# Substrate Dependence of Secondary Ion Intensities from Langmuir-Blodgett Films Investigated by TOF-SIMS

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The difference in secondary ion intensities was investigated in TOF-SIMS analyses of Cd arachidate films on various metal and Si substrates. The dependence of intensities on substrates was clearly observed: e.g., the $[M+Me]^+$ and $[M+H]^+$ intensities showed different dependencies on chemical nature of the substrates, where M and Me denote an arachidate molecule and a metal or Si atom of the substrate, respectively. The $[MeCH_2(CH_2)_n]^+$ intensities as functions of $n$ also vary with substrate materials, and some of them have distinct peaks at $n$=18 and 1. The results were partly interpreted by 'bond-order' calculations.

## *1. Introduction*

In TOF-SIMS, the species and intensities of secondary ions are greatly dependent on the nature of the coexisting substrates [1,2]. In particular, secondary ion emission from a thin organic film sample is seriously influenced by the chemical properties of the substrate on which the sample is deposited. In this study, we investigated the secondary ion emission from Langmuir-Blodgett (LB) films that had tailored structures in layer-by-layer fashion on various substrates [3]. We systematically measured the intensities of fragment and parent-like ions from the LB films, and discussed the differences in the ion intensities with referring to the 'bond orders' obtained by semi-empirical MO calculation [4].

## *2. Experimental*

The LB film samples were Cd arachidate films that were formed on silicon substrates coated with silver, gold, copper, aluminum, and titanium, respectively. TOF-SIMS analyses were performed by a Physical Electronics TFS2000 instrument. Positive-ion spectra were obtained by using a pulsed 12-keV $Ga^+$ beam, which was rastered over120 × 120μm². The primary beam current measured as a continuous beam was about 600 pA and the total ion dose density was about $4.8 \times 10^{12}$ ions/cm². The other experimental conditions were previously reported by the authors [5,6,7].

## *3. Results and Discussion*

Typical mass spectra of positive ions from one-layer LB film samples on Ag, Au and Si and from two-layer sample on Cu are given in Fig. 1, where the mass ranges from 335 to 515. In the following discussion, the various ion species were classified into four categories, i.e., the protonated molecular ions $[M+H]^+$, metal-adduct parent-like ions $[M+Me]^+$, metal-adduct fragment ions $[MeCH_2(CH_2)_n]^+$ and fragment ions from organic molecules $[CH_3(CH_2)_n]^+$ (M and Me denote the arachidate molecule: $CH_3(CH_2)_{18}COOH$ and substrate metal atom, respectively). In the spectra from Ag and Cu substrates, strong metal-adduct parent-like ion peaks such as $[M+Ag]^+$, $[M+Cu]^+$ were observed. In the cases of Au and Si substrates, however, these $[M+Me]^+$ ions were observed to be weak. For Al and Ti substrates, they could scarcely be observed. The metal adduct fragment ions and other fragment ions from the Cd arachidate molecules were also seen in the spectra as well as the substrate metal ions such as $Me^+$, $Me_2^+$ and so on.

