion depth between subsequent mass spectra.

The investigated samples were anodically grown Ta₂O₅ layers of 50 nm thickness on polished Ta sheet metal substrates. Details of the well established preparation procedure of these samples can be found elsewhere /6/ and will therefore not be repeated here.

3. Results and Discussion

Fig. 1 shows depth profiles of a 50 nm anodic Ta₂O₅ layer which were obtained using 15 keV Ar⁺ and 8 keV Xe⁺ ion sputtering, respectively. The quantities displayed in the figure correspond to integrated mass or ToF peaks and comprise the by far dominating signals observed in the mass spectra. The abrupt rise of the Ta⁺ and Ta²⁺ signals indicates the interface between the oxide layer and the metallic substrate. Assuming a constant, i.e. sputtering time independent sample erosion rate throughout the whole depth profile, the 90%-10% interface width can be estimated to be about 3 nm (15 keV Ar⁺) and 5 nm (8 keV Xe⁺), respectively.

From the ion dose necessary to reach the interface, the total sputtering yield of the oxide can be evaluated using the density of Ta₂O₅ taken from literature data (8.2 g/cm³ /7/). The resulting values are displayed in table 1 together with the sputtering

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Y₁₀⁻ (Ta₂O₅)</th>
<th>Y₁₀⁻ (Ta)</th>
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<tbody>
<tr>
<td>8 keV Xe⁺</td>
<td>7.1</td>
<td>4.1</td>
</tr>
<tr>
<td>15 keV Ar⁺</td>
<td>8.7</td>
<td>--</td>
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yield of the Ta substrate which was determined from a stylus profile measurement of a deeply sputtered crater. It is seen that the oxide yield is by roughly a factor of 1.7 larger than the metal yield, a finding which is in good agreement with similar data taken at lower bombarding energies /8/.

The only oxide specific signal observed in fig. 1 is that of sputtered TaO molecules. In a simple statistical model, the partial sputtering yield of monoxide molecules (MeO) and metal atoms (Me) from oxidized metal surfaces or metal oxides can be expressed by /3,9,10/

\[ Y_{MeO} = Y_0 \cdot c_{Me}^t \cdot c_O^t \cdot p \quad \text{and} \quad Y_{Me} = Y_0 \cdot c_{Me}^t \cdot (1 - c_O^t \cdot p) \]  
\[ \text{(1)} \]

where \( c_{Me}^t \) and \( c_O^t \) denote the surface concentration of Me and O, respectively, and \( p \) describes the probability for co-emission of a surface Me atom and a next neighborled O atom. Note that Eq. (1) allows a self-calibration of the oxygen surface concentration at every point of the depth profile by /11/

\[ c_O^t = \frac{1}{2} \left( 1 \pm \sqrt{1 - S_{MeO}/S_{MeO}^{\text{max}}} \right) \]  
\[ \text{(2)} \]

provided a clear maximum \( S_{MeO}^{\text{max}} \) can be observed for the TaO signal at some point in the depth profile. For the data displayed in fig. 1, this maximum is found directly at the interface. The resulting surface oxygen concentration under steady state sputtering conditions is \( c_O^t = 0.69 \) (15 keV Ar\(^+\)) and \( c_O^t = 0.65 \) (8 keV Xe\(^+\)), respectively, which indicates that practically no preferential sputtering of oxygen is observed under bombardment with 15 keV Ar\(^+\) ions.

Using the molecule formation model, we have shown previously, that in a Laser-SNMS experiment under the conditions employed here the measured Ta signal contains a considerable fraction of photodissociated sputtered neutral TaO molecules /2/. More specifically, the detected signals can be described by

\[ S_{TaO}^{\text{ss}} = I_p D_{TaO}^{\text{ss}} Y_{TaO} \quad \text{and} \quad S_{Ta} = I_p \left[ D_{Ta}^{\text{ss}} Y_{Ta} + F_{TaO}^{\text{ss}} Y_{TaO} \right] \]  
\[ \text{(3)} \]

where \( D_X^\text{ss} \) denotes the sensitivity factor for direct postionization of a species \( X \), \( F_{TaO} \) describes the fragmentation probability and \( I_p \) is the primary ion current during a pulse. Plotting the signal ratio \( S_{Ta}/S_{TaO} \) vs. the inverse of the oxygen surface concentration therefore yields a straight line corresponding to

