

Evaluation of Damage Cross Sections by Au Cluster Ion Bombardment

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Received 4 October 2004; Accepted 27 January 2005

The damage cross sections σ of organic materials caused by Au cluster ion (Au_n^+ ; $n = 1-3$) bombardment were evaluated. Three samples in wide variety were investigated: 1) a lubricant of Fomblin Z-DOL as a thin film including an additive of X-1P, 2) a pigment of Cu phthalocyanine as powders, and 3) a polymer of Nylon-6 as a thick film. The determined σ values for selected characteristic secondary ions of all materials were in the order of $10^{-13}\sim 10^{-12}$ cm². The σ increased with increasing n . Ratios of $\sigma(\text{Au}_3^+)/\sigma(\text{Au}^+)$ were in the range of 1.5~5. In the case of Z-DOL, the $\text{CF}_2\text{CH}_2\text{OH}^+$ ions originated from the hydroxyl end groups and deeply concerned with the chemical bonding to the substrate, showed exceptionally high damage cross section. Evaluation of σ is very important not only to perform the most sensitive analysis but also to investigate the chemical interaction.

INTRODUCTION

Surface and interface analysis of organic materials has been interested. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has great advantages in this field, because it can give the information on surface chemical structure with high surface sensitivity, high mass resolution and moderate lateral resolution [1].

Secondary ion formation is strongly influenced by the properties of the bombarding primary ion species. Since the number of available molecules on the outermost surface is very limited, detection of surface organic molecules by ToF-SIMS requires the most sensitive measurement conditions. Recently, Au cluster primary ions produced by a liquid metal ion source (LMIS) have been developed for ToF-SIMS [2]. Not only a monoatomic ions of Au^+ but also polyatomic cluster ions of Au_n^+ are available for the primary ion species. By use of Au polyatomic ions, considerable enhancement of the secondary ion formation efficiency E for molecular ions can be obtained [3].

In order to clarify the improved efficiency,

damage cross section σ (i.e., disappearance cross section [1]) is one of the important parameters [4-6]. The σ determines the average size of the surface area damaged by one single primary ion bombardment. The efficiency E is defined as the secondary ion yield Y per σ [3]. The E corresponds to the number of detected secondary ions if the outermost monolayer of the analyzed surface is completely sputtered.

In this work, the σ of several organic materials caused by Au cluster ion bombardment are discussed. Here we focus on two aspects. One is to compare the order of σ among the investigated materials in wide variety. In order to perform the most sensitive analysis of practical surfaces, experimental works are needed for understanding the differences between monoatomic and polyatomic primary ion bombardment [7]. The second aspect is to investigate the effect of the chemical interaction between organic molecules and substrate upon the damage cross sections. For this purpose, a thin film material is selected. Here it should be noticed that the damage cross section for a thin film

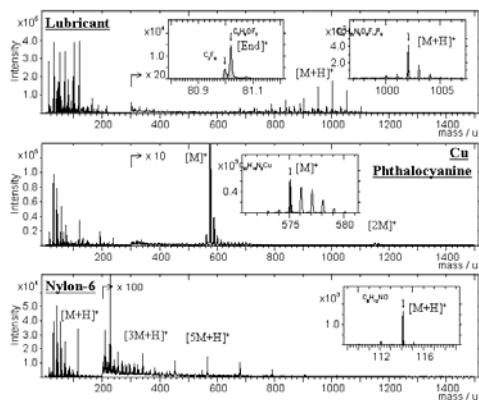


Fig. 1. Positive secondary ion mass spectra obtained from each sample. Au⁺ was used as primary ion species.

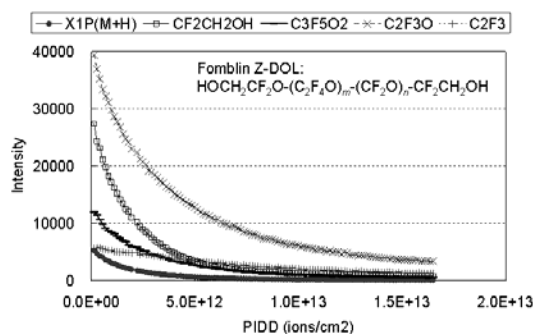


Fig. 2. Dose profile of the lubricant film. Changes in count rate of secondary ion species as a function of Au⁺ primary ion dose density (PIDD) are shown.

