

Desorption and Sputtering from Solids Induced by Polyatomic Projectiles

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I Introduction

Effects induced by cluster ions colliding with solids have been studied for many years. There is actually a renewal of interest due to new experimental possibilities. Thin film deposition [1] shallow ion implantation [2], surface smoothing and polishing [3] with cluster beams have been developed in several laboratories [4]. Enhanced sputtering with clusters by comparison with single atoms has also been demonstrated long ago by Andersen and Bay [5] with Te and Te₂ projectiles and later on by Beuhler and Friedmann [6] using large water clusters. The secondary emission yield from cluster impact is larger than the sum of the yields of individual atoms. The non linear effects in the emission yield were also measured with Sb, Sb₂, Sb₃ at 30 keV/atom [6] and Bi, Bi₂ at 45 keV/atom [7] bombarding metallic surfaces as Au and Ag. A review on non linear effects in sputtering was recently presented by Andersen [8]. A yield enhancement was also found for secondary ion emission. This was first observed with dimers of Ne₂ and Ar₂ [9] and with small hydrogen cluster H_n [10]. Large non linear effects in the emission of molecular ions from solid surfaces were an important finding [11, 12]. These authors emphasized the role of cluster projectiles (as SF₆) for analytical applications in secondary ion mass spectrometry (SIMS), by comparison with single atomic ions of Cs⁺ or Xe⁺. In order to investigate the mechanisms of secondary emission of neutrals and ions (clusters and molecular ions) by polyatomic projectiles and clusters, experiments have been performed at Orsay with projectiles over a large energy range (from keV to MeV per atom) and various types of targets (metals, insulating material as thin or thick organic layers). Cluster ion sources and accelerators were used. Most of the experiments were made in the event by event mode at the limit of single impacts on the target. Experiments with keV polyatomic projectiles were

also performed at Texas A&M [13]. Actually cluster beams of SF₅ and/or (CO₂) are being used in SIMS on commercial instruments. The field of mass spectrometry of organic molecules may gain considerably from these developments.

II Secondary ion emission with gold cluster projectiles

Positive gold cluster ions (Au)_n with 1 ≤ n ≤ 10 can be easily produced with a liquid metal ion source [14]. A double pulsation technique allows to select a given mass and therefore a single cluster can be chosen as a projectile [14]. The source with its beam line and deflection plates was mounted on a reaction chamber that contains short distance time-of-flight mass spectrometers for secondary ion measurements. The ion emission yield is defined as the ratio between the number of emitted secondary ions and the number of incident projectiles (see ref. [14]). A gold target was bombarded with gold cluster (Au)_n (n = 1-5) in the energy range 5 to 60 keV. A non linear effect was observed in the emission of single negative atomic gold ions, induced by impact of Au₁ to Au₅. More spectacular is the emission of gold cluster ions from a solid gold target. It was shown, for example, that the emission of (Au)_n⁻ (with n ≤ 5) is several order of magnitude larger with Au₃ projectile than with Au₁ at 20 keV/atom. These results with a metallic target indicate that the emission of clusters is very much enhanced under impact of cluster projectiles [15]. Insulating materials as CsI targets and organic targets were also bombarded by (Au)_n clusters and polyatomic ions. The secondary ion emission of CsI clusters and of intact molecular ions were severely enhanced with cluster projectiles. The number of constituents in the projectile is a main parameter and the non linear effects are much more important for complex

secondary ions than for atomic secondary ions. The effect of the number of constituents in projectiles has been easily verified by comparing the emission yield of molecular ions produced by the impact of C_{60} and Au_n at the same velocity. These two projectiles have about the same mass. At the bombarding energy of about 25 keV, the emission yield is more than 5 times larger with C_{60} than with Au_4 [15]. Upon impact with the solid the projectile breaks into its constituents and the range of a carbon atom (~ 35 Å) is smaller than the range of gold atom (~ 160 Å). Therefore the density of energy deposited close to the surface is larger with C_{60} . The secondary emission yield simply reflects the amount of energy that can be released out of the surface. Fig. 1 shows the relative variation of yields of an organic ion $(M-H)^-$ from phenylalanine as a function of the energy per unit mass of the projectile ($\sim v^2$).

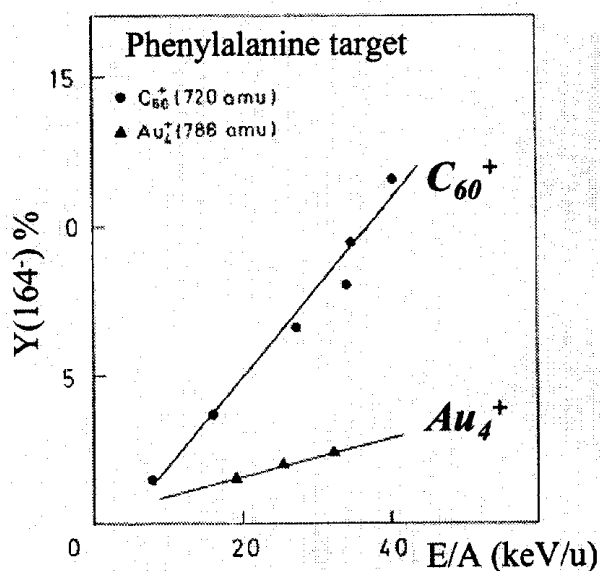


Figure 1. Comparison of emission yields from organic layers after impacts or C_{60} and Au_4 projectiles in the energy range (5-25 keV). The abscissa in E/A (eV/u) is proportional to the square of the projectile incident velocity [15].

