Paper

Simulation of Fragmentation of Polyethylene Glycol by Quantum Molecular Dynamics for TOF-SIMS Spectral Analysis

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For detail analysis of fragmentation of organic molecules in TOF-SIMS spectra, fragmentation process of a polyethylene glycol (PEG) was simulated by using Quantum Molecular Dynamics method. In the simulation, fragmentation process of the PEG model was assumed as thermal decomposition. Initial thermal energies given to the model were 20 ~ 90 eV at every 10 eV step, and the energies were relaxed to 1.5 eV by using Brendsen method. Simulation results of the mass spectra for PEG model were in considerably good accordance with experimental ones of PEG in TOF-SIMS.

1. Introduction

TOF-SIMS is useful surface analytical method for organic materials (polymers, biomaterials and so on). However, for observations of large organic molecules such as polymers and proteins by using TOF-SIMS, it is difficult to obtain the intact molecular secondary ions because of complicated fragmentation. Therefore, we need detailed analysis of such organic molecules in TOF-SIMS spectra. Recently, Aoyagi and coworkers selected specific peaks which can distinguish different protein samples by using spectral analytical method owing to information theory [1] and applied the analytical method to clarify the structure for biosensor materials [2]. On the other hand, in order to determine the structure of complicated fragment ions from organic molecules such as proteins, we think it is useful to simulate fragmentation process of such organic molecules from theoretical standing-points.

Classical molecular dynamics (CMD) simulation has been performed to model ion sputtering of solids including metals [3] and organic thin films on inorganic substrates [4,5]. In these CMD simulations the damage to solid surface was made more reduction by cluster ion bombardments than by mono-atomic ion bombardments. The simulations showed good agreement with TOF-SIMS experimental results. On the other hand, peak position and intensity of mass spectra obtained from CMD simulation of ion sputtering couldn't be compared with the electric charged fragments of experimental TOF-SIMS spectra [6], because they

didn't perform the electric charge analysis for fragments. Recently, we simulated fragmentation process which was assumed as thermal decomposition [7], ion impact [8] and molecular collision [9] by using Quantum Molecular Dynamics (QMD) method with the charge analysis by MO calculations. The calculated fragment spectra correspond considerably well to experimental results. Therefore, we think QMD method is very useful for analysis of fragmentation process of organic molecules.

In this study, fragmentation process of PEG in TOF-SIMS spectral analysis was simulated by QMD method. Fragmentation processes in this simulation were assumed as thermal decomposition. Thermal energy dependence in fragmentation process of PEG model molecule was also discussed in comparison with experimental TOF-SIMS spectra of PEG.

2. Computational method

In experimental condition of TOF-SIMS, molecules on surface area where is bombarded by primary ion have high kinetic energy because of drastic vibration and collision of molecules which are caused by ion bombardments. Therefore fragmentation of molecules in TOF-SIMS can be understood by thermal decomposition. We used 5-mer model molecule ($C_{10}H_{22}O_6$) of PEG, and all calculations were carried out by using QMD method. In QMD method, intra-atomic forces were evaluated by semi-empirical molecular orbital method PM3 by using GAMESS code[10], and the

Journal of Surface Analysis Vol.17 No.3 (2011) pp.208-211

N. Kato et al.   Simulation of Fragmentation of Polyethylene Glycol by Quantum Molecular Dynamics for ...

velocity Velret algorithm was used to solve a equation of motion for atoms in molecule.

Initial thermal energies given to PEG model for thermal decomposition simulation were 20 ~ 90 eV at every 10 eV step. In experimental condition, energy given to material surface by ion bombardments is relaxed because of reconstruction of surface. Therefore thermal energy given to the model molecule in simulation has to be relaxed to a value which corresponded to room temperature. In this simulation, Berendsen method [11] was used for thermal energy relaxation. All number of trajectories in this simulation were 100.

