MOLECULAR SPUTTERING AND DAMAGE INDUCED BY keV IONS IN MULTILAYERED LANGMUIR-BLODGETT FILMS
G. Bolbach, R. Galera, J. Blais

To cite this version:

HAL Id: jpa-00229410
https://hal.archives-ouvertes.fr/jpa-00229410
Submitted on 1 Jan 1989

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
MOLECULAR SPUTTERING AND DAMAGE INDUCED BY keV IONS IN MULTILAYERED LANGMUIR-BLODGETT FILMS

G. BOLBACH, R. GALERA and J.C. BLAIS
Laboratoire de Physique et Chimie Biomoléculaire, CNRS UA-198, Institut Curie et Université Pierre et Marie Curie, 11, rue Pierre et Marie Curie, F-75231 Paris Cedex 05, France

Résumé - Les effets d’irradiation (érosion et endommagement) induits par des ions de faible énergie (keV) dans des films de Langmuir-Blodgett de différentes épaisseurs ont été étudiés à différents angles d’incidence pour des doses $\leq 3 \times 10^{13}$ ions.cm$^{-2}$. Ces films, composés de monocouches superposées et distinctes, permettent de suivre en spectrométrie de masse d’ions secondaires (SIMS) l’évolution, au cours du bombardement, de l’intensité de l’ion moléculaire associé à une profondeur donnée. Au voisinage de l’incidence normale, le volume excité par l’ion primaire est caractérisé par une extension radiale faible par rapport à son extension en profondeur.

Abstract - The irradiation effects (sputtering and damage) induced by keV ion in Langmuir-Blodgett films of different thickness are studied for different incidence angles and for doses up to $3 \times 10^{13}$ ions.cm$^{-2}$. The films composed of different superposed monolayers allow to study, in SIMS, the evolution of the molecular ion intensity as a function of film depth. The volume excited by the primary ion is characterized at small incidence angle by a small radial extension with respect to its depth extension.

INTRODUCTION

The first SIMS studies devoted to molecular films mentioned that extended irradiation by keV ion resulted in a decay of the molecular ion intensity /1/. For a monolayer deposited on a metal substrate this decay is exponential and it is characterized by a disappearance cross section $\sigma$ lying in the range of $10^{-14}$-$10^{-13}$ cm$^2$. This cross section depends on the chemical environment and on the primary particle /1/. It characterizes the radial extension of the excited volume in which the primary ion induces sputtering (neutral or ionized molecules and fragments) and damage (broken molecules in the target). In order to get a better knowledge of the extension of the excited volume we have studied the irradiation effects in multilayered films. These films, composed of different superposed monolayers (ML), allow to study the molecular secondary ion ejection as a function of the depth during the bombardment. Films of 2, 4 and 6 ML have been bombarded by 5 keV Cs$^+$ primary ion at different incidence angles ($20^\circ$, $65^\circ$ and $76^\circ$). Complementary studies have also been carried out with 2 keV Cs$^+$ ions. The irradiation effects have been investigated in the $10^{11}$ - $3 \times 10^{13}$ ions.cm$^{-2}$ dose range.

EXPERIMENTAL

Sample preparation - The 2, 4 and 6 ML films have been built up using the Langmuir-Blodgett (LB) technique /2/. Four different fatty acids have been chosen, $M(n) = CH_3(CH_2)_n COOH$, with $n = 16$ (stearic acid), $n = 17$ (nonadecanoic acid), $n = 18$ (arachidic acid) and $n = 19$ (heicosenoic acid). One of these fatty acids was spread out, from a 10$^{-3}$M solution (hexane), on a water subphase (Millipore) containing $4 \times 10^{-4}$ M CdCl$_2$ at pH = 5.7 and then slowly compressed up to a pressure of 30 mN.m$^{-1}$ /3/. This pressure was kept constant during the transfer. The Au substrates (1000 to 1500 Å Au vacuum evaporated onto glass disks) were dipped at low velocity ($\sim 2$ to 3 mm/nm) into the subphase. Due to the hydrophobic character of the so-prepared Au substrates a first monolayer transfer took place during the first immersion. The subphase surface was thus cleaned, before spreading out another fatty acid. After compression the substrate was raised through the subphase, giving rise to a second monolayer transfer (first emersion). In order to check the cleaning between the two transfers (1st immersion and 1st emersion) a new Au substrate was dipped and raised through the surface. SIMS analysis of this 2 ML sample indicated that only the second fatty acid spread out on the subphase was present in the film. For 4 ML films the procedure previously described was repeated using the two other fatty acids, each monolayer being composed by only one given fatty acid. For 6 ML films, the two first transferred monolayers contained only heicosenoic acid, the third and fourth transferred monolayers contained only arachidic acid and finally the fifth and sixth (surface) transferred monolayers contained nonadecanoic and stearic acids respectively. For all the transfer experiments, the measured coverage rate (transferred molecules area/substrate area) was $1 \pm 0.05$.

