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Molecular Dynamics Study on the Effect of Long-Chain Surfactant Adsorption on Interfacial Heat Transfer between a Polymer Liquid and Silica Surface

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ABSTRACT: The addition of surfactants to polymer-based thermal interface materials applied to improve the heat dissipation efficiency of chip surfaces in contact has attracted attention for the microelectronic processing technology. In the present study, the mechanism by which a long-chain surfactant affects heat transfer across the interface between solid surface and polymer liquid was investigated by non-equilibrium molecular dynamics simulation. We constructed a system where tetracosane was used as a solvent and contained alcohol molecules as a surfactant, and they were placed between two flat silica surfaces under a thermal gradient. The effect of the hydrophilicity of silica surface, the concentration of the surfactant, and chain length of the surfactant on silica-liquid interfacial thermal resistance R_b were examined. Alcohol surfactant molecules preferred



to adsorb onto the hydrophilic silica (Si–OH) surface due to hydrogen bonding between alcohol and silanol hydroxyl groups. It was found that R_b reduced not only with the adsorption amount of alcohol molecules but also with the chain length of alcohol. The van der Waals interaction contribution was dominant for solid-liquid and liquid-liquid heat conduction near the interface. The hydroxyl terminals of alcohol molecules were vertically adsorbed onto the Si-OH surface due to hydrogen bonds, which produced a heat path from silanols to the hydroxyl groups of alcohol. Furthermore, heat was also exchanged between alcohol hydroxyl and alkyl groups via intramolecular interaction and between the alcohol alkyl groups and nearby solvent molecules via van der Waals (vdW) intermolecular interaction. This resulted in an efficient heat path from solid surface silanols to liquid bulk. As the alcohol chain length increased without changing the number of adsorbed alcohol molecules, the heat transfer through this heat path increased, which led to a decrease in R_b. These results provided insight toward the guiding principle for the molecular design of complex surfactants to enhance the interfacial heat transfer.

1. INTRODUCTION

When two electronic components are joined, the local asperities on the surface of the electronic components limit the contact between them. Poor heat dissipation due to this insufficient contact causes performance degradation and malfunction of electronic devices. Polymer materials with good thermal conductivity fillers are often used as a thermal interface material (TIM) to fill the gaps made by the insufficient contact of two substrates.¹ The performance of TIM depends on the interfacial thermal resistance proportional to the surface area of TIM-substrate interface, and the intrinsic thermal resistance proportional to the thickness of TIM. Associated with the miniaturization of integrated electronics, the surface-to-volume ratio of TIM increases, and the interfacial thermal resistance becomes dominant. This fact raised the focus on the application of surface modification²⁻ and surfactant additives⁵ to decrease the thermal resistance at the TIM-substrate contact. We focus on the latter in the present study. In general, surfactants are amphiphilic molecules and are often used as detergents,⁶ emulsifiers,⁷ or lubricants to extend component lifetime.^{8,9} Owing to the amphiphilicity, surfactant molecules in a polymer solvent are preferentially

adsorbed on the solid surface, thereby bridging the thermal connection between the solvent and the solid surface. To understand the bridging mechanism, it is crucial to elucidate the molecular configuration and dynamics near the solventsolid interface since the detail of interfacial heat transfer is determined by them.

Molecular dynamics (MD) simulation is a powerful tool for this aim. Our previous MD studies using monatomic surfactant and solvent molecules^{10,11} showed that when surfactant molecules have a high affinity with solid surfaces and solvent, the solid-liquid interfacial thermal resistance is significantly reduced. While these studies clarified a basic mechanism of thermal energy transfer enhancement aided by a surfactant, it is not possible for systems of monatomic molecules to provide the details of the effect of molecular structure on the heat

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conduction and molecular packing near the interface. Here, we consider more realistic molecular models for surfactants, solvents, and solid surfaces. The mechanism of adsorption is an important factor in selecting these models. Recently several studies confirmed that using thiol-terminated additives to modify Au surface by forming S-Au covalent bonds dramatically improves the Au-organic solvent interfacial heat transfer.^{2,3,5,12,13} However, the formation of covalent bonds between the solid and adsorbent makes it hard to repair the adsorption film if damaged. Another possibility is hydrogen bonding, which is weaker than a S-Au chemical bond. A previous experimental study reported the preferential adsorption of ethanol onto the hydrophilic silica surface from cyclohexane-ethanol mixture, where the ethanol molecules adsorbed onto silica surface are occasionally exchanged with those in the bulk.¹⁴ Thus, a layer of alcohol surfactant on the silica surface is kept by an equilibrium of adsorption and desorption, thereby having a self-repairing nature.

Similar to ref 14 where the surfactant adsorption is characterized by hydrogen bonding, we consider alkane, alcohol, and silica as polymer solvent, surfactant, and solid surface, respectively. Silica is widely used in the microelectronic field due to its intrinsic electrical properties.¹⁵ Alcohol used as surfactant is often added to water in order to reduce the surface tension, for example, in alumina–water interface,¹⁶ and to enhance the heat transfer in spray cooling.¹⁷ Since alcohol is composed of hydroxyl groups and alkyl chains, it has a high affinity with both solvent alkane and hydrophilic silica surface. Therefore, on the basis of the understanding that stronger interaction corresponds to higher heat transfer, alcohol surfactant is expected to reduce the thermal resistance at the silica–alkane interface.

We performed nonequilibrium MD (NEMD) simulations using a system where the liquid was composed of linear alkane (tetracosane, $C_{24}H_{50}$) molecules and contained linear monohydric alcohol and was placed between two silica surfaces. Two typical hydrophilic and hydrophobic silica surfaces were compared, and five linear alcohol molecules from butanol (C_4H_9OH) to dotriacontanol ($C_{32}H_{65}OH$) were selected as surfactants to examine the effects of the hydrophilicity of silica surface and alkyl chain length of surfactant molecules. To analyze the molecular mechanism of interfacial heat transfer, we decomposed the heat flux into the contributions from respective inter- and intramolecular interactions and related them to the molecular details of the adsorption structure.

The simulation details are described in Section 2, the effect of concentration of alcohol is discussed in Section 3.1, and the effect of structural difference in surfactant alcohol molecules is investigated in Section 3.2.

