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Depth resolution and preferential sputtering in depth profiling of sharp interfaces

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ABSTRACT

The influence of preferential sputtering on depth resolution of sputter depth profiles is studied for different sputtering rates of the two components at an A/B interface. Surface concentration and intensity depth profiles on both the sputtering time scale (as measured) and the depth scale are obtained by calculations with an extended Mixing-Roughness-Information depth (MRI)-model. The results show a clear difference for the two extreme cases (a) preponderant roughness and (b) preponderant atomic mixing. In case (a), the interface width on the time scale ($\Delta t(16-84\%)$) increases with preferential sputtering if the faster sputtering component is on top of the slower sputtering component, but the true resolution on the depth scale ($\Delta z(16-84\%)$) stays constant. In case (b), the interface width on the time scale stays constant but the true resolution on the depth scale varies with preferential sputtering. For similar order of magnitude of the atomic mixing and the roughness parameters, a transition state between the two extremes is obtained. While the normalized intensity profile of SIMS represents that of the surface concentration, an additional broadening effect is encountered in XPS or AES by the influence of the mean electron escape depth which may even cause an additional matrix effect at the interface.

1. Introduction

The concept of depth resolution in sputter depth profiling (using mainly SIMS, AES or XPS) has been established since 1976 as a useful means to represent a quality figure for the precision and accuracy of a measured depth profile [1–3]. Progress in quantification of depth profiles during the past twenty years has led to an improved understanding of the basic mechanisms that determine the depth resolution function (DRF) [1,2,4,5]. Its influence on definition and measurement of the depth resolution has been reviewed in a recent publication [6]. In accordance with the Surface Chemical Analysis Vocabulary of ISO [3], the depth resolution is defined as the "depth at an interface over which the signal from an overlayer on a substrate changes from 16% to 84% of their total variation between plateau values, is often used in AES and XPS". In SIMS, instead of a sharp interface usually a thin layer (often a "delta layer" of monoatomic thickness) is used to determine the depth resolution. Therefore the above definition (16–84%) cannot be applied, and the full-width-at-half-maximum (FWHM) of the measured profile of the thin layer is commonly given as a measure

of the depth resolution [2,6–8]. The relation between both definitions for different shapes of the DRF is given in Ref. [6], assuming a constant sputtering rate, independent of sample composition.

However, rather frequently, the different components of a sample are removed by sputtering with different partial sputtering yields. The result is preferential sputtering of one or more components compared to the others (sometimes also called differential or selective sputtering) [2]. Intuitively we may expect an influence on the depth resolution if the sputtering yields of the components are markedly different. For sputter depth profiling of single and multilayer sandwich samples there exist experimental [9–14] as well as theoretical [15,16] evidence that preferential sputtering of a component causes an improved depth resolution for that component. However, to the authors' knowledge, there is still no clear, quantitative relation between depth resolution and preferential sputtering. In the following, an attempt is presented to gain more insight in this relation, based on application of the extended Mixing-Roughness-Information depth (MRI) model [4,5,16]. Here, we only consider depth profiles at a sharp interface.

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2. Preferential sputtering: basic considerations (Fundamentals)

Different sputtering rates of the constituents of a multicomponent sample are known to have a considerable influence on the surface composition during depth profiling and therefore distort quantitative analysis. Thus, preferential sputtering of a component (or more generally, differential sputtering) can be looked upon as an additional matrix effect that has to be taken into account in quantification. The two main mechanisms which lead to preferential sputtering of a component in multicomponent samples are different momentum transfer in the collisional cascade and different surface binding energies [17,18], often accompanied by radiation enhanced diffusion [18,19], surface segregation [19–21] or decomposition of compounds [22]. For multicomponent systems, the component sputtering yields and their dependence on sample composition can be very complicated and are difficult to predict, although the TRIM/SRIM code offers such a possibility [23]. For pure elements, sputtering yields are easier to predict, and a comprehensive table for Ar+ ion sputtering is given in Ref. [24]. Prediction for oxide sputtering is rather difficult [22], but for a number of oxides sputtering rates have been compiled by Baer et al. [25].

At first, samples with constant, depth-independent bulk composition will be considered. Then, the dynamic case of depth profiling in a concentration gradient is treated, which is relevant for depth profiling.

2.1. Preferential sputtering for constant bulk composition

The collisional cascade induced by energetic ion bombardment results in atomic mixing and sputter removal of surface atoms which establish a surface layer of generally different composition of the bulk, the so-called altered layer in sputtering [2,26–28]. Thus, the different elemental sputtering yields are decisive for the composition of the surface layer during sputtering.