It should be noted that for all these fatty acids, compressed at 30 mN.m$^{-1}$ on the water subphase, the molecular areas are similar ($\sim 20$ $Å^2$/molecule). In addition, the four fatty acids exhibit identical chemical
properties and their molecular lengths are very close \((25 \text{ Å for } n = 16 \text{ and } 28 \text{ Å for } n = 19)\). Finally we have verified that for films composed of only one fatty acid, the \((\text{M}(n)\text{H})^+)\, secondary ion yield is similar for all the \(\text{M}(n)\) molecules. Consequently, it was possible, during an irradiation experiment, to study the ejection of molecules well localized in the film.

**SIMS analysis** - The primary beam consisted of \(\text{Cs}^+\) ions \((2 \text{ or } 5 \text{ keV})\). Quadrupolar mass analysis was performed at an angle of 90° with respect to the primary beam direction. The target holder could rotate in front of the primary beam, giving an adjustable incidence angle in the 10°-80° range. In this study only 20°-, 65°- and 76° angles of incidence have been used. It should be noted that this configuration did not allow for a direct comparison of experimental secondary ion yields at different angles of incidence because the optics of the secondary ion extraction depends on the sample orientation.

The primary beam diameter was around 2 mm and the primary ion flux on the target was kept constant \((4 \times 10^9 \text{ ions.s}^{-1}.\text{cm}^{-2})\) for all the experiments. The primary ion beam impact on the target can be easily observed using LB films. A remarkable optical property of such films is their ability to change substrate reflectivity \(/4/\). For \(\text{Au}\) substrates, a change was observed for coverages higher than 6 ML and a minimum reflectivity was observed for about 20 ML. Irradiating such films with a dose of about \(10^{13} \text{ ions.cm}^{-2}\) resulted in reflectivity changes, easily observed at grazing incidence, which allow to determine the area of the beam spot. For smaller film thicknesses \((2, 4 \text{ and } 6 \text{ ML})\) the observation of the impact region is obviously more difficult; the bombarded surface is essentially hydrophilic and the non bombarded surface is of course hydrophobic. This difference can be used in two different ways. Dipping the target into water leads to two different menisci which give a rough idea of the bombarded area. The other method consists of observing the difference of water droplets condensation on the two regions, for example by putting the target on a \(\text{N}_2\) liquid cooled metal plate. From the hydrophilic region, water desorbs faster than from the hydrophobic region; the two regions are thus easily distinguishable.

**RESULTS**

The intensities of the different secondary ions, \((\text{M}(n)\text{H})^+)\, and \(\text{Au}^+\), were sequentially measured in a time of a few tens of seconds. Taking into account the very small variation of these ion intensities in this time range, it can be assumed that they are measured at the same time. Fragments corresponding to a progressive loss of \((\text{CH}_2)\) group were not studied, because they are not representative of a given monolayer. In the following, the first monolayer refers to the surface monolayer, the second one refers to the monolayer located just below the first one and so on.

The charge effects observed in these experiments have already been described for 4 ML films \(/5/\). In the \(1 \times 10^{11} - 5 \times 10^{12} \text{ ions.cm}^{-2}\) dose range, the \((\text{M}(n)\text{H})^+)\, intensity depends on the target potential. We have verified on different sets of experiments with different target potentials that the contribution of a given monolayer to the total \((\text{M-H})^+)\, intensity, i.e. its relative abundance, did not depend on the target potential. Thus, the so-called relative abundances have been used to present the results concerning the angle of incidence effects.

The surface monolayer intensity always exponentially decreases. This exponential decay can be characterized by a disappearance cross section \(\sigma\). The value of \(\sigma\) does not depend on the film thickness and on the angle of incidence within the experimental accuracy, but it clearly depends on the \(\text{Cs}^+\) primary ion energy \(\nu\); typically \(\sigma = (1 \pm 0.3) \times 10^{-13} \text{ cm}^2 \) at 5 keV and \(\sigma = (0.5 \pm 0.15) \times 10^{-13} \text{ cm}^2 \) at 2 keV. Primary particle reflection cannot significantly alter these trends since the reflection coefficients are expected to be very low under our experimental conditions \(/6/\). Figures 1 a, b represent the evolution of the relative abundances for the different films \((2, 4 \text{ and } 6 \text{ ML})\) studied at different incidence angles \((20°\) and \(76°\)) and at different energies \((5 \text{ and } 2 \text{ keV})\). The results at \(20°\), not shown here, are closer from those corresponding to \(20°\). The reproducibility of these data is within \(15\%\). Fig. 2 shows typical \(\text{Au}^+\) signal \(\times\) the \(\text{Au}^+\) signal is normalized in such a way that it represents \(100\%\) at the highest dose \((3 \times 10^{13} \text{ ions.cm}^{-2})\).