2. SIMULATION METHODS

2.1. Molecular Model. All MD simulations were carried out using the LAMMPS package.¹⁸ The NERD force field was used for both polymeric solvent tetracosane¹⁹ and surfactant alcohols.²⁰ This force field is a united-atom model where a CH_n (a methylene or a methyl) group in tetracosane and alcohol molecules is treated as a single interaction site that interacts with each other via non-bonded van der Waals (vdW) and Coulomb interactions and intramolecular bond stretching, angle bending, and torsion interactions. The hydroxyl group of alcohol is expressed by an explicit hydrogen atom and an oxygen atom. Only the hydroxyl group and the neighboring methylene group in an alcohol molecule are electrically

charged; while other sites do not interact via Coulomb interaction. The parameters are listed in the Supporting Information (Table S1). This model was successfully used to predict the thermodynamic properties of molecules.²¹

Functional groups on the silica surface affect alcohol adsorption on the surface. The structure of silica surface covered with silanols has been experimentally well-established. Silanols are considered as an important reason for ethanol to preferentially adsorb onto silica surface.¹⁴ Here, a hydroxylated silica (Si-OH) surface and a hydrogenated silica (Si-H) surface were examined for comparison, where the former with silanol groups is hydrophilic, and the latter with silane groups is hydrophobic. The potential of silica crystal was modeled with an all-atom model, compatible with the CHARMM empirical force field. The parameters of silica adopted in this study are provided by the work of Lopes²² and are listed in the Supporting Information (Table S2). This force field has been successfully used to determine the structure and dynamic behavior of hydrated materials.²³ The interactions between silica surfaces and alcohol molecules and between silica surfaces and tetracosane molecules are modeled by Lennard-Jones (LJ) potential. The Lorentz-Berthelot combing rules were used to acquire the LJ parameters between different interaction sites, which have been used for studying silicaalkane interface in previous works.^{24,25} The electrostatic interaction was evaluated by the particle-particle particlemesh²⁶ method with a relative force accuracy set to 10⁵ and a real space cutoff of 12 Å. The cutoff radius was also set as 12 Å for LJ potential.

2.2. Initial Configuration. The simulation system is shown in Figure 1, where the liquid composed of tetracosane



Figure 1. Side view of the simulation system composed of silica surfaces (hydroxylated) and a liquid layer. The liquid consists of tetracosane (solvent) and alcohol (surfactant) molecules. Bulk area is set away from a silica further than 50 Å from a silica surface.

and alcohol molecules was placed between two silica walls in the z-direction. The x and y dimensions of the simulation system were set as 59 and 63.6 Å, respectively. Periodic boundary conditions were imposed in the *x* and *y* directions. In the initial configuration, the z dimension of the system was set as 600 Å initially. A single silica wall in the geometry of α quartz consisted of 2592 Si atoms and 5184 O atoms. The silica surfaces in contact with the solution were the (100) face, which were fully covered with silanols (Si-OH) or silanes (Si-H) to create two different systems with hydrophilic or hydrophobic surfaces, respectively. Using the RATTLE²⁷ algorithm, the hydrogen (H) atoms in silanols and silanes were constrained at their equilibrium bond lengths. Tetracosane molecules were randomly placed between the two silica walls at least 20 Å away from a silica surface. Alcohol molecules were distributed in the range of 20-50 Å from a silica surface,

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| Table | 1. T | 'he Simu | lation | Conditions | for (| Cases | with | the | Different | Mole | Fraction | of | Butanol, | $c_{\rm sur}^0$ | f |
|-------|------|----------|--------|------------|-------|-------|------|-----|-----------|------|----------|----|----------|-----------------|---|
|-------|------|----------|--------|------------|-------|-------|------|-----|-----------|------|----------|----|----------|-----------------|---|

| | | dimension in the z-direction [Å] c_{surf}^{bulk} (%) | | | bulk den liquid | sity of the [g/cm ³] | thermal conductivity of bulk liquid [W/(m·K)] | | |
|---|---|---|-------------|------------|--------------------|-------------------------------------|--|-------|-------|
| c_{surf}^0 of butanol (#C = 4) (%) | number of alcohol molecules in system | Si-H | Si-OH | Si-H | Si-OH | Si-H | Si-OH | Si-H | Si-OH |
| 0 | 0 | 231.47 | 233.15 | 0 | 0 | 0.741 | 0.741 | 0.122 | 0.113 |
| 5 | 46 | 233.74 | 235.30 | 4.96 | 1.24 | 0.740 | 0.740 | 0.125 | 0.113 |
| 10 | 98 | 236.47 | 237.81 | 9.78 | 2.42 | 0.739 | 0.740 | 0.128 | 0.120 |
| 20 | 220 | 242.06 | 243.60 | 18.89 | 7.26 | 0.738 | 0.738 | 0.131 | 0.137 |
| 100 | 4000 | 234.22 | 235.98 | 100 | 100 | 0.725 | 0.724 | 0.116 | 0.114 |
| ^{<i>a</i>} The number of tetracosane | molecules is 0 in the case of $c_{surf}^0 = 10$ | 00% and i | s 886 for o | ther syste | ems. | | | | |

Table 2. The Simulation Conditions for Cases with Different Alcohol Molecules as a Surfactant at Mole Fraction of $c_{surf}^0 = 5\%^a$

| #C | number of alcohol molecules in system | Si-H | Si-OH | Si-H | Si-OH | Si-H | Si-OH | Si-H | Si-OH |
|----------------------------|---|-----------------------------|------------------------|-------------------------|------------------|--|-------|---|-------|
| | | dimensio <i>z</i> -direc | on in the ction [Å] | $c_{ m surf}^{ m bull}$ | ^k (%) | bulk density of the liquid [g/cm ³] | | thermal conductivity of bulk liquid [W/(m·K)] | |
| 8 | 46 | 235.56 | 236.71 | 4.90 | 1.17 | 0.739 | 0.741 | 0.117 | 0.113 |
| 16 | 46 | 238.20 | 239.46 | 3.85 | 1.74 | 0.741 | 0.740 | 0.121 | 0.115 |
| 24 | 46 | 240.92 | 242.03 | 3.37 | 1.36 | 0.742 | 0.741 | 0.119 | 0.118 |
| 32 | 46 | 243.62 | 245.17 | 3.23 | 1.24 | 0.743 | 0.742 | 0.119 | 0.115 |
| ^{<i>a</i>} The nu | umber of tetracosane molecules is 886 for | r all systems. | | | | | | | |

partly overlapping with the initial tetracosane molecule region. We performed MD simulations on the systems with different mole fraction of butanol (C4HOOH) molecules in order to investigate the effect of the concentration of alcohol surfactant on the silica-alkyl polymer interfacial thermal properties. The mole fraction of surfactant butanol, c_{surf}^0 ranged from 0 to 20% in addition to a single 100% system. Higher c_{surf}^{0} than 20% was not studied because big micelle-like alcohol clusters were easily formed, preventing the system from reaching an ideal mixture.²⁸ Furthermore, in addition to butanol with alkyl chain length (#C) of 4, four additional linear alcohol molecules with alkyl chain length (#C) from 8 to 32, octanol (C₈H₁₇OH), hexadecanol (C₁₆H₃₃OH), tetracosanol $(C_{24}H_{49}OH)$, and dotriacontanol $(C_{32}H_{65}OH)$ molecules, were chosen as the surfactant for the cases of $c_{surf}^0 = 5\%$ to investigate the effect of the molecular structure of the surfactant. The cases with different alcohols were represented as C4, C8, C16, C24, and C32 according to the number of carbon atoms in the molecule, #C. The alkyl chain length of tetracosane solvent molecules is 24. For convenience, #C = 0represents the case of $c_{surf}^0 = 0\%$. The detailed conditions are summarized in Tables 1 and 2.

