Impact of defects in self-assembled monolayer on humidity sensing by molecular functionalized transistors

Takahisa Tanaka*, Takeaki Yajima, and Ken Uchida*

Department of Materials Engineering, The University of Tokyo, Bunkyo, Tokyo 113-8656, Japan

*E-mail: tanaka@ssn.t.u-tokyo.ac.jp; uchikad@material.t.u-tokyo.ac.jp

Received December 2, 2019; revised February 18, 2020; accepted March 18, 2020; published online April 13, 2020

1. Introduction

Toward the realization of the IoT era, chemical sensing by small electronic devices has attracted much attention for a wide variety of applications such as breath diagnosis and detection of biomolecules and toxins. For various applications, chemical sensors are required to detect a certain target gas with high sensitivity and high selectivity. Electrical properties of Si transistors are sensitive to their surface conditions. Therefore, chemical sensors made by Si transistors have been intensively developed both for gas-phase and solution-phase sensings.10–13 To enhance the selectivity, surface functionalization by metals1–3 and self-assembled monolayers (SAM)4,5,7,8,10–13 have been studied. Due to a variability of the functionalized molecular structures, SAM can modulate interactions between the surface and the target molecules maintaining high sensitivity.

Although, numerical calculations based on the density functional theory have been reported for sensing mechanisms of metal functionalized14) and bare Si surfaces,15,16) sensing mechanisms of a SAM functionalized surface have not been completely understood. Usually, sensing mechanisms of the SAM functionalized Si transistors have been understood with an assumption of defectless SAM.17–19 However, SAM defects can be easily generated by a surface roughness and variability in functionalization process. Furthermore, adsorbates easily penetrate into the SAM through the defects.20–22) Although several groups have studied molecular adsorption to defects of SAM by molecular dynamics (MD) calculations,20,21) MD calculations alone cannot calculate electrical sensor responses such as carrier concentration and threshold voltage (Vth) shift by adsorbates in SAM functionalized transistors.

In this work, effects of water adsorption to a defected-SAM-functionalized transistor on Vth shift were studied by MD calculations followed by the carrier concentration calculation in the Si layer of the transistor. The proposed calculation method improves understanding of the electrical sensor response based on the atomic positions resulting from many molecular interactions, which should be considered in actual disordered molecular structures. Although the preliminary results were reported,23) calculated device structure was modified to mimic realistic gas sensors and time dependent Vth was newly analyzed. From atomic positions and time dependent Vth, it was clarified that adsorbates in a SAM defect stacked with the same direction caused large Vth shift.

2. Simulation methodology

Figure 1(a) shows a schematic of calculated structure. In order to calculate a situation close to experiments, nanowires were considered in the present work. However, typical cross-sectional length scale of silicon nanowire (SiNW) was several 10 nm, and there were too many atoms to atomically simulate surface and electrical properties. To suppress the calculation cost, capacitative coupling between SiNW surface and gate electrode was mimicked by the top air region. Thickness of the top air region was defined by $T_{\text{air}} = k_0/C_{\text{AVe}}$, where $k_0$ is the dielectric constant and $C_{\text{AVe}}$ is the averaged capacitance defined from Fig. 1(b). In the top air region, atomic charges whose positions were determined by the MD calculations were introduced.

The MD calculations were done by LAMMPS,24) (111) oriented β-cristobalite whose mass density is similar to that of thermally oxidized SiO2 was assumed as a fixed substrate. For a test case, we considered SAM formed from trichloroethyilsilane and water molecules as adsorbates. This combination of the SAM and the adsorbate was experimentally studied by previous work, and negative Vth shift was reported.5) Although silane-based SAMs were hydrolyzed and desorbed by water immersion,25) we thought the effects of the hydrolyzation should be small in SAMs for gas sensing because of the low water density. As force fields in the MD calculations, we employed modified OPLS-AAA and TIP3P for SAM and water molecules, respectively,26,27) According to reported experimental functionalization,28) three chloro-groups were replaced by three hydroxyl groups. One hydroxyl group was used to connect SAM molecules to the substrate as shown in Fig. 1(c). In order to investigate the effects of SAM defects, three SAM molecules were replaced with three hydroxyl groups as the defects as shown in Figs. 1(d)–1(f). The visualization of atomic position was...
done by OVITO.\textsuperscript{29} From the length/width of 5.04 nm/5.24 nm, the coverage density of SAM with and without the defect is 4.43 nm\(^{-2}\) and 4.55 nm\(^{-2}\), respectively. The densities of assumed SAM were in good agreement with experimental SAM density of 4.4 nm\(^{-2}\)\textsuperscript{30}. As the adsorbates, we assumed 80 water molecules on the SAM as shown in Fig. 1(g). During the MD calculations, temperature of the SAM was fixed at 300 K within canonical (NVT) ensemble by the Nosé–Hoover thermostat. On the other hand, the temperature of the water molecules was changed during the MD calculations. From 0 to 10 ps, the temperature of the water molecules was fixed at 600 K within NVT ensemble by the Nosé–Hoover thermostat. By this approach, the water molecules were scattered in the simulation box as shown in Fig. 1(h). In the following 1 ns, the adsorbates were in microcanonical ensemble. Therefore, the water molecules were gradually cooled by interacting with the SAM at 300 K. Finally, the temperature of the water molecules was coincided with 300 K, and water molecules adsorbed on the SAM as shown in Fig. 1(i). Atomic positions of the last 0.5 ns were used to calculate the carrier concentration and \(V_{\text{th}}\) in the Si layer.