3. Results and Discussion
3.1 Thermal energy relaxation

Fig.1 shows thermal energy relaxation at initial thermal energies of 90 and 40 eV. Thermal energies in both initial conditions increased around at 100 fs and relaxed to room temperature condition at 500 fs. This result corresponds to the simulated curves of cluster ion bombardments [11].
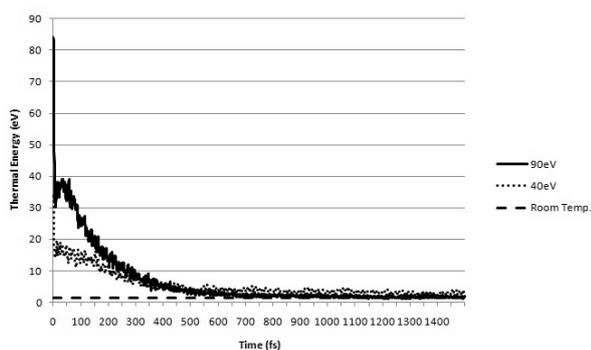
Fig. 1. Thermal energy relaxation at initial thermal energies of 90(solid line) and 40(dotted line) eV. Dashed line shows room temperature.
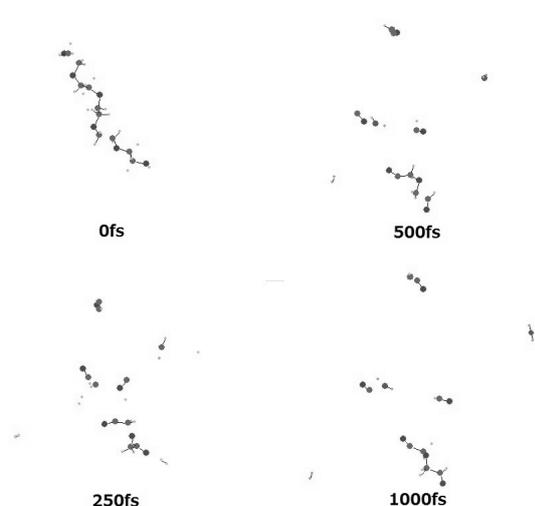
Fig. 2. MD snapshots of thermal decomposition process of PEG model molecule at 0, 250, 500, and 1000 fs. Initial thermal energy was 90eV.

3.2 Thermal decomposition process of PEG

Fig.2 shows MD snapshots of thermal decomposed process for PEG at 0, 250, 500 and 1000 fs. Fragmentation process was almost completed within 500 fs. In sputtering MD simulations for organic utmost surface layer [12], fragmentation of molecule after ion bombardment was also finished within 500 fs.

Fig.3 shows experimental TOF-SIMS spectrum of PEG by using 20keV Au⁺. In Fig.4, we showed calculated mass spectra resulted from thermal decomposition of PEG model molecule in the mass range from 0 to 100 atomic mass unit (amu). In the mass range of 0 ~ 50 amu, when thermal energies are 90, 80, 70, 60, and 50 eV, peak positions in calculated mass spectra correspond to those in experimental spectrum. On the other hand, in the mass range of 50 ~ 100 amu at thermal energy of 70, and 60 eV, peak positions in calculated spectra correspond to the experimental ones in TOF-SIMS.

We showed experimental TOF-SIMS spectrum of PEG in Fig. 5. Fig.6 indicates calculated mass spectra obtained from thermal decomposition of PEG model molecule in the mass range of 100 ~ 250 amu. Calculated peaks at thermal energies of 50 and 40 eV correspond to experimental ones in TOF-SIMS spectra, while we could not simulate similar peaks in the thermal energy ranges of 60 ~ 90 eV. The reason implies that the high initial thermal energy promoted fragmentations in smaller atomic mass units of fragments. On the other hand, in the thermal energies of 20, and 30 eV, intact molecular peaks exist in very high intensity. This means that fragmentation didn't occur due to low thermal energies.
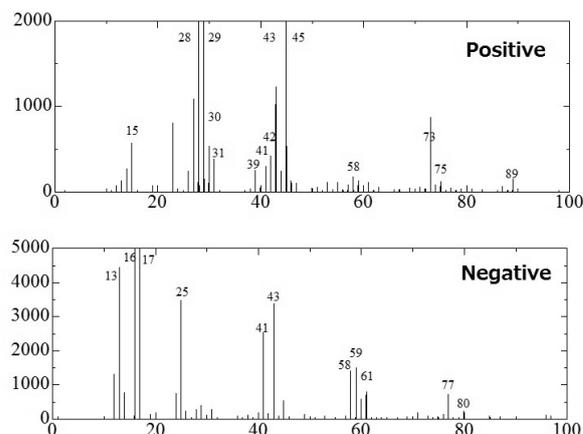
Fig. 3. Experimental TOF-SIMS spectrum of PEG in the mass range of 0 ~ 100 amu. [13]