III Secondary ion emission with organic projectiles

A fabulous projectile seems to be C_{60} at several tens of keV, although C_{60} at several MeV is now being produced as a beam that induces also very peculiar phenomena in solids [16]. It has been shown that complex polyatomic ions [16] are an excellent probe to analyze thin layers of molecules deposited on various substrates as, for example, contaminant layers of organic compounds. The question of damages created at the sample surface is in some cases important; however, in static

TOF-SIMS, and when using a very low dose (sometimes below 10^5 total) secondary molecular ions can be detected at a sensitivity level not attainable with single atomic projectiles. Organic projectiles $73 \leq m/z \leq 1200$ were used at Orsay in event by event coincidence experiments [17, 18] and it was shown that the non linear effect does not extend to large n values (n being the number of atoms in the projectiles). In fact, above n around 20 the non linear effect vanishes and the secondary emission yield follows a linear dependence with n . A simple apparatus producing molecular ions projectiles with $m/z = 385$ has been recently tested for secondary ion mass spectrometry of organic compounds [18]. The method is called "spontaneous desorption mass spectrometry" and Fig. 2 shows a comparison of time-of-flight spectra (recorded during the same time) between the measurements in plasma desorption mass spectrometry and in spontaneous desorption mass spectrometry. The sample was a phosphorylated glycolipid ($m/z = 528.5$). It is shown here that organic projectiles at a few tens of keV are efficient for desorption processes.

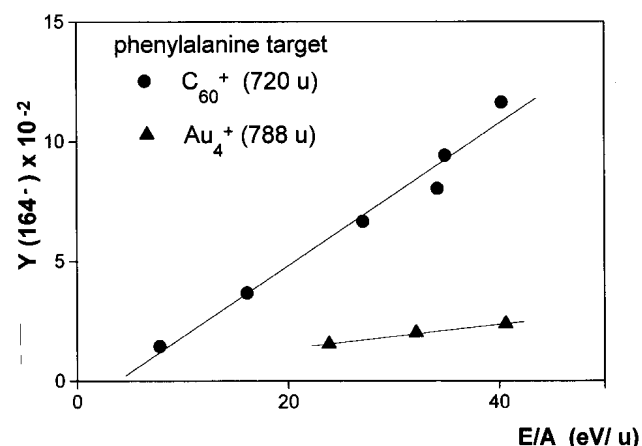


Figure 2. Time-of-flight spectra of C_{60} obtained by fission fragment impacts from a ^{252}Cf source (a) and the brilliant green spontaneous desorption source (b) [18].

IV Total sputtering with (Au_n) projectiles

As mentioned above the non linear enhancement of secondary ions was also observed for neutral species. Recently, total sputtering yield measurements of gold targets bombarded by Au_n ($n = 1$ to 13) clusters were performed in a large energy range from 20 keV to more than 2000 keV per atom. The gold clusters were produced and accelerated by the small tandem accelerator "Aramis" at Orsay and by a 2 MV Van de Graaff at Lyon (Institut de Physique Nucléaire). The mass

eroded from the target was measured with a quartz micro-balance. A thick quartz crystal was coated with 1000 nm of gold and a decrease of the gold thickness due to sputtering gives rise to a proportional increase of the oscillation frequency. A sputtering yield as high as 1200 atoms per impact of Au_{11} was measured while a value of only 50 atoms was obtained for single Au projectiles at the same energy per atom (~ 100 keV). The second main finding of this work was that all the maxima in the sputtering yields do not occur (as expected) at the same velocity of impact of the different Au_n cluster projectiles [19]. Therefore, the strong non-linearity of the emission yield that is observed cannot be given by a simple power law of the nuclear stopping power. With regards to the interpretation of these new results, the shifts of the yield curves maxima towards lower energy per atom for increasing number of constituents in the projectiles is not yet explained. The thermal spike model from Sigmund and Clausen [20] has been applied to try to fit the data. In this model the radius of the spike is a key parameter that should vary both with the number n of atoms and with the energy. This dependence is however not established. These results on total sputtering are now the most complete set of results on the total sputtering of a metal target. A set of results on secondary ion emission has also been obtained with gold clusters in the same energy range as the total sputtering results. The data show that the maxima of yield for molecular ion emission occurs also at relatively low energy with respect to the maxima of the nuclear stopping power [21]. For organic material the maxima of yield with Au_4 is around 80 keV/atom. This is well illustrated in Fig. 3 that shows the yield variation of $(M-H)^-$ from a phenylalanine sample as a function of the energy per atom of Au_n projectiles. The same shape of yield curves with a peak named as "the sugar loaf peak" is observed with different types of samples (organic and inorganic). These new results demonstrate that the projectile energy range of clusters between 40 and 120 keV/atom are of great importance since "resonance" effects may occur in the solid, that lead to an important release of matter from the surface. There are also possible applications with enhanced efficiency and sensitivity for surface and bulk analysis.