2.3. MD Procedure. To gain an equilibrium state for a given pressure and temperature with sufficiently dispersed surfactant molecules, we applied a temperature annealing method, which is commonly used to minimize the energy of molecular configuration.²⁹ Using this method, a 0.2 ns run of equilibrium MD (EMD) simulation followed by a 0.8 ns run of NEMD simulation was repeated 10 times. The x and y dimensions were fixed during these runs. During the EMD simulation, the temperature of the system was controlled at 800 K with a Nosé-Hoover thermostat, while the outmost Si layers each containing 144 Si atoms in the left and right silica walls were fixed. In the NEMD simulation, the Nosé-Hoover thermostat at 800 K was stopped, and the left outmost Si layer was fixed, whereas the right silica wall was subjected to a constant force to control the pressure at 1 atm. The outmost oxygen layers each containing 144 O atoms adjacent to the

outmost Si layers in both silica walls were cooled down to 330 K as a heat sink and 390 K as a heat source, respectively, by a Langevin thermostat with a damping coefficient of 100 fs. These temperatures of the heat source and the heat sink were chosen between the melting point of the tetracosane (\sim 323.75 K³⁰) and the boiling point of butanol (\sim 390.77 K³¹) when the pressure is 1 atm. After the annealing process mentioned above, a 20 ns run of NEMD simulation with the same setting as mentioned above was performed. The average position of the outmost Si layer on the right side was obtained from the last 10 ns in order to determine the volume of the simulation system at specified conditions as shown in Tables 1 and 2.

After the outmost Si layer on the right side of the silica wall was fixed at the average position determined above, the NEMD simulation was continued for 80 ns. The first 20 ns was used for relaxation, and the analysis data was collected from the last 60 ns. The equilibrium mole fractions of alcohol in the bulk area, c_{surf}^{bulk} , listed in Tables 1 and 2, were measured in the bulk area as defined in Figure 1, which were different from the overall mole fraction c_{surf}^0 due to the adsorption of alcohol molecules onto the silica surface. Considering the existence of hydrogen atoms, we chose a small integration time step of 0.5 fs for all cases, which has been utilized in the study of silica/ ethanol interface³² and silica/water interface.³³

2.4. Decomposition of Heat Flux. The expressions of heat flux J_z in the z-direction with respect to a control surface S_{xy} located at z_{xy} and a control volume V for a molecular system interacting with *n*-body potentials are as follows³⁴

$$J_{z}S_{xy} = \sum_{s} E_{s} \frac{\nu_{z,s}}{|\nu_{z,s}|} n_{s}^{*} + \sum_{\text{all } n\text{-body potential}} \sum_{s_{1}} \sum_{s_{1} > s_{2}} \dots$$
$$\sum_{s_{n} > s_{n-1}} \left[\frac{1}{n} \sum_{\alpha=1}^{n-1} \sum_{\beta=\alpha+1}^{n} (\mathbf{F}_{s_{\alpha},U} \cdot \mathbf{v}_{s_{\alpha}} - \mathbf{F}_{s_{\beta},U} \cdot \mathbf{v}_{s_{\beta}}) \\ \left\{ H(z_{s_{\alpha}} - z_{xy}) - H(z_{s_{\beta}} - z_{xy}) \right\} \right]$$
(1)

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Figure 2. Profiles of number density (left axis) and temperature (right axis) for the system composed of solvent tetracosane, surfactant butanol ($c_{surf}^0 = 5\%$), and silica wall (only Si is shown) with silanol (OH) surface modification. The inset shows temperature jump ΔT . The positions of interface and interlayer are also shown as dashed vertical lines.

$$J_{z}V = \sum_{s} v_{z,s}E_{s} + \sum_{\text{all }n\text{-body potential}} \sum_{s_{1}} \sum_{s_{1}>s_{2}} \dots$$
$$\sum_{s_{n}>s_{n-1}} \left[\frac{1}{n} \sum_{\alpha=1}^{n-1} \sum_{\beta=\alpha+1}^{n} (\mathbf{F}_{s_{\alpha},U} \cdot \mathbf{v}_{s_{\alpha}} - \mathbf{F}_{s_{\beta},U} \cdot \mathbf{v}_{s_{\beta}}) (z_{s_{\alpha}} - z_{s_{\beta}})^{*} \right]$$
(2)

where the first term on the right-hand side for both equations represents the heat flux due to the sum of kinetic and potential energy carried by site s, E_{s} ; $v_{z,s}$ is velocity component in the zdirection of site s; and n_s^* is 1 or 0 depending on whether site s has crossed S_{xy} during a single time step or not. The second term denotes the heat flux due to inter- and intramolecular interactions, where z_s is the z-coordinate of site s, \mathbf{v}_s is the velocity vector of site s, and $\mathbf{F}_{s,U}$ is the force exerted on site s due to the *n*-body interaction between *n* sites $U = \{s_1, ..., s_n\}$. In eq 1, $H(z_{s\alpha} - z_{xy}) - H(z_{s\beta} - z_{xy})$ describes the direction of heat transfer, where H(x) is the Heaviside step function and H(x) = 0 if x < 0 and 1 if $x \ge 0$. In eq 2, $(z_{s\alpha} - z_{s\beta})^*$ is the portion of $(z_{s\alpha} - z_{s\beta})$ in the control volume. Using LAMMPS with our in-house package, based on eqs 1 and 2, we decomposed the total heat flux with respect to a control surface or a control volume into the contributions from vdW and Coulomb interactions between corresponding molecules, potential and kinetic energy carried by molecules, and intramolecular contribution (stretching, angle, and torsion). We only calculate the first term of eq 2 because the second term cannot be obtained by LAMMPS correctly when the control volume is small. Similar calculations of respective contributions to heat flux have been done in our previous studies.^{10,11,35}