Carrier concentration was derived from iterative solutions of Poisson equation and an integration of a product of the Fermi–Dirac distribution function and three-dimensional density of states by COMSOL Multiphysics. In the Si layer, we assumed the donor concentration of 10\(^{17}\) cm\(^{-3}\). In this study, we focused on the \(V_{\text{th}}\) shift, and the absolute value of the impurity concentration did not have a significant effect on our results. An increase in gate voltage (\(V_G\)) resulted in a formation of an accumulation layer. From the linear relation of the accumulated carrier concentration and \(V_{G} - V_{\text{th}}\), \(V_{\text{th}}\) value was evaluated.

3. Results and discussion

The tilt angle of SAM depends on a surface coverage density. High coverage density results in the small tilt angle. Figure 2(a) shows time dependent tilt angles of the SAM with and without the defect. Time-averaged tilt angles were compared with the reported tilt angle of the SAM formed from trichlorododecylsilane as shown in Fig. 2(b).\textsuperscript{27}
According to the previous works, alkyl chain length of SAM has almost no contribution to the tilt angle.\textsuperscript{27,31} Therefore, the reproduction of the reported tilt angle validate the assumed SAM structures.

Figure 3(a) shows gate voltage dependences of carrier concentration for transistors with 50 different atomic positions of SAM without defects and adsorbates. For all atomic positions, linear relation between $V_G$ and carrier concentration was confirmed at $V_G > -3$ V. Figure 3(b) shows time dependent $V_{th}$ extracted from the $V_G$ dependence of carrier concentration in Fig. 3(a). Because of the time-dependent difference of atomic positions, there are slight variations in $V_{th}$ in the defect. The negative value of $V_{th}$ around $-3.8$ V originated from positive charges of the bottom Si layer in the fixed SiO$_2$ substrate. To concentrate on the effects by the SAM and its defect, time averaged $V_{th}$ in Fig. 3(b) was employed as a reference value $V_{th,0}$.

