IONIZATION PROBABILITY OF SPUTTERED CLUSTERS

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1. Introduction

It is well known that the flux of secondary ions sputtered from a solid surface generally contains clusters of several atoms as well as purely atomic ions. The formation of these cluster ions during the sputtering process represents one of the most interesting but still unresolved questions regarding the fundamental processes of SIMS. As a general practice, the yield of a specific secondary ion $X^{*+}$ is factorized according to

$$Y(X^{*+}) = Y_X \cdot \alpha_x^{*+}$$

(1)

where $Y_X$ denotes the partial sputtering yield of the species X (regardless of its charge state) and $\alpha_x^{*+}$ defines the ionization probability of the sputtered particle. This treatment divides the formation of a secondary cluster ion into two steps, namely i) the formation of a sputtered cluster and ii) its ionization during its ejection from the surface. While the first process can be reasonably well described - for instance by molecular dynamics computer simulations of the collision cascade initiated by the impinging primary ion [1] - the mechanisms leading to the ionization of a sputtered cluster are still largely unresolved. One of the major reasons for this state of affairs is given by the apparent lack of experimental data characterizing $\alpha_x^{*+}$ for the particular case of sputtered clusters. This, on the other hand, is due to the fact that an experimental determination of $\alpha_x^{*+}$ requires the detection of sputtered neutral species, which must be post-ionized in order to be detectable in a mass resolved manner. Moreover, in order to be quantitative the post-ionization efficiency must be known and secondary ions and neutrals must be detected under otherwise identical experimental conditions. We have recently developed a method which fulfils these requirements and is based on the in-situ determination of secondary ion and neutral particle densities above an ion bombarded surface. The present work describes an application of this method to determine the ionization probability of clusters sputtered from the respective clean surfaces as a function of the cluster size.

2. Experimental

The experimental procedure used in the present work is described in detail elsewhere in this volume [2], and the description will therefore not be repeated here. Briefly, polycrystalline samples are bombarded under UHV conditions with rare gas ions of 15 keV extracted from an ion gun which is used either in dc mode (for sputter cleaning the surface) or in pulsed mode (during data acquisition) with a pulse duration of several microseconds. The number densities of sputtered neutral particles and positively charged secondary ions are detected in situ at a
distance of about 1 mm above the surface, the neutrals being post-ionized by a VUV laser operated at 157 nm. As an essential part of the method, all atoms and clusters are ionized by single photon absorption and the available laser intensity is high enough to drive the post-ionization efficiency into saturation, thus eliminating the influence of the a priori unknown photoionization cross sections of the clusters [3,4]. The ionization probability is then directly determined from the ratio between the mass spectrometric signals of secondary ions (measured without the ionizing laser) and the saturated secondary neutral signals without any further correction.

3. Results and Discussion

Figures 1 - 4 show the resulting values of the ionization probability for the formation of singly positively charged ions measured for Ag$_n$, Ge$_n$, Ta$_n$ and Nb$_n$ clusters sputtered from the respective clean surfaces. In Figure 1, three different sets of data have been included which cover partly overlapping cluster size ranges. The deviation between the different $\alpha^+$-values measured for the same cluster size within these ranges may therefore regarded as a measure of the reproducibility of the experiment.

As a first observation, low $\alpha^+$-values below $10^{-3}$ are found for sputtered Ag, Nb and Ge atoms. This finding is in good agreement with the common sense that the formation probability for atomic ions ejected from the respective sputter cleaned surfaces is generally low [5]. In particular, the absolute values determined here agree within a factor of two with data published by Benninghoven [6], which was obtained by comparing measured total secondary ion currents with tabulated data of total sputtering yields. In view of the fact that our data has been evaluated without the application of any correction factors regarding, for instance, postionization efficiency, instrument transmission etc., we consider this an impressive agreement. The second important observation concerns the cluster size dependence of $\alpha^+$. For small clusters containing less than approximately 10 atoms, the ionization probability is found to increase strongly with increasing nuclearity of the sputtered cluster. This is observed in all cases studied so far and must therefore be regarded as a general trend.