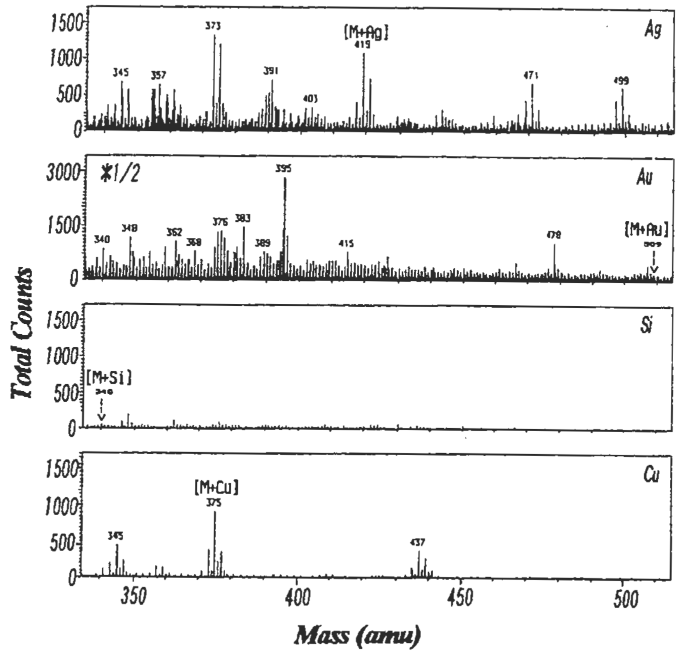

Fig. 1 Typical mass spectra for positive ions obtained from one-layer LB film samples on Ag, Au and Si and two-layer sample on Cu .

The intensities of various secondary ion species from different substrates are summarized in Fig. 2. In this case, all the intensities were normalized by $C_3H_5^+$ since the $C_3H_5^+$ intensities seemed to be almost the same in all of the samples. In the following discussion, intensities are evaluated after normalizing by $C_3H_5^+$. As is summarized in this figure, the $[M+Me]^+$ ion intensities are clearly different with the substrates. The protonated molecular ion peak, $[M+H]^+$, from the samples on Au was observed to be very strong, whereas the other peaks from the samples on Ag, Si, Ti, Al and Cu substrates were not so strong. This is different from the case of $[M+Me]^+$.

Since the $[M+Me]^+$ ion is easily formed through the precursor state of an LB-film molecule combining with a substrate atom [8], the bonding strength and the stability of the state should have an influence on the obtained ion intensity. On the other hand, the $[M+H]^+$ ion can be formed through desorption of the LB molecule from the substrate, which means that the intensity should be influenced by the adsorption strength of the LB-film molecule to the substrate atom.

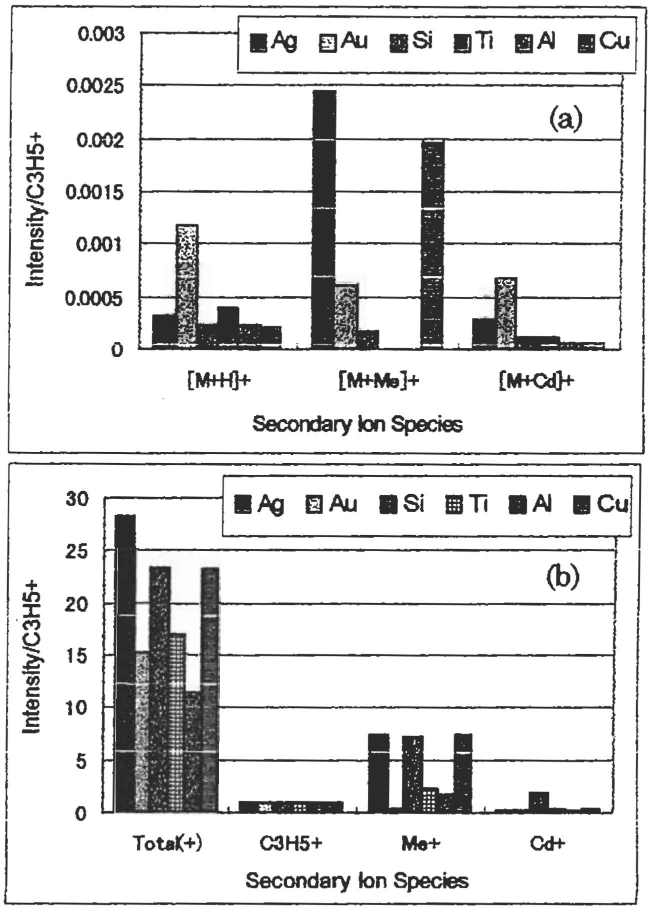

Fig. 2(a), (b) Secondary ion emission from LB films formed on different substrates. The intensities were normalized by the $C_3H_5^+$ intensities, respectively.