- At \(20°\) incidence angle the curves of the relative abundance versus dose are approximatively parallel, except at the beginning of the irradiation for 4 and 6 ML films. They correspond to a same exponential decay for all of the monolayers. However, the relative abundance of a given monolayer is generally greater or equal to the relative abundance of the monolayer located under it. At the beginning of the irradiation, the relative abundance of the surface monolayer represents \(70\%\) to \(50\%\). This strong surface molecular ejection has already been reported in SDMS \(/7/\). Moreover for doses \(> 5 \times 10^{12} \text{ ions.cm}^{-2}\), the surface monolayer relative abundance tends to be smaller when increasing the film thickness or decreasing the primary ion energy.

- At \(76°\) a crossing of the relative abundance versus dose curves is observed \(\times\); the molecular ion ejection of a deep monolayer becomes larger than the molecular ejection of the monolayer located over it. This effect depends on the primary ion energy \(\nu\); for a 4 ML film and doses \(> 1.2 \times 10^{13} \text{ ions.cm}^{-2}\), the relative abundance of the 4th monolayer is the most important for 5 keV but the relative abundance of the 2nd monolayer is the most important for 2 keV. As previously noted the contribution of the deepest monolayers at zero dose is small but not negligible.

The evolution of the \(\text{Au}^+\) signal is also greatly influenced by the film thickness, the energy and the angle of incidence of the primary ion \((\text{fig. } 2)\). In summary, the amplitude of the variation of \(\text{Au}^+\) relative intensity increases with increasing film thickness and the angle of incidence or with decreasing the primary ion energy over the dose range.
Fig. 1.a - Relative monolayer abundance vs Cs+ 5 keV dose (see tex).
Fig. 1.b - Relative monolayer abundance vs Cs+ 2 keV dose (see text).

Fig. 2 - Au relative intensity vs Cs+ (5 and 2 keV) dose (see text).
DISCUSSION

The essential feature of these results is the difference observed in the relative abundance of secondary ions at 20° and 76°. This difference cannot be explained by artefacts connected to eventual inhomogeneities in the LB films.

20° incidence angle - The fast decrease at low dose suggests that instabilities in the film, involving essentially the first monolayer, take place at the beginning of the irradiation. These instabilities may result from a weaker binding energy of the first monolayer and/or from a LB film structure different from the corresponding stable crystal. They may also result from subtle charge effects. The constant contribution of the different monolayers to the molecular ion ejection for higher doses is of more interest. This result cannot be explained from the so-called sequential layer sputtering model, for which only the molecules located in the surface monolayer can desorb. The ejection of molecules located underneath the surface with a constant relative abundance rather suggests that the ejection and damage volume associated with a primary ion impact is a cylinder; no intact molecular ion will be ejected later from this cylinder. The relative abundances of the deepest monolayers are smaller than those of the overayers. It could be expected that in contrary to sputtering, the damage (non-ejected broken molecules) increases with the depth. The radius r of the cylinder has been calculated from the disappearance cross section \( \alpha_1 = \pi r^2 \), \( r \sim 18 \text{ Å} \) (5 keV) and \( r \sim 13 \text{ Å} \) (2 keV). The cylinder depth is at least 150 Å at 5 keV, corresponding to a 6 ML thickness. It is noteworthy that the radial extension of this excited volume is much more smaller that the corresponding depth extension. This may be compared to the spatial distribution of energy deposited by a keV ion. According to Whitelow et al., the calculation of this distribution using the binary-collision code COSIP0/ leads for 10 keV primary ion, in a given depth extension, to a radius \( r \) of 25 Å. The values of these dimensions are similar to those of the excited volume estimated in our study. The large differences between radial and depth extensions result from the small target/primary ion mass ratio \( \mu = 52/197 \), and also from the low primary ion energy (\( \epsilon < 1 \)). The collision of a primary ion with target atoms (C, H or O) is characterized by a small energy transfer and also by a small deflection angle for the primary ion and the recoil atom. Consequently, the collision cascades generated near the surface are mainly forward directed. As predicted by Whitelow et al., only the high order recoils contribute to backward directed collision cascades. If the energy of these collision cascades is large enough they may, in principle, desorb molecules. As also noted by Whitelow et al., most of the primary recoils are generated at large depths, i.e. 100 Å for 10 keV Xe+ primary ions. Thus the damage of the target may essentially be produced in the deep monolayers as suggested by our results. In summary, the cylinder geometry may be explained by sputtering dominating at the surface and damage dominating at larger depths.

