QUANTITATION OF MOLECULAR SNMS SIGNALS

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1. Introduction

It is well known that the particle flux sputtered from an ion bombarded surface contains atomic as well as molecular species. Accordingly, mass spectra obtained by Secondary Neutral Mass Spectrometry SNMS show molecular signals at sometimes appreciable levels /1/. These signals contain quantitative information concerning the composition and structure of the investigated surface. In order to utilize this information, various mechanisms for the formation of sputtered molecules have been proposed in the literature /2/. In particular, the formation of sputtered heteronuclear diatomic molecules with large mass differences and strong ionic bonds between the constituents was shown to be described by the direct emission model DEM /3/. In this conceptually simple mechanism the heavy atom A of the molecule is considered to be hit at the end of a collision sequence, thus gaining sufficient kinetic energy to be sputtered. Co-ejection with a next neighboured lighter atom B being initially at rest is possible if

a) the internal energy of the system A-B (i.e. the energy in the center of mass system) does not exceed the bond strength D between A and B at the surface,

b) the center-of-mass energy is higher than the effective surface binding energy $U_0$ of the molecule A-B.

Utilizing a statistical approach /4/ for a mathematical description of the DEM, we introduce a co-ejection probability $P_{co}$ for the survival of exactly one bond between A and one of its nearest neighbours B during the sputter event.

Assuming a statistical distribution of surface atoms and defining a total average number $N$ of next neighbours to every surface atom, the mean number $\bar{n}$ of next neighbours $B$ of a surface atom $A$ is correlated to the surface concentration $c_B^s$ of B atoms by

$$\bar{n} = N \cdot c_B^s$$  \hspace{1cm} (1).

Hence, as a first approximation assuming $P_{co}$ to be independent of $c_B^s$, the partial sputter yield $Y_{AB}$ of a molecule AB is given by
2. Analytical applications employing molecular SNMS signals

2.1 Determination of oxygen surface concentrations on metals

As a first example SNMS monoxide molecule signals $I_{\text{MeO}}$ ($\text{Me} = \text{metal}$) were used to determine the oxygen surface concentration $c_O^S$ on Ta and Nb. Due to the direct proportionality between measured SNMS intensities and the corresponding partial sputter yields, eq. (2) leads to a parabolic relation for a binary surface composition. With $c_O^S = 1 - c_{\text{Me}}^S$, we obtain

$$I_{\text{MeO}} \sim c_O^S(1 - c_O^S)$$

which yields a maximum signal $I_{\text{MeO}}^\text{max}$ at $c_O^S = 0.5$. Hence, once $I_{\text{MeO}}^\text{max}$ has been measured an unknown $c_O^S$ can be readily determined from the corresponding $I_{\text{MeO}}$ by /5/

$$c_O^S = 0.5 \left(1 + \frac{I_{\text{MeO}}/I_{\text{MeO}}^\text{max} - 0.5}{1 - I_{\text{MeO}}/I_{\text{MeO}}^\text{max}}\right)$$

Polycrystalline Ta and Nb samples were exposed to $O_2$ with varying partial pressure $p_{O_2}$ under simultaneous bombardment with Ar$^+$-ions of 2 keV at 45°. The resulting equilibrium $c_O^S$-values are shown in fig. 1 as a function of $p_{O_2}$. As expected theoretically /6/, a linear correlation is found for low $p_{O_2}$, merging into saturation for high $p_{O_2}$. Note that the observed saturation surface compositions are in both cases close to the pentoxide stoichiometry.

In fig. 2 the $c_O^S$-values obtained from SNMS are compared to results from in situ AES measurements assuming a linear relation between the 510 eV-KLL-peak and

Fig. 1: Equilibrium oxygen surface concentration $c_O^S$ (see text).
the oxygen surface concentration. While the Nb results show fair agreement, significant deviations occur in the case of Ta for low 
\(c_0^S\), which are probably due to a 
\(P_{O_2}\)-dependent change of the 
O-concentration microprofile altering the AES sensitivity factor /7/.

2.2 SNMS investigations of nitrogen implanted steels

As a second example nitrogen implanted steels have been investigated by SNMS and AES depth profile analysis. 1) The x10CrNiTi18.9 steel with a nominal Cr concentration of 18 at% was implanted with 100 keV N⁺ ions until a dose of 1.10⁷ cm⁻².

As seen in fig. 3, the atomic N signal is considerably higher than the molecular signals, and can therefore be used as a monitor for the N content. A corresponding AES measurement indicates no enrichment of Cr on the surface by preferential sputtering or segregation effects. Hence, the atomic surface composition can be assumed to be close to the bulk stoichiometry, i.e. \(c_Fe^S/cCr^S = 3\). The SNMS CrN signal, however, is found to be markedly higher than the FeN signal. Assuming the probabilities \(P_{CO}(FeN)\) and \(P_{CO}(CrN)\) not to differ significantly, this means that the N atoms are preferentially bound to Cr atoms rather than being distributed statistically at the sample surface. Only for the depth regions with higher N contents, the CrN intensity saturates and the FeN signal increases.

1) Sample by courtesy of R. Leutenecker, Fraunhofer Institut für Festkörpertechnologie, München
the oxygen surface concentration. While the Nb results show fair agreement, significant deviations occur in the case of Ta for low \( c^S_O \) which are probably due to a \( P_{O_2} \)-dependent change of the O-concentration microprofile altering the AES sensitivity factor [7].

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Fig. 3: SNMS depth profiles of nitrogen implanted steel. The X10CrNiTi189 steel was implanted by \(1 \times 10^{17} \text{ cm}^{-2} \text{ N}^+\) at 100 keV and a temperature of 200° C.

3. Conclusions

Using the DEM for the formation of sputtered molecules, monoxide molecule SNMS signals can be applied successfully to determine the surface composition of oxidized Ta and Nb. A comparison of the SNMS results with AES data shows small deviations which can be interpreted in terms of the larger information depth of AES. On the contrary, SNMS molecular signals contain information about a surface layer determined by the depth of origin of sputtered particles, i.e. the two outermost atomic layers /8/.

SNMS investigations on N implanted steels show that molecule formation by direct emission can be strongly correlated to the local binding structure at the ion bombarded surface. Hence, information on the local chemical environment of sputtered atoms can be obtained from the comparison of atomic and molecular SNMS signals.

/1/ K.-H. Muller, M. Kopparsi, J.F. Geiger, H. Oechsner: same issue
/6/ G.Blaise, M.Bernheim: Surf.Sci.47(1975), 324