8 Summary

The sputtering of metal surface clusters under bombardment with polyatomic and monatomic projectiles was investigated experimentally by means of time-of-flight mass spectrometry (TOF-MS) characterizing the composition of the sputtered flux. In order to obtain information about the relative abundance of clusters among the flux of sputtered particles independent of their charge state, mass spectra of both secondary ions and sputtered neutral particles are recorded under comparable experimental conditions. The neutral species are post-ionized prior to mass analysis by means of photo-ionization using a intense of UV laser at a wavelength of 193 nm.

As a first step, the formation of sputtered indium clusters under bombardment with SF_5^+ ($m = 1, ..., 5$) and Ar^+ projectiles is investigated. In these experiments, a photon energy of the ionizing laser (6.4 eV) is larger than the ionization energy of indium atoms (5.79 eV) and all indium clusters In_n. Therefore, the photo-ionization of all neutral species is achieved by absorption of a single photon (SPI) and, hence, a high ionization efficiency and low fragmentation rates have been achieved. In addition, the nuclearity and fluorine content of the projectile is systematically varied. Such conditions give us the possibility to unravel the behavior of the partial sputtering yields and ionization probabilities as a function of the fluorine content and nuclearity of the projectile. The investigations demonstrated that the measured secondary ion signals increase much more than those of the corresponding neutral particles if SF_m^+ projectiles are used instead of Ar^+ ions, indicating that the ionization probability under bombardment with SF_m^+ is enhanced by a chemical matrix effect induced by fluorine incorporation into the surface. Interestingly, the largest values of the ionization probability are observed for SF_3^+ projectiles. The total sputtering yield is found to be larger for SF_m^+ compared to Ar^+ projectiles and to increase linearly with increasing m. Both findings are shown to be understandable in the framework of linear cascade sputtering theory. The partial sputtering yields of In_n clusters exhibit a stronger enhancement than the sputtered monomers, the magnitude of the effect increasing with increasing cluster size and projectile nuclearity.

A second step, the formation of sputtered silver clusters under bombardment with Xe^+ and SF_5^+ bombardment is investigated. It is found that measured Ag_n^+ signals increase significantly if SF_5^+ projectiles are used instead of rare gas Xe^+ ions of the same kinetic impact energy. On other hand, the signals of neutral Ag atoms and Ag_n clusters exhibit only a relatively small increase, thus indicating that the enhancement observed for secondary ions is predominantly caused by an increased ionization probability of sputtered particles under SF_5^+ bombardment rather than by enhanced partial sputtering yield. The mass distribution of sputtered particles does not change in favor of large clusters between SF_5^+ and Xe^+ projectiles This finding shows that the use of polyatomic SF_5^+ projectiles does not lead to a higher efficiency in producing sputtered clusters.

Expanding on the comparison between Xe^+ and SF_5^+ projectiles, we have investigated the influence of fluorine projectile nuclearity on sputtering of silver by bombarding the target surface under SF_m^+ ($m = 1, ..., 5$) projectiles. The results demonstrated that the total sputtering yield produced by a set of isoenergetic SF_m^+ projectiles is increased linearly with increasing projectile nuclearity m. This increase can be almost fully explained by linear cascade sputtering theory. For SF_5^+ projectiles the obtained total sputtering yield is slightly larger than that estimated from linear cascade theory. The finding may refer to small contribution of nonlinear cascades to the sputtering process (spike regime).

Finally, the experiments are repeated in a different ultrahigh vacuum system containing an X-ray photoelectron spectrometer in order to obtain more information about the surface chemistry of silver subjected to SF_m^+ bombardment and to determine the concentration of fluorine at the bombarded surface as a function of projectile nuclearity. The results show that the concentration of fluorine atoms at the bombarded surface increases directly with increasing fluorine nuclearity in the projectile. In addition, the silver peaks of photoelectron spectrum are shifted to higher kinetic energy ranging from 0.2 to 0.5 eV depending on the fluorine nuclearity m . This indicates the existence of silver-fluoride (AgF). These results are largely consistent with those obtained by secondary neutral time-of-flight mass spectrometry (TOF-SNMS).

However, the physical reason for the observed, extraordinarily high ionization probability in the case of SF_3^+ bombardment remains unclear.