3. RESULTS AND DISCUSSION

3.1. Effect of Surfactant Concentration. The number density profile of the interaction sites of tetracosane molecules and butanol molecules contacting with Si–OH silica walls for $c_{surf}^0 = 5\%$ are shown in Figure 2 as an example, and those contacting with Si–H silica walls for $c_{surf}^0 = 5\%$ are shown in the Supporting Information (Figure S3). A clear adsorption layer of butanol molecules in the vicinity of Si–OH surfaces is observed. Two liquid–silica interfaces with high and low temperatures formed on the left and right side are represented

as that on the cold and hot side, respectively. The area number densities of interaction sites (CH_n, H, and O sites) in tetracosane and butanol molecules near the Si-OH surfaces and Si-H surfaces were obtained by dividing the number of sites in the first adsorption layer by the xy cross-sectional area of the system, S_{xy} , in order to quantify their corresponding interfacial adsorption amount, where the first adsorption layer is defined between the silica surface and interlayer as shown in Figure 2. The interlayer position is defined at the coordinate of the number density minimum between the first and second tetracosane adsorption layers, and the interface position is defined at the midpoint between the number density peaks of silanols and alcohol hydroxyl groups (Alco). The position of hydroxyl groups (Alco) is represented by the position of alcohol hydroxyl O atoms (Alco). Temperature jump ΔT is the difference between the temperature of a silica wall and liquid at the interface as shown in Figure 2. The interface temperatures of the silica wall and the liquid were obtained by the linear extrapolation method used in our previous studies.^{10,11,36} The local temperatures of liquid near the interface were obtained layer by layer, whereas those for the bulk liquid area were obtained by binning the volume into slabs with a thickness of 10 Å. The local temperatures of silica walls were obtained from binning the volume into slabs with a thickness of 4 Å. These local temperatures, except the points closest to the interface, were linearly extrapolated from both silica and liquid sides to obtain the temperature difference at the interface as exemplified in Figure 2.

The area number density of interaction sites in butanol is plotted in Figure 3A as a function of butanol mole fraction, $c_{\text{suff}}^{\text{bulk}}$, in the bulk area that is indicated in Figure 2. Correspondingly, Figure 3B shows the silica–liquid thermal boundary resistance R_{b} as a function of $c_{\text{suff}}^{\text{bulk}}$. We evaluated R_{b} by

$$R_{\rm b} = \frac{\Delta T}{J_z} \tag{3}$$

where J_z is the heat flux induced in the system in the *z* direction, which was obtained by the accumulation over time *t* of the kinetic energy added from the heat source, E^{source} , and that removed from the heat sink, E^{sink} , by the Langevin thermostat as follows³⁷



Figure 3. (A) Area number density of sites (H, O, CH_n) in butanol molecules in the first adsorption layer near the Si–OH surfaces and Si–H surfaces on the cold and hot side as a function of mole fraction of alcohol molecules, c_{surf}^{bulk} . (B) Thermal boundary resistance R_b as a function of c_{surf}^{bulk} . (C) Thermal boundary resistance R_b as a function of the area number density of sites in butanol in the first adsorption layer for the cases of Si–OH and Si–H surfaces. Error bars display the standard error of the mean which was obtained from evenly dividing the data into 5 parts.

$$J_z = \frac{E^{\text{source}} - E^{\text{sink}}}{2S_{xy}t}$$
(4)

The heat flux flowing from the right to the left results in a negative value; thus, here we switched the heat flux to a positive value in the subsequent analysis for clarity.

Figure 3A,B shows that in the case of the Si-OH surface, adding a small number of butanol molecules distinctly increases the amount of surface adsorption of butanol, and $R_{\rm b}$ decreases accordingly, which confirms our expectations that alcohol works as a surfactant to enhance the heat transfer at silica-alkyl interface. In the case of the Si-H surface, the area number density of butanol is kept negligibly small for all observed c_{surf}^{bulk} in ~20% range, and thus butanol does not play a role as a surfactant to reduce R_b. The hydrophilic Si-OH surface plays a key role in the adsorption of alcohol molecules due to hydrogen bonding between silanols and hydroxyl groups (Alco), and this adsorption mechanism also has been observed for water/silica interface.³⁸ For both types of silica surfaces, butanol molecules adsorb more onto the cold side than onto the hot side, and correspondingly the R_b on the cold side is lower than that on the hot side. When $c_{surf}^{bulk} = 100\%$, the

difference in the adsorption amount of butanol and R_b is mostly due to the temperature difference of cold and hot sides rather than the type of silica surface.

We plot R_b as a function of the corresponding area number density of butanol interaction sites in the first adsorption layer for the cases with c_{surf}^0 from 0 to 20% in Figure 3C. With the increase in the interfacial area number density of butanol, R_b almost linearly decreases independently of the type of silica surface. Therefore, R_b is mostly determined by the adsorption amount of surfactant butanol molecules, which is consistent with our previous research using surfactant monomolecules.^{10,11} Another study has also indicated that the adsorption amount of surfactant determines the thermodynamic property of solid–liquid interface.³⁹

3.2. Effect of Alcohol Chain Length. 3.2.1. Adsorption Amount and Boundary Thermal Resistance. Figure 4A,B shows the area number density of alcohol hydroxyl groups (Alco), alcohol CH, groups (Alco), and tetracosane CH, groups (Tetr) in the first adsorption layer for the cases of Si-OH surfaces and Si-H surfaces with different surfactant alcohols at the interface on the hot side. We use the terminology "groups" instead of previously used "sites" because the OH hydroxyl group is treated as a single unit. The figures on the cold side are shown in the Supporting Information (Figure S4) due to their similarity with the hot side. Although these cases have the same overall surfactant concentration c_{surfv}^0 the interfacial concentration is different, and because of that, the surfactant concentration at the bulk region, c_{surf}^{bulk} , is also different. For the case of the Si-H surface, c_{surf}^{bulk} is much higher than that for the case of the Si-OH surface due to lower adsorption amount, where Si-H system ranges from 3.23 to 4.96% and Si-OH system ranges from 1.17 to 1.74% as shown in Table 2. For the cases of the Si-OH surface, the chain length of alcohol does not significantly affect the number of hydroxyl groups of alcohol molecules in the first adsorption layer, that is, the number of adsorbed alcohol molecules is kept almost constant. Since longer alcohol has more CH_n groups in the molecule, as alcohol chain length increases, more CH_n groups (Tetr) in the first adsorption layer are replaced with the CH_n groups (Alco). On the other hand, the area number density of total alkyl groups remained constant at about 1.5 $Å^{-2}$, independently of alcohol chain length, temperature, and hydrophilicity of the silica surface (see Figure S5 in the Supporting Information). A previous study²⁴ on the silicaalkane interface demonstrated that the adsorption amount of CH_n groups of different alkanes (decane and tetracosane) in the first adsorption layer is very close. This work also showed that there is not much difference in the number of adsorbed alkyl groups between the Si-OH surface and the Si-H surface.