Figure 1. Ionization probability of sputtered silver clusters vs. cluster size.

Figure 2. Ionization probability of sputtered germanium clusters vs. cluster size.
Figure 3. Ionization probability of sputtered tantalum clusters vs. cluster size.

Figure 4. Ionization probability of sputtered niobium clusters vs. cluster size.

For larger clusters containing more than 10 atoms, the ionization probability seems to saturate. Unfortunately, only for the case of silver the cluster sputtering yields are large enough to access this range of cluster sizes within the sensitivity of our experiment. For this system, a tendency towards saturation had already been observed in our previous work [4], the value of $\alpha^+$ in the saturation regime being of the order of several percent. However, from the limited range of cluster sizes accessible at that time (less than 15 atoms), the possibility of a gradual increase towards unity for larger clusters could not be safely ruled out. From the results presented in Figure 1, it is now clear the the ionization probability of sputtered silver clusters actually saturates at a value below ten percent. As a consequence, we must conclude that the vast majority of all sputtered silver clusters is emitted in the neutral state. The same seems to be true for germanium clusters (Figure 2), although in this case the accessible size range is clearly not large enough to decide on the saturation behaviour with increasing cluster size.

The low values of $\alpha^+$ observed for silver and germanium clusters are in marked contrast to the data measured on $\text{T}a_n$ and $\text{Nb}_n$ clusters (Figure 3 and Figure 4), which show that for these systems the ionization probability may be non negligible even for small clusters containing as few as only 4 (Ta) or 7 (Nb) atoms, respectively. Although also in these cases the accessible size range is small and, hence, an assessment of the saturation behaviour is difficult, it is evident that all detected $\text{T}a_n$ clusters containing more than 5 atoms are predominantly emitted in the ionic state. In the case of niobium, it is found that the yields of charged $\text{Nb}_n$ clusters become comparable to those of the neutral counterparts for cluster sizes above 7 atoms. The physical reasons for these findings and, in particular, for the discrepancy between the silver / germanium data on one hand and the tantalum / niobium data on the other hand are unclear at the present time.

Interestingly, the ionization probabilities measured for the tantalum and niobium trimers are comparable to those of the silver and germanium trimer, thus indicating that the difference between the two sets of data are presumably not caused by any systematic error of the experiment. On the other hand, it is known that transition metals like Ta and Nb may exhibit dramatic increases of the ionization probability upon surface reactions with residual gas
contaminants (mostly oxygen) [5]. Although the sample surface was carefully sputter cleaned prior to each experiment, the pulsed nature of the ion bombardment during data acquisition may in principle lead to a gradual buildup of surface contamination during the acquisition of a mass spectrum (which is averaged over several thousand laser shots). We have, however, not detected any significant amounts of mixed neutral clusters containing reactive atoms like oxygen, nitrogen etc., which have been shown to be a good indicator of the contaminant surface concentration [7]. Moreover, the ionization probability measured for the Nb atoms is very low, thus indicating a relatively clean surface. We therefore feel that it is not surface contamination which leads to the large ionization probabilities observed for Taₙ and Nbₙ clusters. In addition, we would expect the magnitude of such an effect to be largest for sputtered atoms and decrease with increasing cluster size.

4. Conclusion

The theoretical interpretation of the data presented in Figures 1-4 is difficult. To the best of our knowledge, only one theoretical model describing the ionization probability of sputtered clusters has appeared in the literature [8]. The results of this calculation, which is based upon the assumption that sputtered clusters are ejected with large internal energies and may therefore exhibit thermionic emission of electrons in order to form a positive ion, qualitatively reproduce the tendency of increasing ionization probability with increasing cluster size. The order of magnitude of the α²-values calculated for larger silver clusters, however, is significantly higher than the data presented in Figure 1. More theoretical work is therefore needed in order to gain a better understanding of the fundamental mechanisms leading to the ionization of a sputtered cluster.

References

[2] A. Wucher, R. Heinrich, and C. Staudt, these proceedings