

First-principles studies of structure of liquid cyclopentasilane and ring-opening reactions of cyclopentasilane

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Recently, a novel method using Cyclopentasilane (CPS) for directly printing of silicon semiconductor devices has been developed.¹ In this method the polymerization of CPS utilized for fabricating liquid silicon materials. For the control of the process it is necessary to clarify the properties and mechanism of the polymerization CPS in liquid phase. For this purpose, numerical simulations are expected to be a useful tool for giving an insight into the nature of the liquid CPS. In this work, microscopic properties of the liquid CPS and the ring-opening reactions of CPS have been studied by first principles simulations. All simulations were done by the Car-Parrinello method implemented in the CPMD code.

In the analysis of the obtained MD trajectory of the liquid CPS, we focus on the RDFs between the centers of mass of CPS molecules and H atoms, $g_{\text{Center-H}}(r)$, and those between the center of mass of CPS molecules and Si atoms, $g_{\text{Center-Si}}(r)$. The RDF $g_{\text{Center-H}}(r)$ shows a peak at approximately 2.1 Å, while $g_{\text{Center-Si}}(r)$ shows a peak at approximately 3.3 Å. These obtained results strongly support a hypothesis that hydrogen bonds between CPS molecules are formed and play a very important role in the liquid CPS.²

For a further understanding the polymerization reaction of CPS in liquid phase, the dissociation of Si-Si bonds and Si-H bonds was investigated by constraint MD simulations with 27 CPS molecules, in which a bond length was gradually increased in the MD simulations. Then, selected critical points on the obtained trajectories were extracted and relaxed by constraint molecular dynamics simulations. We found that the dissociation of a Si-Si bond or a Si-H bond leads to the ring-opening of a neighbor CPS molecule. The hydrogen bonds between broken CPS molecules (radicals) and CPS molecules were found to get involved in intermediate states of the reactions. Especially, we found that the dissociation energies of these bonds in the liquid phase are significantly smaller than that in gas phase.

[1] T. Shimoda and et. al Nature 440 (2006), 783–786

[2] P. T. Lam et. al Chemical Physics 400 (2012) 59–64