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First-principles investigations of low-coverage Ca-induced reconstructions on the Si(001) surface

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ABSTRACT

Using the pseudopotential method and the local density approximation of density functional theory we have investigated the stability, atomic geometry, and electronic states for low-coverage Ca adsorbates on the Si (001) surface within the $(2\times n)$ reconstructions with $n=2, 3, 4, 5$. Our total energy calculations suggest that the (2×4) phase represents the most energetically stable structure with the Ca coverage of 0.375 ML. Within this structural model, each Ca atom is found to form a bridge with the inner two Si–Si dimers. The inner Si–Si dimers become elongated and symmetric (untilted). The band structure calculation indicates that the system is semiconducting with a small band gap. Significant amount of charge transfer from the Ca atoms to neighbouring Si atoms has been concluded by analysing the electronic charge density and simulation of scanning tunnelling microscopy images. The highest occupied and lowest unoccupied electronic states are found to arise from the inner and outer Si–Si dimer components, respectively.

1. Introduction

In the past few decades, studies of elemental adsorption on semiconductor surfaces have been carried out intensively both experimentally and theoretically for the understanding of metal semiconductor interfaces and their potential applications. Of potential technological importance and of scientific interest is the physics of metal adsorbed Si(111) and Si(001) surfaces. While the former surface structures have been widely investigated [1–12], studies of the latter have been inconclusive yet. However, although the adsorption of alkali metals (AMs) on Si(001) surfaces has attracted a lot of interest for several years [13–19], alkaline-earth metals (AEMs) have received little attention.

The change in the behaviour of Ba atoms on the Si(001) surface has been experimentally studied, using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED), as a function of the substrate temperature and Ba coverage [20,21]. Urano et al. [21] have reported that, with less than a monolayer (ML), Ba induces (2×1), (2×3), and (2×4) reconstructions on Si(001). Kim et al. [22] have reported that the adsorption of Ba on the Si(001)(2×1) surface at about 870 °C leads to two well-ordered phases, (2×3) and (2×1), both of which have semiconducting nature. Similar reconstructions, (2×2) and (2×3) have been also reported for the adsorption of Mg atoms on the Si(001) surface using scanning tunnelling microscopy (STM) [23–25]. Kawashima et al. [24] have presented LEED and AES results for the surface structures of the Mg/Si(001) system during the process of thermal desorption. They have observed that as the Mg coverage decreases different structural phases appeared in the order (1×1), (2×3), (2×2) and another (2×3) which correspond to the Mg coverages of 1, 1/3, 1/4, and 1/6 ML, respectively. Hutchison et al. [25] have discussed three different adsorption geometries for Mg in its low-coverage regime using data obtained by STM. They have found that the most preferable geometry consists of a single Mg atom adsorbed on a cave site. Shaltaf et al. [26] have performed first-principles calculations for the adsorption of Mg on the Si(001) surface with different Mg coverages. They concluded that for both 1/4 and 1/2 ML coverages the most favorable site for the Mg adsorption is the cave site between two Si–Si dimers. They also determined that preferable configurations for 1/4 ML coverage is a (2×2) reconstruction while the (2×1) reconstruction corresponds to the 1/2 ML. The adsorption of Sr atoms on the Si(001) surface has also been studied using the ultra-high vacuum STM, LEED, and AES [27]. In their study, Bakhtizin et al. [27] have proposed a structural model of (2×3) with Sr coverage of 1/3 ML. Moreover, it has been reported [28] that at low Sr coverages, (1×2) and (1×5) reconstructions will be also induced whereas (1×3) appears when Sr coverage reaches 1 ML.

However, among various AEM adsorbates on Si(001), Ca has received much less work. Very recently, Cui and Nogami [29] have experimentally studied the growth of Ca atoms on the Si(001) surface using the STM and LEED techniques. It is well known that the room-temperature reconstruction of Si(001) is (2×1) structure. Cui and Nogami first heated the Si(001)(2×1) up to 1150 °C to remove the oxide layer, then annealed at 950 °C, and then reduced the temperature to the range 500–800 °C for deposition of Ca. Depending

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