Depth scale calibration during sputter removal of multilayer systems by SNMS

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Kalibrierung der Tiefenskala beim Sputterabtrag von Vielschichtsystemen durch SNMS

Summary. A key problem in sputter depth profile analysis is the conversion of bombardment time of primary ion dose into eroded depth. In particular during sputter removal of multilayer structures, both the total sputtering yield \( Y_{\text{tot}} \) and the particle density of the sample and, hence, the sputter erosion rate will in general vary between the different individual layers.

The important role of this effect is demonstrated for secondary neutral mass spectrometry (SNMS) depth profile analysis of a model Ta-Si multilayer system where the observed ratio between individual Si- and Ta-layer removal times indicates an average film composition which is far off the TaSi \(_2\)-stoichiometry claimed by the manufacturer. The determination of absolute \( Y_{\text{tot}} \), as a function of sputter time from the recorded SNMS depth profile itself enables a nonlinear calibration of the depth scale which yields a ratio of \( d_{\text{Si}}/d_{\text{Ta}} = 2 \) between the individual Si and Ta layer thicknesses and, hence, confirms the true film stoichiometry.

for accurate sputter depth profile analysis. As a first approximation, the eroded depth \( z \) is usually described by the simple linear relation

\[
z(t) = \dot{z} \cdot t, \quad \text{with} \quad \dot{z} = j_p \cdot \frac{Y_{\text{tot}}}{n}
\]

(\( j_p \): primary ion current density).

During the sputter removal of multilayer systems, however, both the total sputter yield \( Y_{\text{tot}} \) and the particle density \( n \) of the sample will in general vary between the different individual layers. Hence, the erosion rate \( \dot{z} \) becomes a function of the sputtering time \( t \) and Eq. (1) has to be replaced by

\[
z(t) = \int_0^t j_p \cdot \frac{Y_{\text{tot}}(t')}{n(t')} \, dt'.
\]

As a consequence, an accurate calibration of the depth scale is feasible only if the time dependent total sputter yield is known. Several attempts to monitor \( Y_{\text{tot}}(t) \) in situ during depth profile analysis have been published which are based either on optical interferometry [1], electron induced X-ray emission [2] or quartz microbalance [3] measurements. These methods, however, require a substantial amount of additional equipment and are restricted to the analysis of special materials.

The problem can be addressed, however, in a simple manner if Secondary Neutral Mass Spectrometry (SNMS) is used as the analytical method. In SNMS, the flux of sputtered neutral particles is mass analyzed while the surface is eroded by ion bombardment. The sputtered neutrals are post-ionized by the electron component of an inductively coupled low pressure rf-plasma maintained in a noble gas (e.g. Ar). Due to the decoupling of the sputtering and ionization process of the analyzed particles, the neutral-to-ion conversion factor \( \alpha_X \) is an apparatus constant specific for a detected species X. Hence, if the fraction of the sputtered flux ejected as secondary ions is negligible, the SNMS signal \( I_X \) measured for a species X is proportional to the corresponding partial sputter yield \( Y_X \):

\[
I_X = I_p \cdot Y_X \cdot D_{Xo}
\]

(\( I_p \): primary ion current, \( D_{Xo} \): sensitivity factor for X).

Under steady state sputtering conditions and for atomic sputtering, \( Y_X \) is given by

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\[ Y_X = c_X \cdot Y_{tot}, \]  
and quantitation of SNMS is simple and straightforward yielding the bulk concentration of the element X in the sample as
\[ c_X = \frac{I_{X0}/D_{X0}}{\Sigma I_{X0}/D_{X0}}. \]  
The sum in the denominator is performed over all major peaks in the mass spectrum.

2 Depth scale calibration

As seen from Eq. (2), an accurate calibration of the eroded depth scale requires the knowledge of the time dependent total sputter yield \( Y_{tot} \) and particle density \( n \) of the sample. If all sputtered species X are considered, the total sputter yield is simply given by the sum over the partial sputter yields
\[ Y_{tot} = \sum_X Y_X. \]  
Making use of Eq. (3), the time dependence of \( Y_{tot} \) can readily be obtained from the measured SNMS intensities by
\[ Y_{tot}(t) = \sum I_{X0}(t)/D_{X0}, \]  
provided the sensitivity factors \( D_{X0} \) are known and constant throughout the acquisition of the depth profile.