Journal of Surface Analysis Vol.17 No.3 (2011) pp.208-211

N. Kato et al.   Simulation of Fragmentation of Polyethylene Glycol by Quantum Molecular Dynamics for ...
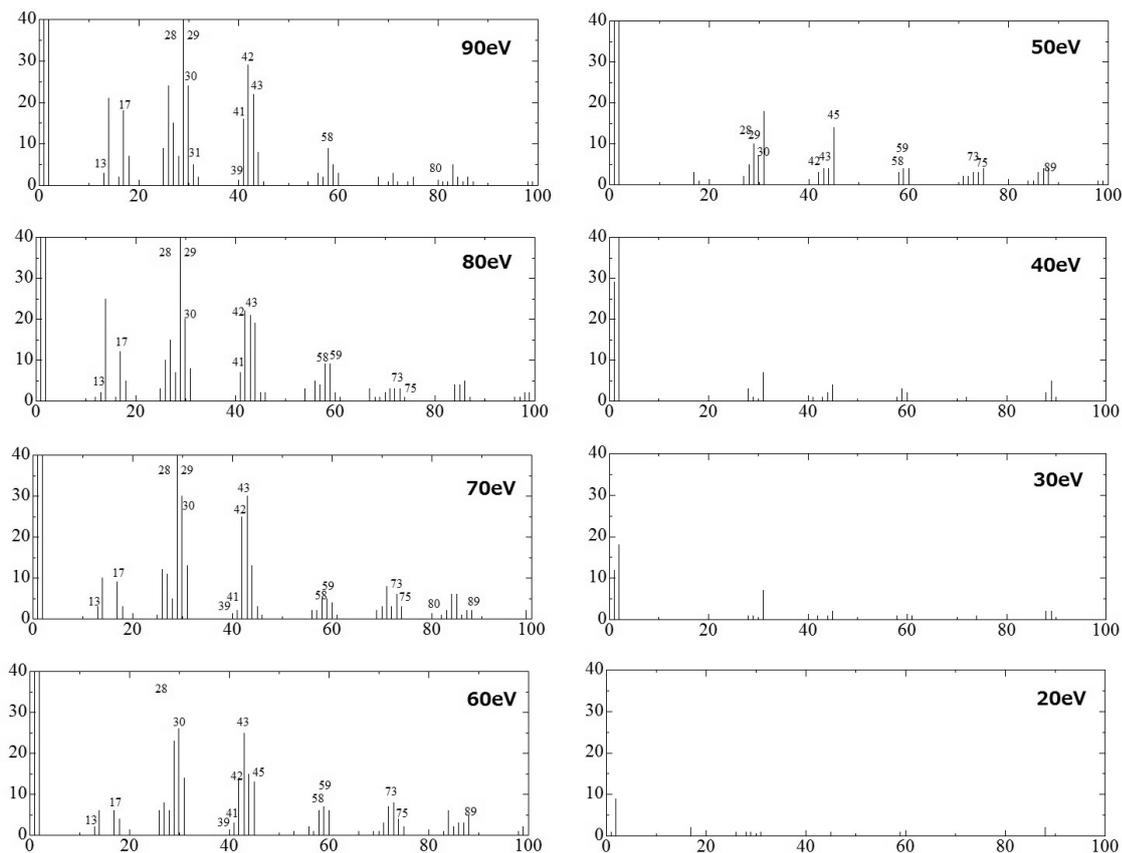
Fig. 4. Calculated mass spectra of PEG model in the mass range of 0~100 amu.

From these results, we can conclude that positions of peaks in experimental TOF-SIMS spectra depend on the energy given to the PEG model molecule.