In Figure 4C, R_b at the Si–OH surfaces and Si–H surfaces on both sides was plotted against #C. In the case of the Si–H surface, R_b does not change distinctly as the alcohol chain length increases because the number of adsorbed alcohol molecules is negligible as Figure 4B shows due to the hydrophobicity of Si–H surfaces. In contrast, that for the Si–OH surface significantly decreases as the alcohol chain length increases. Specifically, R_b for C32 is approximately 63% of R_b for C4 at the cold side. In a previous study⁴⁰ with very high c_{surf}^0 in decane solvent, the bending and entanglement of adsorbed long-chain alkanethiol surfactants prevented the thiol groups of other surfactant molecules from adsorbing at the copper nanoparticle, and thereby the longer the surfactant chain length, the less reduction in R_b was observed. This

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Figure 4. (A,B) Area number density of alcohol hydroxyl (OH) groups (Alco), alcohol alkyl (CH_n) groups (Alco), and tetracosane CH_n groups (Tetr) in the first adsorption layer for the cases of the Si–OH surface and the Si–H surface as a function of the number of carbon atoms in alcohol molecule, #C, with $c_{surf}^0 = 5\%$. (C) Thermal boundary resistance (R_b) at the Si–OH surfaces and Si–H surfaces as a function of #C, with $c_{surf}^0 = 5\%$. (C) Thermal boundary resistance (R_b) at the Si–OH surface area between a silica surface with Si–OH and liquid molecules into the vdW and Coulomb contributions as a function of #C, with $c_{surf}^0 = 5\%$ and $c_{surf}^0 = 5\%$ and $c_{surf}^0 = 6\%$. The standard error of the mean for C is shown as an error bar. The error bars of subfigures A, B, and D were too small to be observable.

phenomenon was not seen in our case because we chose systems with low c_{surf}^0 and surfactant chain length was limited. Section 3.1 discussed strong dependence between the number of adsorbed alcohol molecules and R_b . However, there is no obvious increase in the adsorption amount of hydroxyl groups (Alco) when the alcohol chain length increases under a constant c_{surf}^0 as shown in Figure 4A,B. Therefore, the reduction in R_b in this case is attributed to another mechanism relevant to the chain length of alcohol. As no clear relation was displayed between adsorption amount of alcohol molecules and R_b for the cases of the Si–H surface, further discussion in Section 3.2 will only apply to the cases of the Si–OH surface.

3.2.2. Interfacial Potential Energy and Local Heat Transfer. To explore further the relationship between the solid-liquid affinity and alcohol chain length, we next examine the strengths of solid-liquid interaction. The solid-liquid interfacial potential energy consists of silica-alcohol potential energy and silica-tetracosane potential energy, where the former is composed of vdW and Coulomb interaction, and the latter is composed of only vdW interaction. These decomposed interfacial potential energies per unit area are plotted in Figure 4D for the cases from C4 to C32 with $c_{surf}^0 = 5\%$ and $c_{surf}^0 = 0\%$ at the hot side. The total vdW interfacial potential energy for the cases of $c_{surf}^0 = 5\%$ remains almost constant as #C increases, which is consistent with the fact mentioned in Section 3.2.1 that the area number density of total alkyl groups is almost kept constant for different #C. The alcohol-silica Coulomb contribution leads to a slightly higher total interfacial potential

energy for the cases with alcohol than for the case without alcohol. Because of that $R_{\rm b}$ for the cases of $c_{\rm surf}^0 = 5\%$ is lower than that of $c_{\rm surf}^0 = 0\%$ as shown in Figure 4C.

As the alcohol chain length increases, the vdW alcoholsilica potential energy increases, and the vdW tetracosanesilica potential energy decreases corresponding to the adsorption amount in the first adsorption layer as shown in Figure 4A. Overall, no obvious change is observed for alcoholsilica Coulomb potential energy for the cases with different alcohol chain lengths. This dependence on specific molecular structure distinguishes the present study from many previous studies^{10,11,41,42} on monoatomic molecules where R_b is proportional to solid-liquid interfacial potential energy. As shown in Figure 4D, the total potential energy of solid-liquid interaction, which was almost constant regardless of alcohol chain length, cannot explain the reduction in $R_{\rm b}$. Rather, it is likely due to the increasing portion of the solid-surfactant intermolecular interactions, but unlike monoatomic systems, this was not reflected in the interfacial energy, therefore a different mechanism exists than just simple interaction strength.

The local temperature and number density distribution for each interaction site are shown in Figure 5 for the case of C16 as an example. In the present study, the O–H bond distance in silanol is constrained as noted in Section 2.2. Therefore, when calculating the local temperature of silanols, the reduction of the degrees of freedom due to this constraint was taken into account via the equipartition theorem⁴³

Temperature Density 0 SiO_2 Si OH (Si) OH (Si) H (Alco) Δ H (Alco) O (Alco) O (Alco) CH_n (Alco) ∇ CH_n (Alco) CH_n (Tetr) CH_n (Tetr) 335 0.25 Number density [Å⁻³] 330 0.2 Temperature [K] 325 0.15 Ć 320 0.1 315 0.05 310 0 15 20 25 30 35 40 10 45 z [Å]

Figure 5. Local temperature shown with marks (left axis) and number density distribution shown with dashed and solid lines (right axis) of SiO₂ (only number density of Si is shown), silanols, alcohol hydroxyl groups H and O (Alco), alcohol CH_n groups (Alco), and tetracosane CH_n groups (Tetr) for hexadecanol surfactant ($c_{surf}^0 = 5\%$) with the Si-OH surfaces. The standard error of the mean for temperature is shown as an error bar.

$$\left(\frac{3N-C}{2}\right)k_{\rm B}T = \frac{1}{2}\left\langle\sum_{\rm atom \, i}m_i v_i^2\right\rangle \tag{5}$$

where N is the number of atoms, and C is the number of constraints.

The overlap of density distributions between hydroxyl groups (Alco) and silanols can occur because the sparse distribution of silanols on the (100) silica surface allows the penetration of hydroxyl groups (Alco) into the void space between silanol groups. A similar phenomenon has been reported for the adsorption of water onto the (100) silica surface with Si-OH modification.⁴⁴ The hydrogen atoms in alcohol hydroxyl groups H (Alco) are closest to the silica surface followed by the oxygen atoms of the same alcohol hydroxyl groups O (Alco), which is due to the vertical adsorption of terminal groups of alcohol onto the Si-OH surfaces. The adsorption peaks of alkyl layers of alcohol and tetracosane molecules overlap, indicating that there is sufficient contact between CH_n groups (Alco) and CH_n groups (Tetr) for possible energy exchange.