A larger problem is the accurate determination of the time dependent particle density \( n(t) \). As an approximation, \( n(t) \) is taken as
\[ n(t) = \sum_X c_X(t) \cdot n_X, \]  
where \( n_X \) denotes the density of the pure bulk material X and the \( c_X(t) \) are calculated from the SNMS signals according to Eq. (5). Combining Eqs. (2), (7) and (8) the time dependence of the depth \( z \) actually eroded at a sputter time \( t \) can then be calculated by
\[ z(t) = \frac{1}{\sum_X n_X \cdot I_{X0}(t')/D_{X0}} \int_0^t \left( \frac{\sum_X I_{X0}(t')/D_{X0}}{\sum_X I_{X0}(t')/D_{X0}} \right)^2 dt'. \]  
If relative sensitivity factors \( D_{X0}/D_X \) are determined for all sputtered species (for instance from the SNMS analysis of standard materials), the proportionality constant in Eq. (9) must be calibrated at one point either by using a known layer thickness or, for example, by a mechanical stylus profile subsequent to the sputter depth profile analysis.

An interesting point of discussion is the question whether the depth scale calibration method described above is still valid during depth profiling across a relatively sharp interface between two adjacent layers A and B. Then, if the interface width is comparable to or smaller than the depth interval needed to achieve sputter equilibrium, the establishment of steady state sputtering conditions becomes questionable. It should be stressed here that the evaluation of \( Y_{tot}(t) \) according to Eq. (7) does not require steady state sputtering conditions and, hence, remains valid without any restriction even in this case. A problem, however, may arise if the densities \( n_A \) and \( n_B \) differ significantly. In this case, the time dependence of \( n \) across the interface has to be taken into account. Since the quantitation scheme leading to Eq. (5) is based on the assumption of sputter equilibrium, the depth scale calibration according to Eq. (9) may then be inaccurate, but only within the sharp interface region considered here. The order of magnitude of the effect depends on the particular material under investigation and ranges from some ten percent (e.g. most metal-metal-, metal-oxide- or metal-silicon-interfaces) to a factor of two as a worst case estimate.

3 Experimental results

The experimental setup for SNMS as being used in the present investigation has been described previously [4]. Hence, only the essential parameters of the particular apparatus being employed here (Leybold INA 3) will be reviewed briefly.

The system was mounted in a UHV-chamber with a base pressure of \( 3 \cdot 10^{-9} \) mbar. The SNMS-plasma was operated at an Ar pressure of about \( 1.6 \cdot 10^{-3} \) mbar. The samples were bombarded under normal incidence with a 250 eV Ar\(^+\) ion beam of 1 mA/cm\(^2\) extracted from the plasma. The sputtered neutral particles were partly post-ionized in the plasma and subsequently energy and mass analyzed with an energy window of 20 eV and unit mass resolution.

Two different model samples were chosen in order to examine the depth scale calibration described above which were a) a single 50 nm Ta layer and b) a sandwich-like Ta-Si multilayer system with a double layer thickness of \( d = 20 \) nm and a total film thickness of 200 nm. In both cases the film was sputter deposited onto a (100)-orientated Si substrate. The average film stoichiometry of the multilayer system was claimed by the manufacturer to be TaSi\(_x\), with \( x \) being slightly below 2. The Ta-Si system was chosen for two reasons. First the densities of bulk Ta and Si differ only by about 10\%. Hence, the time dependence of the particle density can be neglected during depth profiling. Second, a comparison of the relative sensitivity factor (RSF) \( D_{tot}/D_{Ta,Si} \) determined from an NBS steel standard with Ta and Si impurities and from a TaSi\(_{2}\)-sample revealed agreement within 10\%. Therefore the RSF are confirmed to be matrix independent for this particular system.

Figure 1 shows the SNMS depth profile of the single Ta layer on Si. The original plot of the normalized SNMS intensities for Ta and Si vs. the sputter time \( t \) is displayed in Fig. 1a. Assuming a linear relation between sputter time and eroded depth and using the known layer thickness of 50 nm, a 90\% – 10\% width of the Ta-Si interface is evaluated from the Ta signal to be \( d_{Ta} = 3.15 \) nm. If literature data [5] of the sputter yields for bulk Ta and Si are taken and a linear interpolation of \( Y_{tot} \) is employed across the interface region, a corrected width of \( d_{corr} = 2.62 \) nm is obtained. Figure 1b, however, shows the variation of \( Y_{tot} \) with sputter time as evaluated from Eq. (7) using the RSF between Si and Ta. The absolute calibration of \( Y_{tot} \) in Fig. 1b was obtained from the known layer thickness and from the time needed to remove the Ta-layer. As seen from the figure, a pronounced increase of \( Y_{tot} \) is found across the Ta-Si interface leading to a maximum sputter yield at a time where the Ta signal has already decayed to 30\% of its maximum value. Since for the bombarding conditions employed here the ratio between the documented sputter yields for bulk Si and Ta is \( Y_{Si}^{bare}/Y_{Ta}^{bare} = 0.7 \) [5], this drastic increase of \( Y_{tot} \)
has to be specific for the sputtering of a two component Ta-Si phase generated within the interface region. In the silicon substrate, $Y_{\text{tot}}$ is found to decrease significantly below the value of $Y_{\text{Si}} = 0.24$ taken from ref. [5]. This is presumably due to surface charging caused by the poor conductance of the Si wafer which reduces the effective bombarding energy. (This effect does not occur during sputtering of the Ta layer due to surface conduction towards the sample holder.)