76° incidence angle - The relative abundances exhibit a behaviour in better agreement with the predictions of the sequential layer sputtering model. The relative abundances have been calculated using the value of \( \alpha_1 \) at low doses is experimentally higher than that predicted by the model. In addition the experimental contribution of the deepest layer becomes larger than the contribution of the overayers at smaller doses than those expected from the model. The first effect could be related to coverage inhomogeneities. If only a few percent of the target are inhomogeneously covered, the contribution of the monolayers to the molecular ion ejection for higher doses is of more interest. This result cannot be explained from the so-called sequential layer sputtering model, for which only the molecules located in the surface monolayer can desorb. The ejection of molecules located underneath the surface with a constant relative abundance rather suggests that the ejection and damage volume associated with a primary ion impact is a cylinder; no intact molecular ion will be ejected later from this cylinder. The relative abundances of the deepest monolayers are smaller than those of the overayers. It could be expected that in contrary to sputtering, the damage (non-ejected broken molecules) increases with the depth. The radius r of the cylinder has been calculated from the disappearance cross section \( \alpha_1 = \pi r^2 \), \( r \sim 18 \text{ Å} \) (5 keV) and \( r \sim 13 \text{ Å} \) (2 keV). The cylinder depth is at least 150 Å at 5 keV, corresponding to a 6 ML thickness. It is noteworthy that the radial extension of this excited volume is much more smaller that the corresponding depth extension. This may be compared to the spatial distribution of energy deposited by a keV ion. According to Whitelow et al., the calculation of this distribution using the binary-collision code COSIP0/ leads for 10 keV primary ion, in a given depth extension, to a radius \( r \) of 25 Å. The values of these dimensions are similar to those of the excited volume estimated in our study. The large differences between radial and depth extensions result from the small target/primary ion mass ratio \( \mu = 52/197 \), and also from the low primary ion energy (\( \epsilon < 1 \)). The collision of a primary ion with target atoms (C, H or O) is characterized by a small energy transfer and also by a small deflection angle for the primary ion and the recoil atom. Consequently, the collision cascades generated near the surface are mainly forward directed. As predicted by Whitelow et al., only the high order recoils contribute to backward directed collision cascades. If the energy of these collision cascades is large enough they may, in principle, desorb molecules. As also noted by Whitelow et al., most of the primary recoils are generated at large depths, i.e. 100 Å for 10 keV Xe+ primary ions. Thus the damage of the target may essentially be produced in the deep monolayers as suggested by our results. In summary, the cylinder geometry may be explained by sputtering dominating at the surface and damage dominating at larger depths.

The similar \( \alpha_1 \) values found at a given primary ion energy, for the different angles of incidence, show that the excited volume at 76° does not correspond to a simple projection of the cylinder determined at 20°. Indeed, a simple projection would give a cosine law \( \alpha_1 = \alpha_1^0 \cos \theta \), \( \alpha_1^0 \) Two different explanations could be invoked. The effect may result from the anisotropy of collision cascades. If the collision cascades distributions are similar at small and large incidence angles, i.e. these distributions are independent of the primary ion beam direction with respect to the molecular orientation, the desorption is generated at small incidence angle by backward directed collision cascades while it is generated, at large incidence angle, by collision cascades essentially directed perpendicular to the primary ion direction. At small incidence angle, the backward directed collision cascades are isotropically distributed round the incident direction. This is not the case at large incidence angle, given an excited surface area smaller than expected from a simple projection; moreover this area is probably located far from the primary ion impact. The second explanation may result from a difference of energy propagation in the target for small and large incidence angles. The LB films are far to be isotropic. The molecules consist of long linear C chains oriented perpendicular to the substrate, they interact through (hydrophobic-hydrophobic) Van der Waals bonds or through (hydrophilic-hydrophilic) ionic bonds. Thus it could be expected that a first order recoil produces different high order recoils, depending on its direction, perpendicular or parallel to the surface plane. Other phenomena
must be also taken into account, in particular the importance of H atoms constituting 64 % of the target atomic composition; for these light atoms, the energy loss of the primary ion is essentially due to electronic processes. As also noted by Whitelow et al., the H recoils preferentially transfer energy to other H atoms [11].

CONCLUSION

These preliminary results clearly show that the study of the irradiation effects under keV ion bombardment of Langmuir-Blodgett films is well adapted to give information on the mechanisms involved in the secondary ion emission. The possibility to build up films composed of different superposed monolayers is particularly useful to obtain informations about the volume effect; this is not possible using the classical target preparation techniques. More information could be gained by measuring the absolute secondary ion yields which are directly connected to sputtering yields. Moreover the choice of amphiphilic molecules giving characteristic fragment secondary ions could be of interest to investigate more precisely the damage distribution in the organic film. A complementary study should also concern the ejection of clusters.

REFERENCES