\[ \frac{S_{Ta}}{S_{TaO}} = \frac{D_{TaO}^{\text{ss}}}{D_{Ta}^{\text{ss}}} \cdot \frac{1}{P} \left[ \frac{1}{c_O^t} - P \left( 1 - \frac{F_{TaO}}{D_{Ta}^{\text{ss}}} \right) \right] \]  
\[ \text{(4)} \]

which can be used to check the validity of the model. Fig. 2 shows such a plot for the two depth profiles depicted in fig. 1. Using a known value of \( p = 0.8 \) determined earlier /10/, relations between the quantities \( D_{TaO}^{\text{ss}} \), \( D_{Ta}^{\text{ss}} \) and \( F_{TaO}^{\text{ss}} \) can be deduced from the slope and intercept of the resulting fitting lines which are displayed in table 2. It is seen that i) the probability for dissociative ionization of sputtered neutral TaO molecules is significantly higher than that for its direct ionization and ii) the sensitivity factor of Ta is higher than that of TaO. These findings agree well with similar data extracted from depth profiles of ultrathin passivation layers on tantalum metal /2/. Interestingly, the values of \( D_{TaO}^{\text{ss}}/D_{Ta}^{\text{ss}} \) as well as \( F_{TaO}^{\text{ss}}/D_{Ta}^{\text{ss}} \) differ between the different measurements presumably due to slightly different laser focusing conditions employed in the two depth profiles. The ratio \( F_{TaO}^{\text{ss}}/D_{Ta}^{\text{ss}} \), on the other hand, is practically the same as that found in ref. 2 and therefore seems to be largely inde-

<table>
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<tr>
<th>Table 2</th>
<th>8 keV Xe(^+)</th>
<th>15 keV Ar(^+)</th>
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<tr>
<td>( D_{TaO}^{\text{ss}}/D_{Ta}^{\text{ss}} )</td>
<td>4.4</td>
<td>2.5</td>
</tr>
<tr>
<td>( F_{TaO}^{\text{ss}}/D_{Ta}^{\text{ss}} )</td>
<td>1.8</td>
<td>3.0</td>
</tr>
<tr>
<td>( F_{TaO}^{\text{ss}}/D_{Ta}^{\text{ss}} )</td>
<td>7.5</td>
<td>7.8</td>
</tr>
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Fig. 2: Straight line fits to the data displayed in a) Fig. 1a and b) Fig. 1b according to eq (4) in the text.

ependent of the laser power density.

Using the data of table 2, it is possible to examine the quantitation of the measured Ta signal. According to eq. (1), the total yield of Ta atoms sputter removed from the sample is given by \( c_{Ta}^2 Y_{Ta} \). Under steady state sputtering conditions (the plateau in the depth profiles), this number must be equal to \( c_{Ta}^2 Y_{Ta} \left( Ta_{2}O_{5} \right) \), where \( c_{Ta}^2 \) is the bulk concentration of Ta within the oxide and \( Y_{Ta} \left( Ta_{2}O_{5} \right) \) denotes the total sputtering yield of the oxide. Inserting this into eqs. (1) and (3) yields the ratio between the Ta signals measured in the oxide and the Ta substrate as

\[
\frac{S_{Ta}^{oxide}}{S_{Ta}^{metal}} = c_{Ta}^2 \cdot \frac{Y_{Ta} \left( Ta_{2}O_{5} \right)}{Y_{Ta} \left( Ta \right)} \cdot \left( 1 - c_{Fe}^2 p \left( 1 - F_{Ta}^2 \right) \right),
\]

where \( Y_{Ta} \left( Ta \right) \) is the total sputtering yield of the Ta substrate. For the depth profile of fig. 1b, we can insert the values of table 2, \( p = 0.8 \) and \( c_{Ta}^2 = 0.65 \) to obtain \( S_{Ta}^{oxide}/S_{Ta}^{metal} = 0.67 \). The experimentally measured signal ratio deduced from fig. 1b is 0.46 and, hence, by 30% lower than expected. This indicates a change of the sensitivity factor \( D_{Ta}^2 \) between the oxide and the metal by the same amount, a finding which may in principle arise from matrix dependent variations of the angular and energy distributions of the sputtered particles /

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