The total sputtering yield of a multicomponent system, Y_t, can be expressed as the sum of the different partial sputtering yields Y_i and their respective surface concentrations X^s_i (in mole fractions) [2]:

$$Y_t = \Sigma_i X^s_i Y_i \tag{1}$$

In sputter equilibrium, for constant sample composition, the material removed from the surface is given by the surface composition (actually the composition of the so-called altered layer in sputtering [2–4]) and the corresponding partial sputtering yields of each component. As required by mass conservation, the surface concentration of component I, X^s_i, which is removed from the surface layer with the partial sputtering yield Y_i, is equal to its bulk concentration, X_i, removed with the total sputtering yield Y_t [2,4,29,30]:

$$X^s_i Y_i = X_i \frac{\sum_i (X^s_i Y_i)}{\sum_i X_i} = X_i Y_t \tag{2}$$

where $\sum_i X_i = 1$, and the total sputtering yield Y_t is given by Eq. (1).

Whereas the sputtering yield is defined as sputtered atoms per incident ion, the sputtering rate dimension is length/time. This is the dimension we need in order to characterize a composition-depth profile measured as a function of the sputtering time. For a given primary ion flux and a pure element, the connection between the sputtering yield and sputtering rate (in terms of depth z removed in time t), dz/dt = q, is given by [2,4,31]

$$q = (j_P Y)/(eN) \tag{3}$$

with the primary ion current density j_p (A/m²), the elementary charge e (1.6×10^{-19} As), the total sputtering yield Y(atoms/ion), and N (atoms/m³) the atomic density of the sample. Keeping j_p constant and assuming N to be practically constant yields the sputtering rate q (m/s).

The relation between sputtering rate and sputtering yield for pure elements, Eq. (3), can be reformulated for multicomponent systems according to Eq. (2), where the total sputtering rate q_t is given by [14,32]

$$q_t \sum_i X_i = q_t = \frac{j_p}{e} \frac{\sum_i Y_i X^s_i}{N_m} = \sum_i X^s_i q_i \tag{4}$$

Where $\sum_i X^s_i = 1$ and N_m is the average atomic density of the surface layer. When N_m does not change during sputtering, and the sputtering yield of component i is constant and independent of composition, the component sputtering rate q_i is constant. Since these changes usually are small, this simplification is adopted in the following.

An important consequence of Eq. (4) is the fact that, if the concentration and the sputtering rate of each element are found by quantification of $n-1$ elements from a total of n components the sputtering rate and concentration of the last unknown component can be adjusted to satisfy the equation through the measured q_t. This theorem was applied in Ref. [14].

For simplicity, a binary system with components A and B is considered in the following. In such a system, the consequences of preferential sputtering for the change in surface composition were first pointed out by Shimizu et al. [30]. The basic connection between the surface concentrations X^s_A, X^s_B, of a sample with homogeneous bulk concentrations X_A, X_B, follows from Eqs. (2) and (4) and is given by [14,30,32]

$$\frac{X^s_A}{X^s_B} r_{A,B} = \frac{X_A}{X_B} \tag{5}$$

where $r_{A/B} = q_A/q_B = 1/r_{B/A}$[1] is the ratio of the sputtering rate of pure A, q_A, and that of pure B, q_B. According to Eq. (4), the total sputtering rate, q_t, is given by [2,14,33]:

$$q_A X^S_A + q_B X^S_B = (X_A X_B) q_t \tag{6}$$

Because $X_A + X_B = 1$,

$$q_t = q_B \left[X^s_A \left(r_{A/B} - 1 \right) + 1 \right] \tag{7a}$$

or

$$q_t = q_A \left[X^s_A \left(r_{A/B} - 1 \right) + 1 \right] \tag{7b}$$

Note the equivalence of Eqs. (7a) and (7b).

2.2. Preferential sputtering in a concentration gradient

In sputter depth profiling, the main interest is in determination of a changing concentration with depth, usually represented by an elemental intensity as a function of the sputtering time, t. The sputtered depth $z(t_1)$ at a sputtering time t_1 is given by

$$z(t_1) = \int_0^{t_1} \left(\frac{dz}{dt} \right) dt = \int_0^{t_1} q_t(t) dt \tag{8}$$

where (dz/dt) is the instantaneous, total sputtering rate $q_t(t)$ defined by Eqs. (7a), (7b). Absence of preferential sputtering means

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[1] Note that the basic condition for the validity of Eq. (5) with $r_{A/B}$ = constant is that components A and B have the same sputtering rate in an alloy of A and B as they have as pure elements. If the elemental sputtering effect depends on sample composition, the MRI model has to be extended by a respective matrix dependence.