

First-Principles Study on Formation of Freestanding Silicene and Germanene

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Abstract

Silicene and germanene, which are single layer Si and Ge crystals, have been theoretically predicted to possess supreme electronic properties. However, they are synthesized on metallic substrates, and thus they cannot show the inherent electronic properties owing to strong interactions with metallic substrates. In this study, we investigate whether free-standing silicene/germanene can be created from the hydrogenated one, using statistical-mechanical approach coupled with the first-principles calculations. Our results show that the free-standing germanene can be created from the hydrogenated one.

1. Introduction

Two-dimensional crystals consisting of group IV element heavier than carbon, such as silicene and germanene, are supreme thin-film materials. They have been theoretically predicted to possess high carrier mobility and some intriguing functions such as band-gap control and topological insulator [1,2]. They have been recently synthesized on metallic substrates [3-6]. However, it has been reported that the electronic states of silicene on a metallic substrate are dramatically modified by the strong interactions with the surface atoms [7,8]. Accordingly, it is difficult to measure the intrinsic electronic properties.

A hydrogenation of CaSi_2 [9] or CaGe_2 [10] crystal is one of the most promising methods to fabricate a free-standing silicene or germanene. The crystal consisting of hydrogenated silicene (silicane) or germanene (germanane) can be obtained by the hydrogenation, and the free-standing silicane/germanane can be easily exfoliated from the crystal because the interlayer interaction is the van der Waals interaction. In this study, we theoretically investigate whether hydrogen atoms can be desorbed from the silicane/germanane by controlling temperature and hydrogen partial pressure, and discuss whether a free-standing silicene/germanene can be created from the free-standing silicane/germanane.

2. Calculation Method

To discuss the hydrogen adsorption and desorption property of silicene/germanene, we calculate the Gibbs free energies of reactant and products. Considering the primitive cell of silicene/germanene as the calculation box, the reactant is silicane/germanane, and the products are silicene/germanene and a hydrogen molecule. The free-energy difference between reactant and products, ΔG , determines the direction of

this reaction. If ΔG is negative, silicene/germanene is created. If positive, silicane/germanane is created. The free energy consists of two parts: contributions of electrons and lattice vibration. We used VASP code [11] to calculate the electronic contributions and ALAMODE code [12] to calculate the vibrational contributions. The hydrogen molecule has additional contributions: translational and rotational contributions. They can be analytically calculated according to the ideal gas approximation [13].

3. Results

Figures 1 and 2 show the phase diagrams for silicene and germanene formation, respectively. The horizontal axis is temperature, and the vertical axis is hydrogen partial pressure. The color contour indicates ΔG . We find from Fig. 1 that silicene can be created from silicane at relatively higher temperatures but it cannot be created at low temperature unless the hydrogen pressure is decreased. On the other hand, we observe from Fig. 2 that ΔG is negative over a wide area, which means that germanene can be created from germanane at ordinary temperatures and pressures.

Our results show that the free-standing silicene/germanene can be created from the silicane/germanane by controlling temperature and hydrogen atmosphere. However, considering the stability of the two-dimensional crystal, it is more likely that the free-standing germanene is created from the hydrogenated one.

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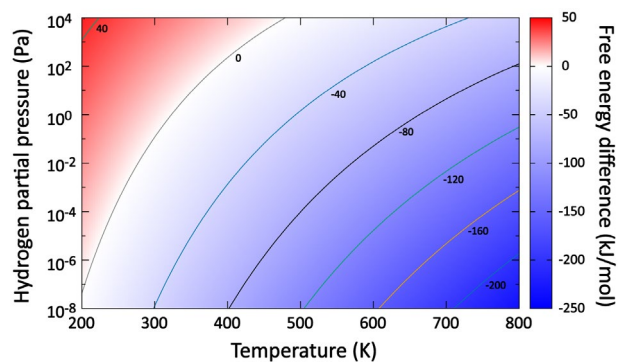


Fig. 1 Phase diagram on hydrogen adsorption and desorption of silicene.

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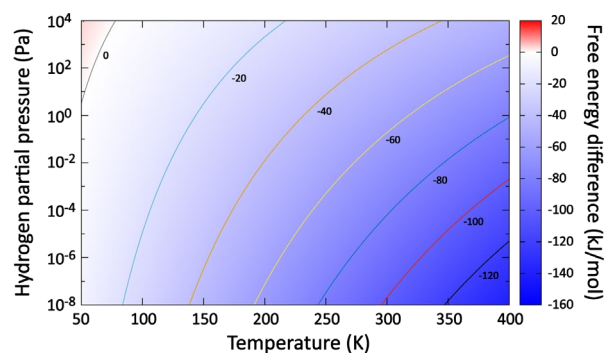


Fig. 2 Phase diagram on hydrogen adsorption and desorption of germanene.