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Theoretical study on hydrogen reaction processes on H/Si(0 0 1) surface

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Abstract

The reaction processes of an incident H atom with the H- or D-terminated Si(0 0 1)-(2 × 1) surface are theoretically investigated by using first-principles molecular dynamics simulations. Because the atomic hydrogen reaction process producing an H_2 (HD) molecule is exothermic, this reaction is considered to be observed in many cases. It is found that an H_2 (HD) molecule is produced in all of the cases treated in this study. The final kinetic energy of the resultant H_2 (HD) molecule is found to be mostly distributed to the vibrational energy, whereas the translational energy of the resultant molecule is estimated to be relatively low. In this reaction process, a resultant H_2 (HD) molecule is weakly trapped into a bound state site between two Si dimer rows on the surface followed by the desorption from the surface. This type of reaction processes corresponds to the direct abstraction of Eley-Rideal mechanism, which is in good agreement with the previous experimental results.

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Keywords: Si surface reaction; Atomic hydrogen; Hydrogen termination; First-principles calculation; Exothermicity; Energy distribution

1. Introduction

Adsorption, abstraction and desorption of hydrogen on silicon surfaces are deeply involved in many processes of semiconductor fabrication such as plasma CVD, etching, epitaxial growth and surface cleaning. Therefore, atomic H reaction processes on the H- or D-terminated Si(0 0 1) surface are of great interest from both theoretical and experimental viewpoints [1–6].

Many researches about the structures of the Si surface have been done up to now. However, details about the kinetics, dynamics and mechanisms of the reaction have not yet been clarified in many points. In

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the atomic H reaction processes on the H- or D-terminated Si(0 0 1) surface, several kinds of the reaction model are proposed such as Langmuir–Hinshelwood mechanism (thermal reaction), Hot Atom mechanism and Eley-Rideal mechanism (non-thermal reaction).

Kubo et al. have studied the abstraction and desorption kinetics in the reaction of atomic H on D/Si(0 0 1) surface [1]. They have measured the desorption rates of the HD and the D_2 molecules at different surface temperatures and demonstrated the coexistence of thermal (the D_2 desorption is dominant) and non-thermal (the HD abstraction of Eley-Rideal mechanism is dominant) processes. They have also shown that only the non-thermal process is observed at the lower temperatures <400 K. Shimokawa et al. have also studied the abstraction and desorption kinetics in the reaction of atomic H on D/Si(0 0 1) surface at 573 K [2]. They have explained the reaction kinetics of collision-induced D_2 desorption as well as in the abstraction of the HD molecule by the model proposed by Flowers et al. [4], and concluded that the abstraction of the HD molecule may be due to an Eley-Rideal mechanism rather than to a Hot Atom mechanism.

The reaction mechanisms have also been theoretically investigated [5,6]. Hansen and Vogl performed classical molecular dynamics simulations for the atomic H incidence to the H-terminated Si surface [5]. They have showed that the hydrogen adsorption is the dominant process with a probability of ∼0.6 and an Eley-Rideal abstraction mechanism is the other efficient reaction process with a probability of ∼0.4.

Although much effort has been both experimentally and theoretically devoted to elucidate the reaction mechanisms of atomic H reaction processes, there are few reports based on the analysis at the microscopic level. In this paper, we show that the kinetics and dynamics of atomic H reaction processes on the H- or D-terminated Si(0 0 1) surface by using the first-principles molecular dynamics simulations. Our results are shown to be in good agreement with the previous experimental results [1].

2. Calculation method

First-principles molecular dynamics (MD) simulations are applied to the H-terminated Si(0 0 1) surface modeled as the repeated slab geometry containing five Si atomic layers. Si atoms of the top layer are terminated by H or D atoms with the coverage of 1.0 (monohydride or monodeuteride), which corresponds to the H(D)/Si(0 0 1)-(2 × 1) surface. Si atoms of the bottom layer are terminated by H atoms with the coverage of 2.0 (dihydride). A $c(4 \times 4)$ supercell is used as the unit cell. One H atom is injected toward the surface terminating H atom under several initial conditions. Our MD simulations are performed within

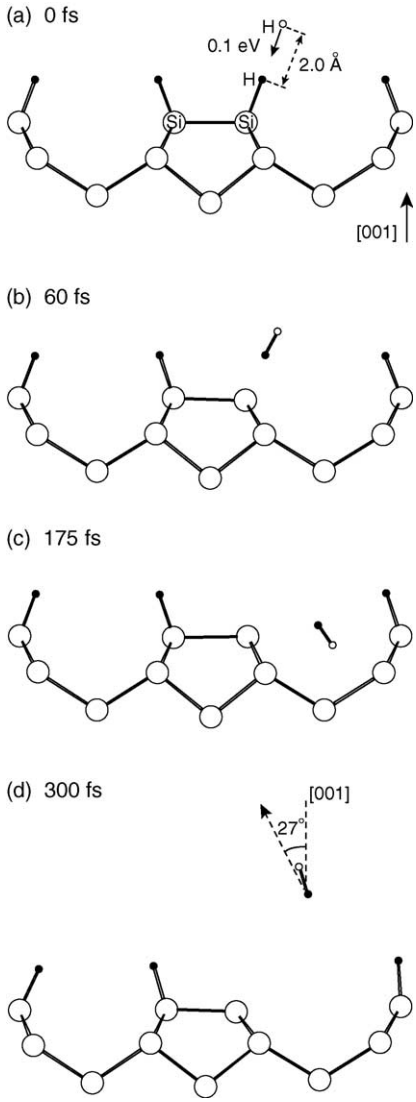

Fig. 1. Snapshots of the atomic H reaction process of the case I at (a) 0 fs, (b) 60 fs, (c) 175 fs and (d) 300 fs.