Figure 3(c) shows the time dependence of $V_{th}$ for SAM with the defect. The shift of $V_{th}$ from $V_{th,0}$ was averaged to be approximately $-17$ mV. Therefore, the shift of $V_{th}$ due to the SAM defect was small. Then, we calculated the $V_{th}$ shift by the water adsorption. Figure 4(a) shows the time dependent $V_{th}$ with considering water adsorption on the SAM without the defect. The adsorption of water causes $-41$ mV shift of $V_{th}$ from $V_{th,0}$. The negative $V_{th}$ shift agrees with MD calculation of water molecules on hydrophobic surface in previous works.\textsuperscript{32} For the SAM without the defect, penetration of water was not observed in the MD calculations. On the other hand, the penetration of the water was occurred for the SAM with the defects as shown in Figs. 4(b)–4(f). The SAM molecules around the defect were attracted to each other by the van der Waals interaction, making the defect less visible [Figs. 4(b) and 4(c)] unless the penetration occurred [Figs. 4(d)–4(f)]. In order to define the amount of the penetration, we counted the number of water molecules below the half height of the alkyl chains. Figure 4(g) shows the time dependent $V_{th}$ and number of penetrating water molecules for the defected SAM. The averaged $V_{th}$ shift of $-110$ mV was larger than that for the SAM without the defect. Furthermore, large $V_{th}$ shift appeared after the penetration occurred. In order to suppress a variability of MD calculations and to confirm a relation between the water penetration and the $V_{th}$ shift, penetrating water number dependence of $V_{th}$ shift was extracted from an average of several MD calculations started from different initial velocities. Figure 5(a) shows the averaged result of penetrating water number dependence of $V_{th}$ shift from 10 MD calculations. We can confirm the linear relation between number of penetrating water and $V_{th}$ shift. The $V_{th}$ shift at no penetration of water molecules almost coincide with the sum of the $V_{th}$ shift by the SAM defect itself and the adsorption of water molecules on the defectless SAM. The $V_{th}$ was shifted by a stacking of the water molecules with the same direction in the defect as shown in Fig. 5(b). A dipole moment linearly depends on the number of the stacked water molecules, and $V_{th}$ was shifted by the dipole. Such stacking in the defect originated from the Coulomb interaction among the water molecules. On the hydrophobic SAM surface, water molecules often exist with hydrogen down and oxygen up.\textsuperscript{32} As a result of molecular motion, the first trapped water molecule is pushed into the defect without turning the direction. Compared to the carbon and the hydrogen in the alkyl chains, water molecules have a strong polarization. From the Coulomb interaction of water molecules, it is more energetically stable for a secondary trapped water molecule to stack the same direction to the firstly trapped water molecule than to stack with the opposite direction. Experimentally reported $V_{th}$ shift of $-1.8$ V by 40% of relative humidity was larger than that derived from our calculations.\textsuperscript{31} In our calculation, the removal of the three SAM molecules resulted in the $V_{th}$ shift of $-0.2$ V. In order to satisfy the experimentally reported $V_{th}$ shift, SAM density was estimated to be $3.5 \times 10^{12}$ cm$^{-2}$, which is 73% of the full coverage. In actual SAM functionalization, some groups reported a short alkyl chain resulted in a disordered SAM because of a weak van der Waals interaction.\textsuperscript{33,34} Therefore, defect induced water sensing can reasonably explain the experimental $V_{th}$ shift.

The stack of adsorbates in the SAM defects would depend on both the size of the SAM defects and the size of the adsorbates. If a SAM defect was too large, the initially trapped adsorbate could be rotated in the defect, and the averaged $V_{th}$ shift would be canceled out. On the other hand, if the adsorbates were too large to stack or to penetrate into a defect, linear $V_{th}$ shift depending on the number of stacking would not be observed. Therefore, the stacking of adsorbates

Fig. 3. (Color online) (a) Gate voltage dependence of carrier concentration in the Si layer calculated from 50 different atomic positions derived from the MD calculations. In the MD calculations, SAM has no defect and water molecules were not included. (b) Time dependent threshold voltage calculated from the gate voltage dependences of carrier concentration in Fig. 5(a). Dashed line represents the time averaged reference value $V_{th,0}$. (c) Time dependent threshold voltage shift for the SAM with defect and without water adsorption. Dashed line represents the time averaged value.
in defects indicated the possibility to enhance not only the sensitivity but also the selectivity of SAM functionalized transistors.

4. Conclusions

We investigated the effects of SAM defects on the electrical sensing properties of the SAM functionalized transistors. Based on the MD calculations of the SAM and the water molecules, atomic position dependent carrier concentration in the Si layer was derived. From the $V_{th}$ calculated from the carrier concentration, it is revealed that the stacking of the adsorbed water molecules in the SAM defect causes the large threshold voltage shift. Our results imply the defect can enhance not only the sensitivity but also the selectivity of sensors, if the size of the SAM defect was precisely controlled.

Acknowledgments

This work is supported by JSPS KAKENHI Grant No. 19K15050. This work was partly supported by JST CREST Grant No. JPMJCR1912, Japan.