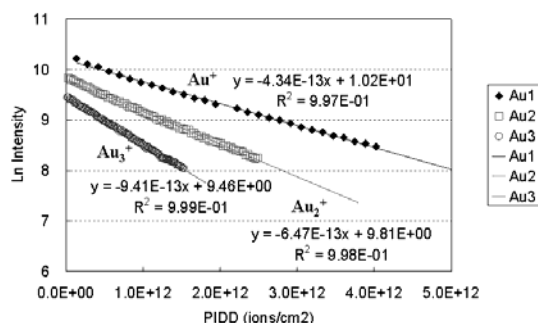


Fig. 3. Evaluation of damage cross sections for CF₂CH₂OH⁺ caused by Au⁺, Au₂⁺ and Au₃⁺ ion bombardment.

material is a combination of damage and removal of material.

EXPERIMENTAL

Materials

Three samples were prepared. One was a lubricant film (~1 nm) covered on the amorphous carbon overcoat of magnetic recording disk. The lubricant used was Fomblin Z-DOL, HOCH₂CF₂O-(C₂F₄O)_m-(CF₂O)_n-CF₂CH₂OH, including an additive of X-1P. The X-1P has a chemical structure of (p-FC₆H₄O)_n-N₃P₃-(m-OC₆H₄CF₃)_{6-n}. The lubricant film was prepared by dip coating from the mixed solution of Z-DOL and X-1P. The additive content of the solution was 10 wt%.

The second was powders of Cu phthalocyanine (Cu pc) with a chemical structure of (C₈H₄N₂)₄Cu. Cu pc is known as a typical pigment.

The third was a polymer film (~100 μm) of Nylon-6. Its chemical structure is (C₅H₁₀CONH)_n.

TOF-SIMS MEASUREMENTS

All ToF-SIMS measurements were performed in an ION-TOF, TOF-SIMS IV system. Pulsed Au cluster ion beams operating at 25 keV was used. Au⁺, Au₂⁺ and Au₃⁺ ions generating at the ion source were separated with the mass filter, and were introduced to the analysis chamber. The typical currents of each primary ion species were 0.50 pA for Au⁺, 0.12 pA for Au₂⁺ and 0.06 pA for Au₃⁺, respectively, with pulse frequency of 5 kHz. Positive secondary ions were detected with reflectron-type mass spectrometer. Dose profiles of the interested peaks were measured from the bombarded area of 150 μm x 150 μm on the each specimen surface.

RESULTS AND DISCUSSION

Figure 1 shows positive secondary ion spectra of each sample obtained by Au⁺. The acquisition time was 80 s. Corresponding primary ion dose (PID) and primary ion dose density (PIDD) were 2.50 x 10⁸ ions and 1.11 x 10¹² ions/cm², respectively. Characteristic secondary ions of each

Table 1. Evaluated damage cross sections ($/10^{-13} \text{ cm}^2$) for tested materials.

Materials	Positive secondary ion species	Mass	Primary ion species		
			Au+	Au2+	Au3+
Fomblin Z-DOL	CFO+	47	1.53	3.36	5.43
	CF2+	50	1.46	3.25	5.40
	CF3+	69	1.59	3.52	5.44
	C2F3+	81	1.01	3.00	4.65
	CF2CH2OH+	81	4.34	6.47	9.41
	C2F3O+	97	2.35	4.25	6.30
	C2F5+	119	-	4.44	7.00
	C3F5O2+	163	3.14	5.59	8.30
	C3F7O+	185	2.94	5.56	8.45
	C4F7O2+	213	3.35	5.72	8.31
X-1P	P+	31	0.40	2.41	5.36
	C6H4F+	95	1.58	3.07	5.18
	C6H4CF3+	145	1.85	3.36	5.65
	[M+H]+ (n=2)	1002	4.49	6.92	11.63
Cu Phthalocyanine	C8H9N+	119	0.04	0.10	-0.22
	C8H4N2Cu+	191	1.85	2.55	3.48
	[M]+	575	3.09	3.68	4.83
	[2M]+	1150	2.6	3.3	4.4
Nylon-6	[M+H]+	114	1.22	-	3.44
	[2M+H]+	227	2.5	-	9.3
	[3M+H]+	340	3.0	-	16

material are observed in Fig.1. Some of their chemical formula and nominal mass will be found in Table 1.

