Extended Abstracts of the 2014 International Conference on Solid State Devices and Materials, Tsukuba, 2014, pp588-589

Elucidation of semiconductor / bio-interface structure by molecular dynamics simulation

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Abstract

The comprehension of aqueous structure is very important to the improvement of the biosensing devices. In this study, we simulated the oxide/electrolytes bio-interfacial properties by a classical molecular dynamics method. As a result of the simulation, we could propose a novel bio-interface structure with DNA molecule in a concentrated salt solution.

1. Introduction

In recent years, various kinds of biosensors have been developed and utilized in the field of biology, clinical diagnosis, and pharmaceutical development. Most biosensing devices are generally used in the aqueous environment, forming the bio-interface structure which consists of a solid state for detection, a liquid state for sustenance of living environment, and a bio-molecule as a target. Therefore, the comprehension of the bio-interface structure is very important to the improvement of the performance of biosensors.

In particular, since the mechanism of semiconductor-based field effect transistor (FET) biosensors is based on the potentiometric detection of the bio-molecular charges at the sensing surface [1], the importance of the aqueous structure near the solid/liquid interface is tremendously high. The FET biosensors were applied to the detection of various targets such as enzymes [2], antigen-antibody reactions [3], DNA [4], and living cells [5].

The biggest problem of biosensors is whether their detection abilities have the selectivity and the specificity for the biological targets or not. The measurement of FET biosensor is often performed including a lot of ions in the aqueous solution besides the bio-molecules as a target. Therefore the elucidation of the ionic behaviors gives a guide for the elimination of the influence of the unwanted charge in the electrical detection. However, it is difficult to investigate experimentally the aqueous structure of interface, especially under the existence of the bio-molecules.

Our purpose of this study is to develop a pseudo-experimental system of FET biosensors and investigate the effect of the bio-molecules on the ionic behaviors around the device/solution interface by use of the molecular dynamics (MD) simulations.

2. Methodology

Simulation cells

To compare the influence of the existence of the bio-molecules on the aqueous structure around the solid/liquid interface, we prepared the simple oxide/electrolytes interfacial simulation cells (solid/liquid model) and the bio-interfacial simulation cells tethering ds-DNA on the oxide surface (bio-interface model). The (100) SiO_2 (alpha-quartz) was chosen for the oxide solid surface. The SiO_2 is used broadly for the material of the insulator of FET devices. The SiO_2 surface was protonated in a solution depending on the pH, and adjusted to the ratio of $N_{SiO^-}/N_{SiOH} = 1/5$ in the simulations [6]. The electrolytes were 1.0M NaCl solutions. In case of the bio-interface cells, the 19 Na^+ was inserted additionally for the neutralization of the charge of the DNA. The initial DNA strand was the B chain consisted of the dodecamer d(AAAAAAAAAA) and the complementary strand of base-T. The SiO_2 and DNA were bonded by the DNA linker comprised of opened epoxide and amine.

Molecular dynamics simulation

The geometry optimization was carried out for each cell in advance of the main MD calculations by way of a complex calculation of the steepest descent and the conjugate gradient method with a total of 5000 steps. All cells were relaxed by MD in the NVT ensemble at 100 K, 200 K, and 300 K for 0.5 ns, respectively after geometry optimizations. The main MD calculations were performed at 300 K for 3.0 ns in the NVT ensemble. The last 0.5 ns were used for various analyses. All simulations were carried out using Materials Studio simulation package [7] including Condensed Phase Optimized Molecular Potentials for Atomic Simulation Studies (COMPASS) [8,9].

3. Results and Discussions

Fig. 1 shows the snapshot of the tethered DNA for the temporal change of the dynamics. The double strand structure was also remained and the DNA seemed to swing in the solution. The DNA was rigid due to the structure of the double strand, however the DNA linker was inflected because of the carbon chain, resulting in leaning of the tethered DNA.

The comparison of the aqueous structure around the SiO_2 interface between the solid/liquid model and bio-interface model is shown in Fig.2. In both the solid/liquid model and bio-interface model, the Na^+ adsorbed at around the SiO_2 interface, forming two layered structure, and the oxygen and hydrogen of water molecules took three

or four layer structure. There were no significant differences between those two models for the configuration of ions and water molecules. Although the DNA has many negative charges derived from the phosphate ester, why did not the tethered DNA affect the aqueous structure?

Fig.3 shows the Na^+ behavior around the tethered DNA. The Na^+ played an important role in remaining the double strand structure. In fact, if there were much fewer ions in the solution, the DNA cleaved immediately. In this MD simulation, the Na^+ adsorbed strongly at the site of the phosphate of the DNA and stayed nearby the double strand. These Na^+ prevented the DNA from cleaving and screened the negative charge of the phosphate. Therefore the aqueous structure around the interface could take less affect from the DNA.