1) H. M. Fahad, N. Gupta, R. Han, S. B. Desai, and A. Javey, ACS Nano 12, 2948 (2018).
2) H. M. Fahad et al., Sci. Adv. 3, e1602557 (2017).
3) B. Choi, J. H. Ahn, J. Lee, J. Yoon, J. Lee, M. Jeon, D. M. Kim, D. H. Kim, I. Park, and S. J. Choi, Solid. State. Electron. 114, 76 (2015).
4) B. Wang, J. C. Cancilla, J. S. Torrecilla, and H. Haick, Nano Lett. 14, 933 (2014).
5) R. Ermanok, O. Assad, K. Zigelboim, B. Wang, and H. Haick, ACS Appl. Mater. Interfaces 5, 11172 (2013).
6) A. O. Niskanen, A. Colli, R. White, H. W. Li, E. Spigone, and J. M. Kivioja, Nanotechnology 22, 295502 (2011).
7) V. Pussi, E. Dubois, C. Celle, S. Clavaguera, J. P. Simonato, and J. P. Raskin, ECS Trans. 35, 313 (2011).
8) S. Clavaguera, A. Carella, L. Caltieri, C. Celle, J. Pécaut, S. Lenfant, D. Vuillaume, and J. P. Simonato, Angew. Chemie - Int. Ed. 49, 4063 (2010).
9) A. Henning, N. Swaminathan, A. Godkin, G. Shalev, I. Amit, and Y. Rosenwaks, Nano Res. 8, 2206 (2015).
10) T. Kim, K. Kim, H. Cho, W. Jeong, J. S. Yoon, Y. Kim, M. Meyyappan, and C. K. Baek, IEEE Sens. J. 17, 667 (2017).
11) Y. Engel, R. Elnathan, A. Pezvner, G. Davidi, E. Flaxer, and F. Patolsky, Angew. Chemie - Int. Ed. 49, 4063 (2010).
12) E. Stern, J. F. Klemic, D. A. Routenberg, P. N. Wyrembask, D. B. Turner-Evans, A. D. Hamilton, D. A. LaVan, T. M. Fahmy, and M. A. Reed, Nature 445, 519 (2007).
13) Z. Li, Y. Chen, X. Li, T. I. Kamins, K. Nauka, and R. S. Williams, Nano Lett. 4, 245 (2004).
14) Y. Qin, L. Zhao, and Y. Jiang, Appl. Surf. Sci. 467–468, 37 (2019).
15) F. De Santiago, A. Trejo, A. Miranda, F. Salazar, E. Carvajal, L. A. Pérez, and M. Cruz-Irisson, Nanotechnology 29, 204001 (2018).
16) A. Miranda, F. de Santiago, L. A. Pérez, and M. Cruz-Irisson, Sensors Actuators, B Chem. 242, 1246 (2017).
17) Y. Paska, T. Stelzer, S. Christiansen, and H. Haick, ACS Nano 5, 5620 (2011).
18) B. Wang and H. Haick, ACS Appl. Mater. Interfaces 5, 2289 (2013).
19) B. Wang and H. Haick, ACS Appl. Mater. Interfaces 5, 5748 (2013).
20) G. Gannon, J. C. Greer, J. A. Larsson, and D. Thompson, ACS Nano 4, 921 (2010).
21) J. M. D. Lane, M. Chandross, C. D. Lorenz, M. J. Stevens, and G. S. Grest, Langmuir 24, 5734 (2008).
22) I. Díez-Pérez, M. Luna, F. Teherán, D. F. Ogletree, F. Sanz, and M. Salmeron, Langmuir 20, 1284 (2004).
23) T. Tanaka, T. Yajima, and K. Uchida, 32nd Int. Microprocess. Nanotechnol. Conf., 2019, 31C-10-4.
24) S. Plimpton, J. Comput. Phys. 117, 1 (1995).
25) B. M. Silverman, K. A. Wieghaus, and J. Schwartz, Langmuir 21, 225 (2005).
26) D. J. Price and C. L. Brooks, J. Chem. Phys. 121, 10096 (2004).
27) J. M. Castillo, M. Klos, K. Jacobs, M. Horsch, and H. Hasse, Langmuir 31, 2630 (2015).
28) C. P. Tripp and M. L. Hair, Langmuir 11, 149 (1995).
29) A. Stukowski, Model. Simul. Mater. Sci. Eng. 18, 015012 (2010).
30) I. M. Tidwell, T. A. Rabedeau, P. S. Pershan, S. D. Kosowsky, J. P. Folkers, and G. M. Whitesides, J. Chem. Phys. 95, 2854 (1991).
31) S. R. Wasserman, Y. T. Tao, and G. M. Whitesides, Langmuir 5, 1074 (1989).
32) M. Jensen, O. G. Mouritsen, and G. H. Peters, J. Chem. Phys. 120, 9729 (2004).
33) D. M. Spori, N. V. Venkataraman, S. G. P. Tosatti, F. Durmaz, N. D. Spencer, and S. Zürcher, Langmuir 23, 8053 (2007).
34) S. A. Kulkarni and K. P. Vijayamohan, Surf. Sci. 601, 2983 (2007).