Figure 1c shows the concentration depth profile evaluated from the raw data in Fig. 1a by means of Eqs. (5) and (9). Because of the linear relation between the SNMS signals and the corresponding sputtering yields [cf. Eq. (3)] which enables the calibration of both the depth and the concentration axis, Fig. 1c is assumed to describe the true concentration profile. It is easily seen that the interface width in Fig. 1c is larger than $\Delta z_{\text{Si}}$ and $\Delta z_{\text{Ta}}$, namely $\Delta z_{\text{int}} = 6.70$ nm. As a consequence, interface widths determined from intensity-time profiles are questionable unless sputtering yield variations are explicitly excluded.

The SNMS depth profile measured for the sandwich-like Ta-Si multilayer structure is shown in Fig. 2. From the original intensity-time plot (Fig. 2a) the ratio of the time intervals $t_{\text{Si}}$ and $t_{\text{Ta}}$ needed to remove a single Si or Ta layer, respectively, is determined as $t_{\text{Si}}/t_{\text{Ta}} \approx 0.8$. Assuming a linear relation $z(t)$, this would give an average film stoichiometry of TaSi$_{0.8}$ which is far off the expected film composition. The time dependent total sputter yield $Y_{\text{tot}}(t)$, however, as determined from Eq. (7) and displayed in Fig. 2b, exhibits a variation by as much as a factor 2 between a Si and Ta layer. Interestingly, the sputter yield of the Si layer is found to be the higher one which again is quite in contrast to the data for pure bulk Si and Ta given in ref. [5]. Figure 2c shows the concentration depth profile as evaluated from Eqs. (5) and (9). It is apparent from the figure that a single Si layer is thicker than the following Ta layer. Defining individual layer thicknesses $d_{\text{Si}}$ and $d_{\text{Ta}}$ between points where $c_{\text{Ta}} = c_{\text{Si}} = 0.5$, we obtain a ratio $d_{\text{Si}}/d_{\text{Ta}} = 2.0$ according to an average TaSi$_{2}$ stoichiometry.

A different way to determine the average film composition involves time integration of the measured SNMS intensities. For a periodically structured multilayer system, it is sufficient to perform this integration over one periodicity.
interval $T$ corresponding to one double layer. For the profile shown in Fig. 2a the resulting average concentration ratio is

$$\frac{c_{Si}}{c_{Ta}} = \frac{D_{Ta} \int_{t}^{t+T} I_{Si}(t')dt'}{D_{Si} \int_{t}^{t+T} I_{Ta}(t')dt'} = 1.5.$$  (10)

This is in reasonable agreement with the average film composition as claimed by the manufacturer.

A striking feature of the depth profile shown in Fig. 2c is the fact that the maximum concentrations of both Si and Ta always remain below unity. Interestingly, the element with the larger layer thickness (Si) shows a lower concentration modulation. Hence, poor depth resolution of the depth profiling method is apparently ruled out as a possible explanation for this behaviour. Considering also the different widths observed at the Ta-Si and Si-Ta transitions, the individual Si and Ta layers have presumably been intermixed during the film deposition. The nature of the transport mechanism which apparently works differently at Ta-Si and Si-Ta interfaces has not been determined yet and will be the subject of a forthcoming paper.

4 Conclusions

It has been shown that during sputter depth profiling of multilayer systems the layer-to-layer variations of the total sputtering yield cannot a priori be neglected. As a consequence, the sputter erosion rate becomes time dependent and the assumption of a simple linear time-vs.-depth relation which is usually employed may be seriously misleading. It is therefore the objective of this study to show that SNMS depth profiles intrinsically contain all information needed to convert the sputter time or primary ion dose axis into a true depth scale.

In connection with the well known quantitation scheme of SNMS, model experiments on a Ta-Si multilayer system yield concentration depth profiles which are in good agreement with the film properties given by the manufacturer. Hence, the simple and straightforward depth scale calibration described here is believed to contribute towards fast, accurate and quantitative depth profile analysis of solids.

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References


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