V Energetic MeV clusters

It must be recalled also that increasing the energy of cluster projectiles might be useful for applications. Both aspects of pulverisation and production of thin layers by redeposition as well as material modification of materials may be gained from the increase of energy. Surface analysis and depth profiling are only some aspects of secondary ion mass spectrometry. For example

C_{60} projectiles at 20 MeV are very efficient to emit and identify intact molecular ions of mass larger than 25000 u or large clusters. A time-of-flight mass spectrum can be recorded with a good statistics with only 10^4 incident ions since the emission yield of very large molecules is much more than one secondary ion/impact [22]. For example the desorption yield of insulin molecules by 20 MeV C_{60} as shown in Fig. 4 is about 100 times larger than with MeV atomic ion projectiles. The desorption of molecules with masses above 100.000 u could also be investigated in the future. Some surfaces are strongly modified in one impact, others are not. Fast clusters can create in metals [23] permanent defects which are not produced by single ions having the same energy loss. Whatever the energy loss domain (nuclear or electronic) it is the amount of energy density deposited in the material which is important for the induced effects.

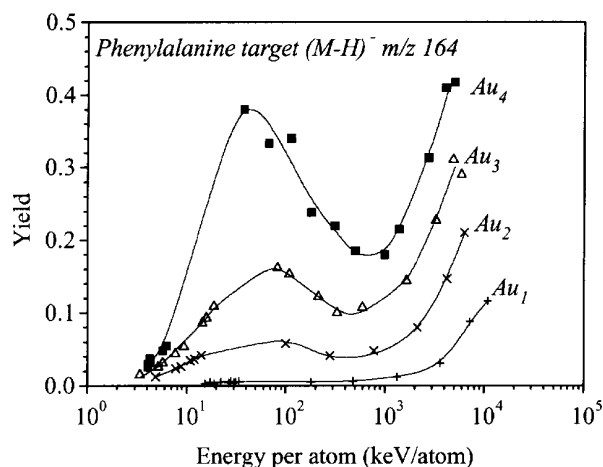


Figure 3. Desorption yield of the ion $(M-H)^-$ from phenylalanine layers (~ 2000 Å) bombarded by gold clusters Au_n projectiles over a large energy range per atom. It is clearly observed the importance of the so-called "sugar loaf peak" at the energy per atom around 60 keV.

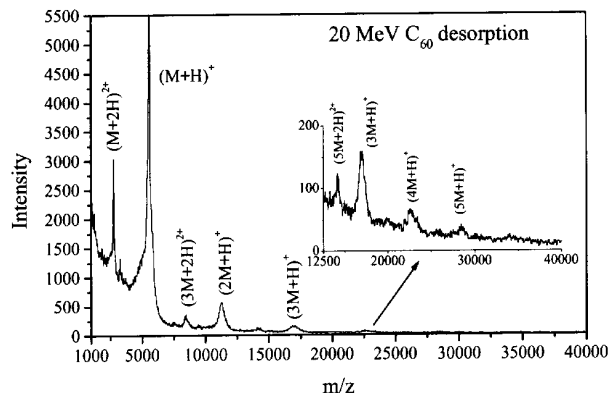


Figure 4. Example of PDMS-type time-of-flight spectra obtained by the impact of 20 MeV C_{60} projectiles on an insulin sample. A spectrum with good statistics can be obtained in a few minutes of beam.

VI Conclusion

When using polyatomic ions as projectiles the enhancement of emission yield of secondary ions and neutrals is clearly established in a large range of incident energies. The larger the secondary ions the more important the non linear effects. Damage cross sections must be considered but at projectile energies below 50 keV and for organic samples the rate of emission seems to be larger than the rate of damages. Molecules and clusters which are not seen with single atomic projectiles can be easily observed with polyatomic projectiles. The use of fast complex projectiles has considerably broadened the field of collisions of ions with solids in fundamental research. With atomic projectiles it has been shown for many years that the velocity was an important parameter. Fast atomic ions, in the electronic regime of energy loss, were the most efficient for desorbing intact molecular ions from solid samples. It appears now that polyatomic projectiles at much lower velocities seem to be even more efficient. MeV ion beams require sophisticated equipment and the use of fission fragments from ^{252}Cf is rather limited (and sometimes restricted). From the results presented here, cluster ions at a few tens of keV/atom are certainly promising. In the future the use of large multiply charged clusters or molecules may also be a unique way to study phenomena related to a high energy deposition in solids.

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