These considerations lead to the expectation that the $[M+Me]^+$ and $[M+H]^+$ intensities might show complementary behaviors to each other, if there is no difference in ionization mechanism. The observed results, however, do not agree with this prediction. Because there is no reliable data for the adsorption energy or the bonding energy between the Cd arachidate molecule and the substrate metals, it is not possible to precisely correlate the present experimental data with chemical and physical properties of this investigated system at this moment. The tendency of $Me^+$ intensities in Fig. 2 does not agree with that expected from the secondary ion yield, either. We here used the values of secondary ion yields in 12-keV $Ar^+$

bombardment [9] for interpreting our experimental results because we have no reliable systematic data for 12-keV $Ga^+$ bombardment. Since it is regarded that the general tendency of the relative secondary ion yield by $Ga^+$ excitation is similar to that of $Ar^+$ excitation. This analysis is reasonable as the first order approximation. The discrepancy between the $Me^+$ tendency and the secondary ion yields implies that the intensities of $Me^+$ may be influenced by the effect of surface oxidation of the substrates. This further dose not contradict with the fact that only the intensity ratio $[M+Au]^+$ to $Au^+$ is located at much a higher value than the five data points for other substrates, as is shown in Fig. 3, that is, Au is free of surface oxidation.

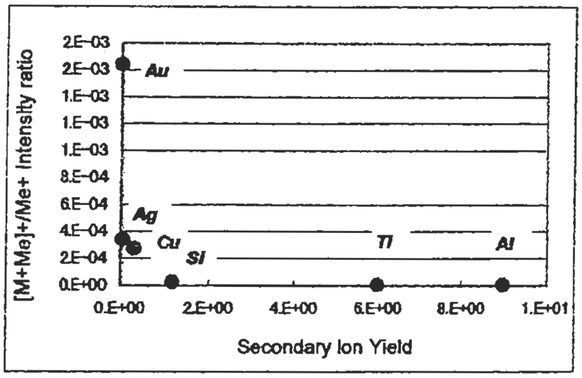

Fig. 3 Intensity ratio $[M+Me]^+$ to $Me^+$ versus secondary ion yield of Me.

Fig. 4 and Fig. 5 illustrate the intensity variations of the metal-adduct fragment ion species ($[MeCH_2(CH_2)_n]^+$) and other fragment ions from Cd arachidate molecules ($[CH_3(CH_2)_n]^+$) as functions of the number of $CH_2$ groups ($n$), respectively, using one-layer samples on Ag, Au and Si and two-layer samples on Ti, Al and Cu. As can be seen in Fig. 4, the variation in the $[MeCH_2(CH_2)_n]^+$ intensities showed a clear dependence on the substrate materials. For the samples on Ag and Cu, there was observed a distinct peak at $n$=18, whereas for the samples on Au and Si, there could not be seen a peak at $n$=18 but an intense peak at $n$=1.

On the other hand, as shown in Fig. 5, the changes in $[CH_3(CH_2)_n]^+$ intensities with $n$ was found to be almost identical and independent of the substrate materials except that the intensities from Au were a little higher than those from other substrate when $n$ is larger than 5. The intensity variations show a broad peak around $n$=2 and a clear intensity depression at $n$=0.