Typical dose profile of the lubricant film caused by Au⁺ ion bombardment is shown in Fig.2 as a representative example. The count rates (counts per 3 scans) of interested secondary ion species are plotted against the PIDD. The acquisition was continued for 1200 s. One can see the exponential decay curve with increasing PIDD. The σ can be calculated from the slope of the respective exponential decay curve. An example for CF₂CH₂OH⁺, which is originated from the hydroxyl end groups of Z-DOL, is shown in Fig.3.

The σ was determined for characteristic secondary ion species of each material. Typical fragment ions, molecular ions (quasi-molecular ions) and oligomer ions were selected. The results are tabulated in Table 1 and shown in Fig.4. Obtained σ values were in the order of $10^{-13} \sim 10^{-12} \text{ cm}^2$. In

general, the σ values increased with increasing n , where n means the number of Au atoms composing the cluster primary ions. Ratios of $\sigma (\text{Au}_3^+) / \sigma (\text{Au}^+)$ were in the range of 1.5~5. It seems to be reasonable because an increase in n may lead to increase the impact area on the surface, which is believed almost proportional to the number of atoms.

FOMBLIN Z-DOL

Fomblin Z-DOL has a long chain composing of [-C₂F₄O-] and [-CF₂O-] repeating units. From the Fomblin backbone, fragment ions of C_xF_yO_z⁺ were dominantly observed [8]. Their σ values showed a tendency to increase with increasing secondary ion mass, as shown in Fig.5. One can see the linear increase versus the secondary ion mass on a logarithmic scale. Using this correlation, we can easily estimate the σ values of interested secondary ions originated from the thin lubricant film.

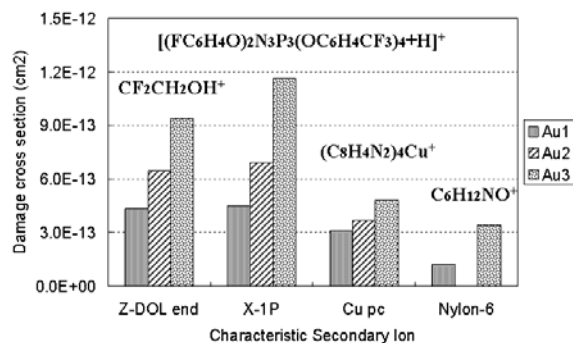


Fig. 4. Obtained damage cross sections for characteristic secondary ions of each material.

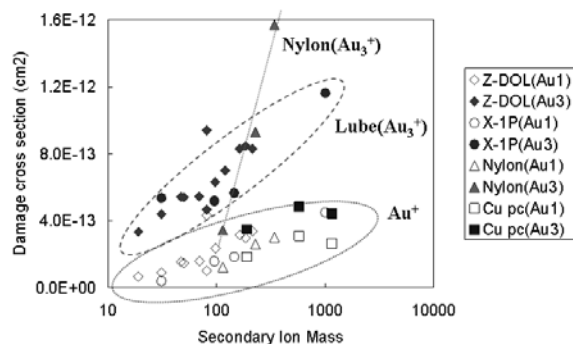


Fig. 5. Damage cross sections obtained from each material are compared as a function of secondary ion mass.

However, $\text{CF}_2\text{CH}_2\text{OH}^+$ at m/z 81 showed exceptionally high σ (Table 1.) The $\text{CF}_2\text{CH}_2\text{OH}^+$ ions are originated from the hydroxyl end groups, and deeply concerned with the chemical interaction between Z-DOL molecules and the substrate [8]. The enhanced σ of the end groups is supposed to result from energy distribution within the collision cascade via the chemical bonding.

X-1P

X-1P has a cyclic phosphazene structure with side chains of $(p\text{-OC}_6\text{H}_4\text{F})_n$ and $(m\text{-OC}_6\text{H}_4\text{CF}_3)_{6-n}$. Its molecular ions of $[\text{M}+\text{H}]^+$ appeared at m/z 1052 ($n = 1$), 1002 ($n = 2$), 952 ($n = 3$) and so on. From the side chains, fragment ions of $\text{C}_6\text{H}_4\text{F}^+$ and $\text{C}_6\text{H}_4\text{CF}_3^+$ were observed at m/z 95 and 145. As well as Z-DOL, their

σ values showed the linear increase versus the secondary ion mass on a logarithmic scale, as shown in Fig.5. Although the chemical structure of Z-DOL and X-1P are far different, the tendency of their damage cross sections seems to be almost similar.