The local temperature difference between different molecules at the solid-liquid interface is observed in Figure 5. For the first (27.75 Å < z < 32.15 Å) and second (32.15 Å < z < 36.65 Å) adsorption layers, the temperature of CH, groups (Alco) is closer to the temperature of the silica surface than the temperature of tetracosane molecules. This local temperature difference indicates that the alcohol molecules exchange thermal energy with silica surface more easily than tetracosane molecules. Also, because of temperature difference, there might be a heat flow within the adsorption layers between alcohol and solvent molecules, which we will investigate in later sections.

3.2.3. Decomposition of Microscopic Thermal Energy Transfer. The scheme for the decomposition of heat flux across the solid-liquid interface, liquid-liquid interlayer, and central plane in the bulk area is shown in Figure 6. The decomposition of heat flux across the solid-liquid interface $J_z^{interface}$ is calculated between the silica wall and alcohol or tetracosane

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(7)



Figure 6. Scheme for the decomposition of heat flux across the control surface S_{xy} (represented by the dashed line, including solidliquid interface, liquid-liquid interlayer, and central plane in the bulk area) via van der Waals (vdW) and Coulomb interactions between different molecules (silica surface, liquid including alcohol, and tetracosane molecules) and in the control volume V (represented by the rectangle, enclosing the corresponding S_{xy} via potential and kinetic energy transfer and intramolecular energy transfer (stretching, angle, and torsion).

molecules in the liquid, where only intermolecular interaction terms contribute to $I_{z}^{\text{interface}}$, thus the intramolecular interactions terms, potential and kinetic energy transfer terms in eq 1, must be zero. The positions of liquid-liquid interlayer were defined as shown in Figure 2, and a central plane was set at z_{xy} = 120 Å in the bulk areas. The intramolecular interaction, potential and kinetic energy contributions, were obtained by measuring the heat fluxes inside a thin volume V enclosing the corresponding S_{xy} ; the details are shown in Section 3 of the Supporting Information According to the molecular mechanism of thermal energy transfer by eqs 1 and 2, the heat fluxes across the solid-liquid interface, the interlayer, and the central plane, are decomposed as

$$J_{z}^{\text{interface}} = J_{\text{vdW}}^{\text{si-alco}} + J_{\text{Coul}}^{\text{si-alco}} + J_{\text{vdW}}^{\text{si-tetr}}$$
(6)
$$J_{z}^{\text{interlayer}} = J_{\text{vdW+Coul}}^{\text{si-bulk}} + J_{\text{vdW}}^{\text{alco}(1)-\text{bulk}} + J_{\text{Coul}}^{\text{alco}(1)-\text{bulk}} + J_{\text{vdW}}^{\text{alco}(1)-\text{bulk}} + J_{\text{vdW}}^{\text{alco}(1)-\text{bulk}}$$
(7)

and

$$J_{z}^{\text{bulk}} = J_{\text{vdW}}^{\text{alco-bulk}} + J_{\text{Coul}}^{\text{alco-bulk}} + J_{\text{vdW}}^{\text{tetr-bulk}} + J_{\text{pot}} + J_{\text{kin}} + J_{\text{stretch}} + J_{\text{bend}} + J_{\text{torsion}}$$
(8)

respectively. The subscripts represent the type of contributions, including the vdW, Coulomb, intramolecular interactions (stretching, angle, and torsion), and kinetic and potential components. The superscripts for vdW and Coulomb components represent the corresponding interacting objects, where "si", "alco", "tetr", "alco(1)", "tetr(1)", and "bulk" represent the silica wall, alcohol molecules, tetracosane molecules, the alcohol and tetracosane molecules in the first adsorption layer, and the liquid molecules in the bulk area, respectively. In case of heat flux decomposition over the central plane, the contribution terms of alcohol and tetracosane on the right side of S_{xy} are treated as a single type "bulk" for clarity. The respective components are shown in Figure 7. The terms of kinetic and potential energy transfer in $J_z^{\text{interlayer}}$ (Figure 7C) are smaller than those in J_z^{bulk} (Figure 7D) because hardly any migration of liquid molecules across the control surface occurs. The decomposition for $J_z^{\text{interlayer}}$ on the hot side is similar to that



Figure 7. Decomposition of heat flux (A,B) across the solid–liquid interface on the cold and hot sides, (C) across the liquid–liquid interlayer on the cold side, and (D) across the central plane in the bulk area for the cases of C4 to C32 with $c_{surf}^0 = 5\%$ and the Si–OH surfaces. The standard error of the mean for respective interaction contributions is shown as an error.

on the cold side and is not shown in Figure 7. For $J_z^{\text{interface}}$ (Figure 7A,B), $J_{\text{Coul}}^{\text{si-alco}}$ has no significant change with alcohol chain length, and for $J_z^{\text{interlayer}}$ (Figure 7C), $J_{\text{Coul}}^{\text{alco}(1)-\text{bulk}}$ is negligible because hydroxyl groups (Alco) are mostly in the first adsorption layer and almost absent in the bulk area. Most intermolecular contribution to J_z^{bulk} (Figure 7D) is from $J_{\text{vdW}}^{\text{tetr-bulk}}$ because the liquid in the bulk area is mostly tetracosane molecules. Therefore, the Coulomb interaction only slightly contributes to the interfacial heat transfer between silica and alcohol and hardly contributes to the heat transfer at liquidliquid interlayer. The vdW interaction is the dominant contributor to all of $J_z^{\text{interlayer}}$, $J_z^{\text{interlayer}}$, and J_z^{bulk} . Our previous study also indicated that Coulomb interaction promotes the formation of hydrogen-bond networks but has limited direct contribution to heat transfer.⁴⁵ As the alcohol chain length increases, $J_{vdW}^{si-alco}$ (Figure 7A,B) at the interface increases, which indicates that the path of heat transfer from silica surface to alcohol molecules in the first adsorption layer gradually becomes dominant. The increase in the alcohol chain length enhances the alcohol intramolecular contribution J_{intra} and adsorbed alcohol to bulk liquid intermolecular contribution $L_{vdW}^{\text{alco}(1)-\text{bulk}}$ to interfacial heat transfer as Figure 7C shows, which lead to the decrease in the temperature jump ΔT approximately from 3.55 to 2.17 K. Therefore, the reduced $R_{\rm b}$ is due to the increase in interfacial heat transfer mediated by the alcohol molecules from silica surface to bulk liquid.