From the above simulated results by the MD,, it could be predicted that the bio-molecules did not affect the aqueous structure around the solid/liquid interface in the concentrated solution. This suggestion would give a novel inspiration to obtain the detection selectivity of the FET biosensors.

4. Conclusions

In this study, we investigated the difference in the surface aqueous structure between the solid/liquid model and bio-interface model. The MD simulations resulted in that the large difference in the configuration profile was not found between two models. There may be some possibilities of measuring selectively the specific ions such as hydrogen ion in the concentrated solution in spite of the existence of the bio-molecules. We will examine the effect of bio-molecules in the dilute solution on the surface aqueous properties in the next research.

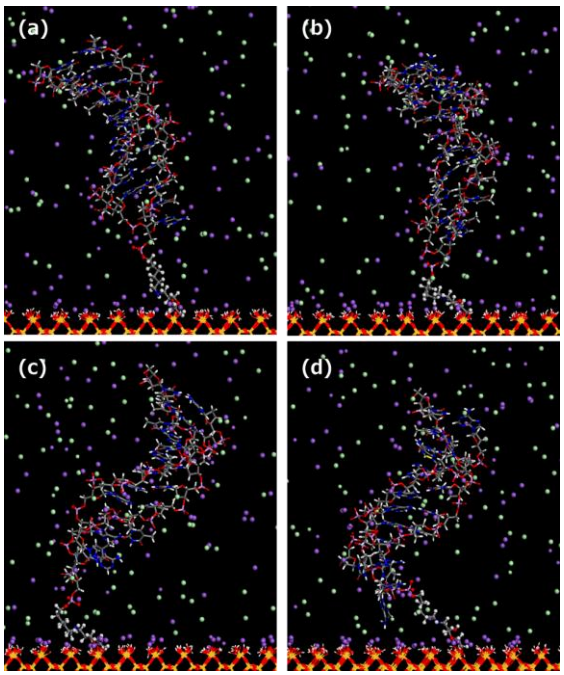

Fig. 1 Snapshot of the dynamics of the tethered DNA at (a) 0 ns, (b) 1.0 ns, (c) 2.0 ns, and (d) 3.0 ns.

Acknowledgements

This work was partly supported by the CREST project, Japan Science and Technology Agency (JST). We thank Dr. Abhijit Chatterjee of Accelrys K.K. in Japan for help and discussion.

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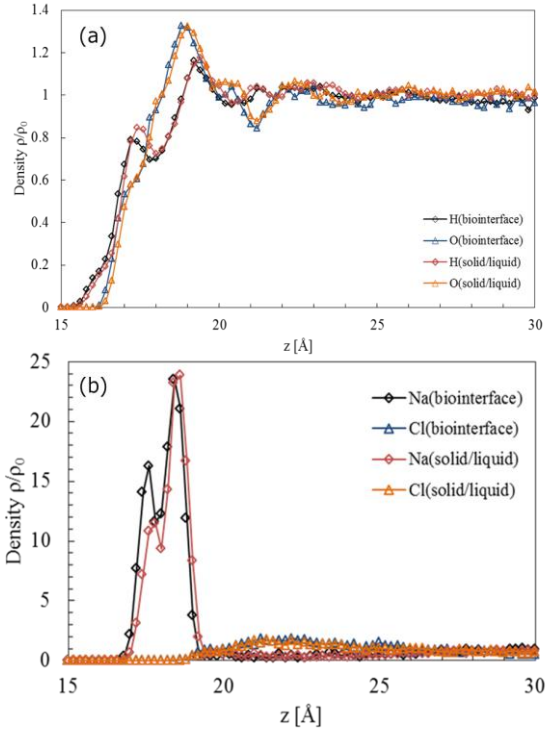

Fig. 2 Density profiles of (a) water molecules and (b) ions.

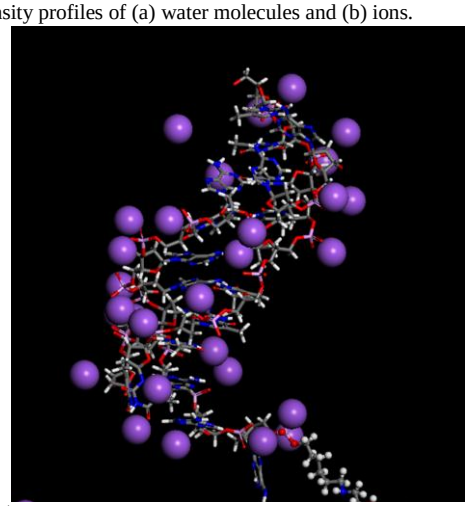

Fig. 3 Na^+ location around the DNA.