CU PHTHALOCYANINE

Cu pc has a cyclic phthalocyanine structure of $(\text{C}_8\text{H}_4\text{N}_2)_4\text{Cu}$. Its molecular ion of $[\text{M}]^+$ and dimer ion of $[2\text{M}]^+$ appeared at m/z 575 and 1150, respectively. From the phthalocyanine, fragment ions of $\text{C}_8\text{H}_9\text{N}^+$ and $\text{C}_8\text{H}_4\text{N}_2^+$ were observed at m/z 119 and 191. The σ values of $\text{C}_8\text{H}_9\text{N}^+$ were quite low, and its intensity was not decreasing against PIDD. The $\text{C}_8\text{H}_9\text{N}^+$ ions are considered as fragmentation products. Such a fingerprint fragment ion with small σ can tolerate higher dose densities and may be useful for imaging purpose.

NYLON-6

Nylon-6 has one repeating unit of $[-\text{C}_5\text{H}_{10}\text{CONH}-]$. Its oligomer ions of $[n\text{M}+\text{H}]^+$ appeared at m/z 114, 227, 340 and so on (at m/z $113n+1$). Their σ values showed a tendency to increase with increasing n , as expected. In particular, the σ caused by Au_3^+ showed the rapid increase versus the secondary ion mass on a logarithmic scale, as compared with those of the lubricant in Fig. 5. Although the tested polymer has a linear structure as well as Fomblin Z-DOL, its damage cross sections caused by polyatomic ion bombardment are rather high in the higher mass region.

One of the possible origins might be the difference in film thickness. The bombardment of the surface and the formation of the collision cascade causes the damage not only at the surface but also in the deeper layers. However, it is difficult to compare thin film materials and thick films, because the damage cross section for thin film materials is really a combination of damage and removal of material.

SUMMARY

We have evaluated the damage cross sections of three samples including four organic materials caused by Au cluster ion bombardment.

Obtained σ values for the selected characteristic

ions of each material were in the order of $10^{-13} \sim 10^{-12}$ cm^2 . Ratios of $\sigma(\text{Au}_3^+) / \sigma(\text{Au}^+)$ were in the range of 1.5~5, which were consistent with the number of Au atoms composing the cluster primary ions.

In the case of lubricant thin film, the σ values of both Fomblin Z-DOL and X-1P show a linear increase versus the secondary ion mass on a logarithmic scale. However, the $\text{CF}_2\text{CH}_2\text{OH}^+$ ions, originated from the hydroxyl end groups and deeply concerned with the chemical bonding to the substrate, showed exceptionally high damage cross section. The enhanced σ of the end groups is supposed to result from energy distribution within the collision cascade via the chemical bonding.

In conclusion, evaluation of σ is very important not only to perform the most sensitive analysis of each interested material but also to investigate the chemical interaction between the organic molecules

and substrate.

REFERENCES

- [1] A. Benninghoven, *Surf. Sci.*, **299/300**, 246 (1994).
- [2] B. Hagenhoff, R. Kersting, D. Rading, S. Kayser and E. Niehuis, Proc. SIMS XII, 833 (2000).
- [3] F. Kollmer, *Appl. Surf. Sci.*, **231-232**, 153 (2004).
- [4] F. Kotter and A. Benninghoven, *Appl. Surf. Sci.*, **133**, 47 (1998).
- [5] D. Stapel, O. Brox and A. Benninghoven, *Appl. Surf. Sci.*, **140**, 156 (1999).
- [6] D. Rading, R. Kersting and A. Benninghoven, *J. Vac. Sci. Technol. A*, **18**, 312 (2000).
- [7] B. Hagenhoff, K. Pfitzer, E. Tallarek, R. Kock (2004).
- [8] Y. Abe, M. Shibayama and T. Matsuo, *Surf. Interface Anal.*, **30**, 632 (2000)