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Simulation of SiH_4 adsorption on H/Si(100) surfaces

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Abstract

Using quantum-chemical calculations, we have studied the adsorption mechanism, geometry and energy states of silane on H/Si(100) surfaces (with a monohydride phase). Adsorption can take place both with and without dimer bond rupture. As a result of the calculations, it has been established that adsorption of silane on the H/Si(100) surface can result in the formation of structures of different types. The SiH_2-fragment can be adsorbed onto atoms of one surface dimer (models 1 and 3) and onto atoms of two neighboring dimers of one dimer row (models 2 and 4).
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Keywords: Computer simulation; Adsorption; Silane; Si(100) surface

1. Introduction

Nowadays, great efforts are made to study the processes of silicon film growth on Si(100) surfaces by chemical vapor deposition (CVD) methods. Silane is the most frequently used gas for low-temperature CVD growth. Growth of hydrogenated amorphous silicon (a-Si:H) and nanocrystalline silicon (nc-Si:H) films on hydrogen-terminated silicon surfaces through CVD from silane (SiH_4) is widely used in electronic, optoelectronic and photo-voltaic device manufacturing technologies [1–4]. Despite the wide experimental study of CVD processes [5,6], mechanisms of silicon deposition (silicon film growth) and its quality monitoring methods are still not fully comprehended. The role of surface hydrogen is of high importance, as it provides the growth of high quality silicon films [1]. Hydrogen reduces the surface disorder during silane adsorption by saturating the dangling bonds of surface atoms and reducing the adsorbing activity of the surface.

2. Calculations

Our calculations were carried out using a semi-empirical modified neglect of differential overlap (MNDO) method for Si_{33} and Si_{63} clusters. The Hartree–Fock method (restricted or unrestricted) serves as a basis for Roothaan equations set calculation. Determination of optimized cluster geometry, corresponding to system energy minimum, is carried out by Baker's Eigen Following (EF) method. Calculation methods are described in detail in [7,8]. Cluster geometry and total energy, atom bond orders, electron density, atomic orbital populations and molecular localized orbitals were calculated. In the simulation of silane adsorption on the Si(100) surface, the reaction coordinate was the distance between the Si atom of silane and one of the cluster surface atoms, while positions of all other atoms were freely optimized. As a result of the calculation, the total system energy depending on the reaction coordinate was obtained, and the geometry and electron characteristics of equilibrium states of adsorbed particles were determined. The accuracy of the method used (~5–15%) can be estimated by comparison with other calculations [9–11] and experimental data [12].

3. Results and discussion

It is known that the hydrogen adsorbed on clean Si(100) surface forms monohydride and dihydride phases, thus reducing adsorption activity of the surface.

The monohydride phase is formed as a result of hydrogen saturation of dangling bonds of surface dimers. Adsorption

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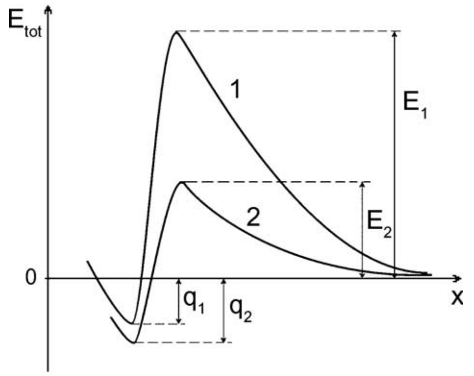

Fig. 1. Dependence of surface total energy $E_{tot}(x)$ on reaction coordinate with a silane molecule. E_1, E_2—are adsorption barriers, q_1, q_2—heats of adsorption. Curve 1 corresponds to adsorption accompanied by surface dimer bond rupture; curve 2 corresponds to adsorption without surface dimer bond breaking.

activity of such a surface is low, because all the bonds of the surface atoms are saturated, thus silane adsorption occurs with a significant energetic barrier. Silane adsorption take place by breaking a dimer bond between surface dimer atoms (curve 1 on Figs. 1 and 2) or by hydrogen desorption from the monohydride phase (curve 2 on Figs. 1 and 3). Both of these processes result in the formation of dangling bonds of surface silicon atoms.