Similarly to our previous paper,^{10,11} we also investigated the per-site contribution to the interfacial thermal conductance as shown in the Supporting Information (Section 6). As with

monoatomic molecules in our previous work, the per-site contribution was mostly invariant of the alcohol chain length and only depended on the affinity toward silica atoms. Specifically, the per-site ITC contribution of alcohol sites was approximately 1 pW/K, while that of solvent sites was about 0.7 pW/K.

3.2.4. Adsorption Chain Structure. The number density profiles of the CH_n groups (Tetr) and CH_n groups (Alco) are shown in Figure 8A–C, where the CH_n groups (Alco) are grouped into three types: CH₂ groups adjacent to hydroxyl O (CH_{2a}), terminal CH₃ groups, and other CH₂ groups (CH_{2o}). As the alcohol chain length increases, tetracosane molecules are displaced by CH_n groups (Alco) near the Si–OH surfaces. The terminal CH₃ groups for C4 are distributed in the first adsorption layer, while for C8 to C32, they are mainly concentrated in the first and second adsorption layers with small amounts further away, indicating that adsorbed alcohol molecules favorably lie on the Si–OH surfaces.

Understanding the shape and orientation of molecules in the adsorption layer is necessary for investigating the mechanism of interfacial heat-transfer enhancement due to the addition of long-chain alcohol molecules at the solid–liquid interface. We calculated the average angle between the *z*-axis and a connecting line between two specified sites (s_1 and s_2) in the molecules, $\theta_{s_1-s_2}^z$ (see Figure S2 in the Supporting Information for examples of $\theta_{s_1-s_2}^z$ as a function of #C). The typical configuration of alcohol molecules at the interface, on the basis of these angles, is shown in the left panel of Figure 9. The

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Figure 8. (A–C) Number density distributions of the alcohol CH_2 groups adjacent to hydroxyl O (CH_{2a}), the end terminal alcohol- CH_3 groups against the left axis, other alcohol CH_2 groups (CH_{2a}), and tetracosane CH_n groups (Tetr) against the right axis near the Si–OH surface on the cold side for the cases for C4, C16, and C32 of $c_{surf}^0 = 5\%$, respectively. (D,E) Orientation distributions of tetracosane and butanol (C4) molecules for the system with $c_{surf}^0 = 5\%$, respectively. (F) Orientation distribution of octanol (C8) molecules for $c_{surf}^0 = 5\%$. Panels (D–F) have the number density profiles of corresponding sites (tetracosane CH_n , alcohol CH_n , alcohol hydroxyl H, and O) plotted by dashed lines in the right axis.



Figure 9. Illustration of adsorption structure of terminal groups of alcohol molecules onto the Si–OH surface (left panel) and a snapshot near the Si–OH surface for the case of C8 with $c_{surf}^0 = 5\%$ (right panel), where the tetracosane molecules are not shown. Two types of hydrogen bonds, (1) SiOH···O(H)R and (2) ROH···O(H)Si, are formed between hydroxyl groups of alcohol and silanols.

hydroxyl groups of alcohol tilted away from the silica surface with an average angle between the z-axis and a connecting line between hydroxyl O and H (Alco), $\theta_{\rm O-H}^z \approx 55^\circ$, which closely matches the spectroscopic experimental study⁴⁶ where $\theta_{\rm O-H}^z$ for ethanol molecules is from 45 ± 6 to 39 ± 5°. The subtle orientational differences between different short alcohol molecules adsorbed onto Si–OH surface have also been observed in the spectroscopy experiment.³² The $\theta_{\rm O-H}^z$ for

silanols exhibited a similar orientation to θ_{O-H}^{z} for the investigated alcohol molecules (see Figure S2).

The orientation of short-chain alcohol molecules in the adsorption layer with their OH terminal groups hydrogenbonded to the silica has been observed in previous experiment studies, ^{14,32,46,47} which demonstrate that our results are reasonable. The orientation order parameter P(z) is used in the present study to describe the orientational ordering of molecules near Si–OH surfaces and is defined as follows⁴⁸

$$P(z) = \frac{1}{2} \langle 3 \cos^2 \theta_{s_1 - s_2}^z - 1 \rangle$$
(9)

where the average is taken over all $\cos \theta_{s_1-s_2}^z$ between the *i*th site and the (i + 2)th site from either end of the molecule. Sites for alcohol include O, H, and CH_n groups and for tetracosane include CH_n groups. The value of P(z) ranges from 1 to -0.5, where zero value indicates that the molecules are oriented randomly; a positive value specifies that the molecular chain is oriented parallel to the z-direction, and a negative value indicates that the molecular to the z-direction.

Figure 8D shows P(z) and density distributions of tetracosane molecules for the cases of C4. The results for other alcohol surfactants were similar and are not shown. The curves of P(z) and the density of CH_n groups (Tetr) exhibit oscillations in opposite phases. In each molecular layer, the value of P(z) is negative because tetracosane molecules prefer

to align parallel to the silica surface in each monolayer which has been also observed in previous studies.^{24,49} Distributions P(z) of C4 and C8 alcohol molecules and their corresponding number density profiles are shown in Figure 8E,F, respectively. The hydroxyl groups and the CH₂ groups of adsorbed alcohol molecules show strong anisotropic orientation ordering in a vertical direction toward the silica surface (see also $\theta_{s_1-s_2}^z$ in Figure S2). This phenomenon is induced by hydrogen bonding with silanols regardless of alcohol chain length. Different from the adsorbed CH_n groups (Tetr) parallel to the silica surface, the vertical adsorption structure of alcohol molecules implies that there is a heat path from the silica surface to the nearest hydroxyl groups (Alco) via hydrogen bonds and from the hydroxyl groups (Alco) to CH_n groups (Alco) via intramolecular interactions. With the distance from the silica surface being more than 15 Å, the orientation of alcohol molecules becomes isotropic, that is $P(z) \approx 0$.

3.2.5. Structure of Hydrogen Bonds. Geometric criteria are often used to determine hydrogen bonds.^{50,51} Here, we assumed a hydrogen bond XH···O if the H···O distance is $r \leq 2.75$ Å and \angle XHO $\geq 130^{\circ}$ to investigate the structure of hydrogen bonding between silanols and hydroxyl groups (Alco). Distance criteria were obtained by calculating the radial distribution functions g(r) for the O···H distance in the two configurations SiOH···O(H)R (type 1) and ROH···O(H) Si (type 2), where the central atom was set as alcohol hydroxyl H and O, respectively. The results for C8 are shown in Figure 10 as an example, where 2.75 Å is taken as the first minimum



Figure 10. Radial distribution functions g(r) of SiOH···O(H)R (type 1) and ROH···O(H)Si (type 2) distance for octanol at the Si–OH surfaces.

position of g(r) which is the same for type 1 and type 2. All other cases with different alcohol molecules produced similar graphs with the same peak positions because these peaks correlate with the strong hydrogen bond interaction.⁵² The angle criteria for hydrogen bond does not have a unique definition, thus $\angle XHO \ge 130^{\circ}$ was chosen from the previous research⁵³ dealing with water and organic compounds where a high probability of $\angle XHO$ appears in this area.