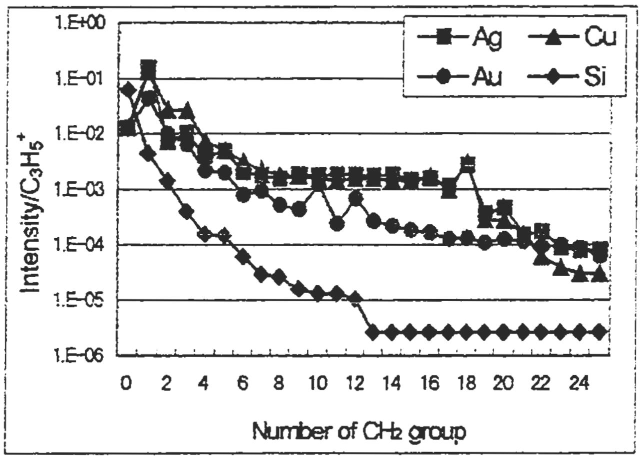

Fig. 4 $[MeCH_2(CH_2)_n]^+$ intensities from the LB films on the different substrates as functions of the number of $CH_2$ groups.

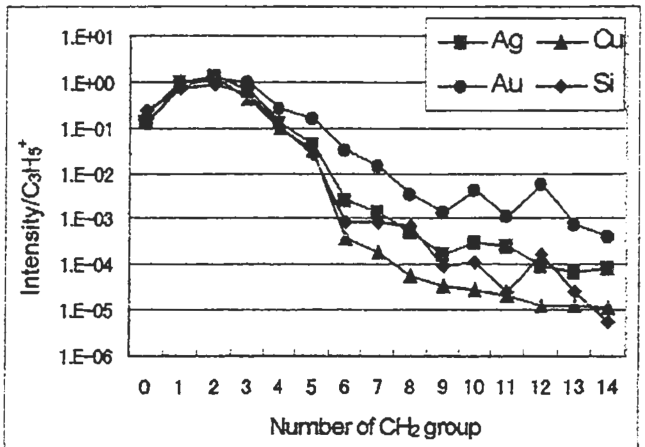

Fig. 5 $[CH_3(CH_2)_n]^+$ intensities from the LB films on the different substrates as functions of the number of $CH_2$ groups.

Some of these results can be interpreted with the aid of the chemical bond strength of the arachidate molecule estimated by MO calculation. The following discussion will be made with referring to the estimated bond orders obtained with the AM1 Ver.6 program package [4]. In this calculation, the Cd and Ag atoms were temporally replaced with Hg and K because of the lack of the proper parameters for the strict calculation. As the result, the bond order between the $CH_2$ chain and the carbonyl carbon -COOHg was estimated to be 0.877 and is smaller than the other values of the C-C bonds in the $CH_2$ chain (from 0.974 to 0.976). This analogously suggests that the bond between the $CH_2$ chain and the -COOCd is easily scissioned by the primary ion bombardment and might result in the emergence of the peak at $n$=18 in Fig. 4. Furthermore, the bond order of the $CH_3$-$CH_2$, which may explain the peak intensity at $n$=0, was estimated to be higher (0.983) than those of other C-C (0.975) in the $CH_2$ chain. This successfully explains the intensity depression at $n$=0 for the samples on Cu, Ag and Au. There still remain some other results unexplained, such as the data for Au at $n$=18 and Si at $n$=1 in Fig. 4.

The peaks around $n$=2 in Fig. 5 could not be explained either with the preliminary calculation using Hg instead of Cd. Stricter calculations using precise parameters are necessary.

## 4. Conclusion

The difference in secondary ion intensities was investigated in TOF-SIMS analyses of Cd arachidate films on various metal and Si substrates. The $[MeCH_2(CH_2)_n]^+$ intensities as functions of the number of $CH_2$ chain $n$ also vary with substrates, and some of them have distinct peaks at $n$=18 and 1. These results were partly interpreted by the preliminary bond-order calculations. This suggests that this kind of calculation method should be useful for interpreting secondary ion formation. On the contrary, the variation in $[CH_3(CH_2)_n]^+$ intensities with $n$ was almost independent of substrate materials and could not be explained by our preliminary calculations. To fully understanding the intensity differences of the ions objected from these systems, various ion-formation processes should be considered in addition to the sample bond-scission mechanism used here. Furthermore, the lifetime and stability of fragment ions should also be taken into account.

## 5. References

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