According to our calculation, the dimer bond length on the H/Si(100) surface with a monohydride phase is 2.22 A. Hydrogen saturation of surface dangling bonds results in removal of the dimer asymmetry. The silane adsorption, causing the surface dimer bond rupture, goes through a significant energy barrier, $E_1=4.8$ eV. As a result of adsorption, the SiH–SiH surface dimer bond breaks. The silane molecule dissociates into H and SiH_3 radicals, saturating the unsaturated bonds that are formed due to dimer bond rupture. Thus, the dihydride phase is formed on one surface atom (it is bounded with two hydrogen atoms), while the other surface atom is bounded with a hydrogen atom and an SiH_3 fragment (Fig. 2a). The heat of adsorption of the SiH_3-fragment is $q_1=0.43$ eV.

It is known that the SiH_3-fragment is unstable and dissociates into SiH_2 and H [10,13]. Furthermore, the SiH_2-fragment can be adsorbed onto silicon atoms of one surface dimer and silicon atoms of two neighboring dimers of one dimer row (Fig 2b,c). The total energy minimum corresponds to the state of "cluster–adsorbate" system, which is shown in Fig. 2b (model 1). Transition into such a state from the initial adsorption stage (Fig. 2a) is accompanied by molecular hydrogen desorption (one hydrogen atom from an SiH_3-fragment abstraction and another from a surface silicon atom). The energy barrier of H_2 desorption is 1.25 eV. As a result, the SiH_2-fragment saturates the bonds of two neighboring surface atoms. It is typical for model 1 that the dimer bond break results in repositioning of silicon atoms, which are bounded with silane dissociation products. The surface silicon atoms then occupy positions close to ideal bulk geometry, i.e. adsorption of silane results in reconstruction of the 2×1 surface structure. Hybridization of surface atoms 1 and 2 (Fig. 2b) is close to sp^3, meaning that the geometry of the surface is close to the 1×1 structure.

Model 2 corresponds to the state when the SiH_2-fragment saturates the dangling bonds of silicon atoms of two neighboring dimers. In this case, the rupture of the dimer bond between surface atoms in the neighboring dimer takes place. The hydrogen atom that saturates the dangling bond of one surface atom is abstracted from an SiH_3-fragment adsorbed on the surface. The resulting SiH_2-fragment saturates the bonds of two surface atoms of neighboring dimers. The barrier of this transition from the state, shown in Fig. 2a, is approximately 2.45 eV. The total cluster energy in such a state is 0.5 eV higher than the state corresponding to model 1. Though all the bonds of the surface atoms are saturated, the increase in system energy compared to model 1 can be explained by uncharacteristic angles between bonds in model 2 (91°, 99°, 82°, 109°) for crystals with a diamond structure. The values of the adsorption barriers, which have to be overcome to form the corresponding structures of models 1 and 2, indicate that their formation is possible either at high temperatures, or at high energies of silane molecules impinging on the surface.

Silane adsorption can take place without the breaking of surface dimers:

1) During the interaction of SiH_4 with the surface, silane dissociates into SiH_3 and H. The hydrogen atom recombines with another hydrogen atom, saturating the

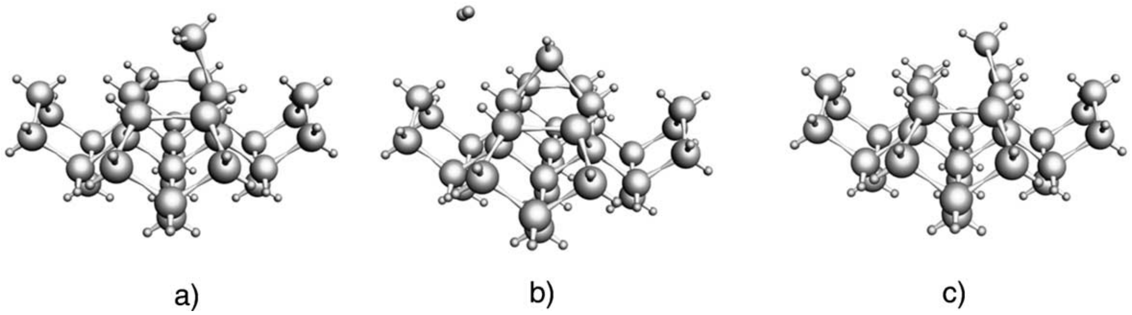

Fig. 2. The result of silane adsorption on the monohydride-terminated Si(100) surface: (a) hydrogen atom and SiH_3-fragment saturate dangling bonds of surface silicon atoms, formed due to dimer bond rupture; (b) model 1; (c) model 2.