# Tight-Binding Molecular Dynamics Simulation of Desorbed SiO Molecule during the Oxidation of Si(111) Surface

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### 1. Introduction

Due to the technological importance of silicon integrated circuit, the oxidation of Si surface has received considerable attention. The high temperature (T > 900K) oxidation of the Si surface leads to SiO gas formation and at lower temperatures  $SiO_2$  film is formed. The study related to desorption of SiO during  $O_2$  molecular beam scattering has been reported [1-3] recently, however the

reaction dynamics is still unknown.

On the other hand, computational chemistry has became a powerful tool to obtain such useful information that can not be provided by experiments. Particularly, Car and Parrinello (CP) [4] method is very accurate and can consider the effect of temperature. From computational points of view, however, the demand to much faster method is rapidly increasing. Hence it is worthwhile to apply computationally faster tight-binding molecular dynamics (TBMD) to such materials. In this study, we have investigated the dynamics and rovibrational state of desorbed SiO using TBMD where extended Hückel approximation is applied to solve the electronic state.

## 2. Computational method and model

TBMD calculations were performed by Colors code developed by our group. This program is based on the method reported by Laasonen et al. [5]. In this program, we introduced the external potential as a short-correction potential as proposed by Calzaferri et al. [6]. To solve the electronic problem, simulated annealing technique was used. We used the molecular cluster  $Si_9H_{15}O_3$  to model the Si(111) surface and the dynamics of desorbed SiO from the surface was considered. All the hydrogen atoms saturating the dangling bonds of bulk silicon were fixed, and three silicon atoms were also fixed to prevent irrelevant motion at high temperature. The velocity form of the Verlet algorithm was used with a time step of 0.2  $\times 10^{-15}$  s to integrate the equations of motion. The total of 8000 MD steps was performed. To investigate the dynamic behavior of SiO, the phonon spectrum was obtained by taking the Fourier transformation of the velocity-velocity autocorrelation function and the rovibrational energy of desorbed SiO was also calculated.

# 3. Results and discussion

The empirical parameters used in the TB hamiltonian are determined so as to satisfy the bond lengths, binding energies and frequencies of  $Si_2$  and SiO molecules (Table I). Experimental data were referred in SiO interaction, while in Si-Si interaction the data obtained by *ab initio* calculation were referred.

On Si(111) surface molecular oxygen is dissociatively adsorbed and the O atoms are located in both the on-top and bridge sites. Previous report on the properties of oxygen on silicon surface shows that the adsorption on the on-top site is less stable [7]. As it will be easy to desorb from the less stable site, we determined the initial structure to be on-top site model and one oxygen to be inclined in order to facilitate the desorption.

Table I Comparison of experimental and calculated data of diatomic molecules.  $r_e$  - equilibrium nuclear distance.

molecule		r <sub>e</sub> (Å)	binding frequency energy (eV) (cm <sup>-1</sup> )	
Si <sub>2</sub>	TB	2.27	3.43	520
	ab initio	2.23	3.02	507
SiO	TB	1.45	8.17	1254
	experiment	1.51	8.26	1241

In Table II, the phonon spectra of the adsorbed oxygen at 300 K and 1270 K are presented. The frequency value 1150-1197 cm<sup>-1</sup> is attributed mainly to the SiO stretching vibration and 1267 cm-1 corresponds to the desorbed SiO stretching vibration. In comparison with the temperature of substrate (1019 K) and that of desorbed SiO (1334 K), it is assumed that SiO desorbed at thermal equilibrium state. This tendency is equal to the experimental results [1]. Fig. 1 shows the snapshot of the results of MD simulations. At 600th step (120 fs) SiO wags severely because of the high bending energy related to inclination. Finally at ca. 1300th step (260 fs), SiO is desorbed from the on-top site. It is observed from the animation that after SiO rotates very little at the moment of SiO desorption, at 2500th step SiO started to rotate again.

Turning our attention to the energetics in the system, we calculated rovibrational and translational energy of SiO molecule (Fig. 2). In the region of 1300th-1800th step, a decrease in bending (Erot) and stretching (Evib) energies was observed and was used to break the Si-Si bond. Subsequently, the decreased energy was recovered by the week interaction between SiO and the substrate (1800th-2500th step). This mechanism supports the experimental results that the rovibrational temperature of desorbed SiO is almost equal to that of Si substrate.

### 4. Conclusion

We have reported the results of vibrational frequencies at oxygen adsorption site on Si(111) surface and rovibrational energy of the desorbed SiO. We proposed SiO desorption mechanism as follows: bending (Erot) and stretching (Evib) energy resulted from thermal energy of substrate is converted to the dissociation energy of Si-Si, which was further recovered by the weekly physisorbed state of SiO on the substrate so as to attain thermal equilibrium.

#### References

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Table II Calculated vibrational frequencies and intensities of Si-O and temperature of desorbed SiO. Those labeled stretching\* corresponds to the desorbed SiO molecule.

		temperature of	emperature of the system (K)	
		300	.1250	
	bending	35 (0.98)	24 (1.00)	
frequencies	stretching	1053 (0.75)	1150 (0.42)	
(cm-1)		1193 (0.89)	1197 (0.52)	
	stretching*		1267 (0.55)	
substrate tempe	erature (K)		1019	
temperature of	desorbed SiO (K	- (;	1334	



Fig. 1 A snapshot (1300 step) for our simulation at 1270 K.



Fig. 2 Rovibrational and translational energy of SiO.