It was observed that g(r) of type 1 has one peak, but g(r) of type 2 has two peaks (Figure 10), suggesting that the number of type 1 hydrogen bonds is more than type 2. We have also conducted some preliminary analysis and discovered that a hydroxyl group (Alco) could mostly form either a single (type 1) or double (type 1 and 2) hydrogen bond with a silanol. The ratio of the hydrogen bond type 2 to type 1 was about 40% for all alcohol species on both hot and cold sides, which indicates that for adsorbed alcohol molecules, the proportion of conformation of the double hydrogen bonds is independent

of temperature and alcohol chain length. To investigate the dynamical properties of the adsorption structure due to hydrogen bonds, the dynamic lifetimes of hydrogen bonds type 1 and type 2 were obtained. However, although the hydrogen bond lifetime was strongly correlated to the temperature, we could not find a correlation between the hydrogen bond lifetime and $R_{\rm b}$ (see Figure S1 in the Supporting Information). This is because even if the hydrogen bond breaks in a short time, the hydroxyl groups (Alco) remain localized to adjacent silanols,⁵⁴ while also the total number of hydroxyl groups (Alco) in the first adsorption layer is almost invariant. Thus, we conclude that the effect of hydrogen bond lifetime on $R_{\rm b}$ is not significant.

According to the results in Figure 7, Coulomb contributions to heat flux are not significant, and vdW contributions are dominant. Here, for convenience, our definition of vdW interaction includes the attractive component due to dispersion force and the repulsive component due to the Pauli repulsion, although vdW interaction originally stands for the former only. By attracting atoms closer to each other, Coulomb interaction rises the repulsive vdW interaction, which enhances the thermal conductivity. This mechanism has also been discussed in previous works.^{55–59} So, it appears that hydrogen bonds, to which Coulomb interaction dominantly contributes, are essential to determine the adsorption structure of alcohol, which enables more favorable energy transfer.

3.3. Discussion on Other Possible Surfactants. Our study highlights the importance of the molecular structure of surfactants in enhancing interfacial heat transfer using surfactants. We chose alcohol as a surfactant because it has a high affinity with both Si–OH surface and polymer liquid. If we used water as a solvent, for example, the function group of the surfactant that is directed to water should be hydrophilic.

In this study, $R_{\rm b}$ decreased with the increase in the alcohol chain length up to #C = 32. Whether R_b would continue increasing for longer chains depends on many factors. If the increase in chain length does not affect the number of adsorbed hydroxyl groups (Alco), as in our case here, the increase in chain length would only increase the number of CH_n groups (Alco) in the first adsorption layer and R_h is expected to decrease due to the increase in intramolecular heat transfer in surface alcohol and intermolecular heat transfer between surface alcohol and bulk liquid. However, while the adsorbed hydroxyl terminal groups of alcohol molecules would remain vertical to the surface, the alkane end of adsorbed alcohol would orient horizontally in the vicinity of the surface because CH_n groups (Alco) prefer to spread near the Si-OH surface as shown in Figure 8A-C. In the case of much longer alcohols, the alkyl chain may prevent the hydroxyl groups of other alcohols from approaching the silica surface, and in such cases, an increase in chain length would possibly result in an increase in R_b^{40} The property of alcohol with a very long chain would be closer to the property of alkane solvent, as the volume density of hydroxyl groups becomes low, and this longchain alcohol would be easier to desorb from the Si-OH surfaces, which would also reduce the interfacial heat transfer. $R_{\rm b}$ is possibly lower for polyol than monoalcohol because an increase in the number of hydroxyl groups in a molecule causes increased organic adsorption on a hydrated surface,⁶⁰ and multiple hydroxyl groups would increase the number of heat path from hydroxyl groups to alkyl groups via alcohol intramolecular interaction.

4. CONCLUSIONS

To explore the mechanism of a surfactant that is capable of enhancing heat transfer at the solid-liquid interface applied in microelectronic devices, we performed MD simulations of a system in which a polymer liquid containing alcohol as the surfactant is in contact with silica surface. These molecules and the solid surface were chosen to study the effect of molecular structures of solvent, surfactant, and solid surface on the interfacial heat transfer. Our simulations showed that alcohol molecules are preferentially adsorbed onto the hydrophilic Si-OH surface compared with polymer molecules because of strong hydrogen bonding with silanols, while no obvious adsorption of alcohol was observed on the hydrophobic Si-H silica surface. The thermal boundary resistance $R_{\rm b}$ between the Si-OH surface and the polymer liquid decreased with the increase in the adsorption amount of alcohol molecules. This reduction in $R_{\rm b}$ can be explained by the increased affinity between the polymer solvent and the silica surface due to the adsorption of amphiphilic alcohol surfactant and is consistent with the conclusions in many studies that heat transfer at a solid-liquid interface is correlated with the affinity between the liquid and the solid.^{10,11,41,42} Here, we also found that $R_{\rm h}$ decreases with increasing the chain length of alcohol surfactant if the adsorption amount of alcohol is kept constant. This reduction was due to the heat path from the silica surface to the polymer solvent, formed with the help of the adsorbed alcohols. First, thermal energy is transferred from a surface silanol to a hydroxyl in alcohol via hydrogen bond. This energy is then carried by intramolecular interactions through the alkyl chain of alcohol, and it finally diffuses from alcohol to the polymer molecules due to the intermolecular van der Waals (vdW) interactions between alkyl chains. The increase in the alcohol chain length facilitates the last two mechanisms of heat transfer, thereby reducing $R_{\rm h}$. The interfacial heat transfer was mostly due to vdW interactions, whereas Coulomb interaction plays a crucial role in maintaining the adsorption structure of surfactant alcohol molecules to stabilize the heat path. This chain length dependence is purely an effect of specific molecular structures and suggests that there are various ways of the interfacial heat transfer enhancement depending on different molecular structures of solvent, surfactant, and solid surface.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c08940.

Parameters of the molecule models, lifetime of hydrogen bonds, calculation details for respective heat flux, angle distribution of silanol and alcohol at silica–alcohol interface, the density profile with Si–H silica walls, area number density and interfacial potential energy for both hot and cold sides, and description of mechanism of interfacial thermal conductance (PDF)

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Notes

The authors declare no competing financial interest.

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