4. Conclusion

In order to analyze fragmentations of PEG model molecule in TOF-SIMS spectra, the process of the model molecule was simulated by quantum molecular dynamics method. From simulations which was assumed as thermal decomposition, it can be seen that positions of peaks in experimental TOF-SIMS spectra depend on the energy given to the PEG molecule. Some peaks appeared in experimental TOF-SIMS spectra were not compared with calculated ones by thermal decomposition calculation with QMD method, because recombinations of proton atoms with small fragments are enhanced in the thermal decomposed process by QMD method.
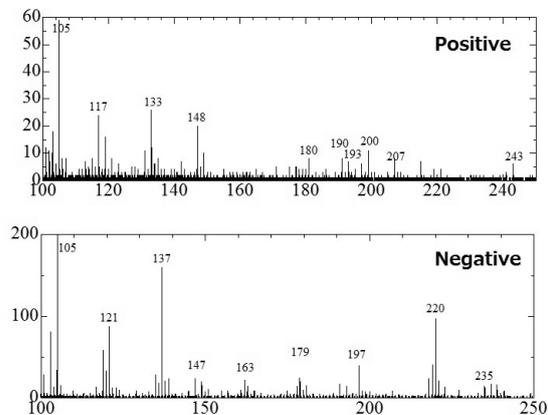
Fig. 5. Experimental TOF-SIMS spectrum of PEG in mass range from 100 to 250 amu. [13]
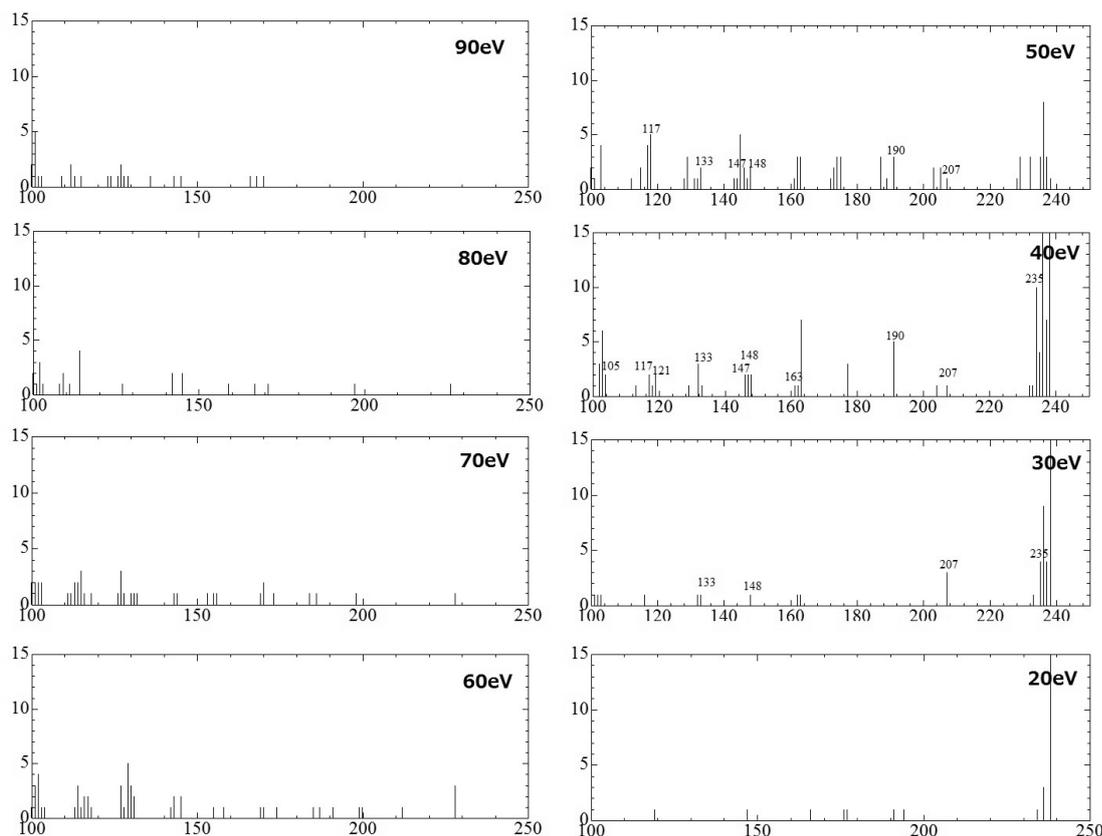
Fig. 6. Calculated mass spectra of PEG model molecule in mass range of 100 ~ 250 amu.

5.References

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