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Experimental and *ab initio* study of Si(111)(2/3)√3×(2/3)√3-Mg models

M.V. Ryzhkova [1] ✉, L.V. Bondarenko [1], D.A. Tsukanov [1, 2]

[1] Institute of Automation and Control Processes FEB RAS, Vladivostok, Russia;
[2] Far Eastern Federal University, Vladivostok, Russia
✉ lavric@iacp.dvo.ru

Abstract. In the present work, using VASP and AIRSS, we have modelled possible structures of Si(111)(2/3)√3×(2/3)√3-Mg. *Ab initio* density functional theory (DFT) calculations using pseudopotentials were employed to investigate structural models of the Si(111)(2/3)√3×(2/3)√3-Mg surface. A number of models were analyzed in a 2×2 surface cell. The study identifies the most energetically favorable structure in the 2×2 configuration as the “7-3_random” model, which contains 1.75 monolayers (ML) of Mg and 0.75 ML of Si. The results of ab initio calculations are well confirmed by experimental methods (STM and LEED observations).

Keywords: magnesium silicide, silicon surface, ultrathin films, density functional theory, ultra-high vacuum, surface structure, surface structure simulation, surface energy

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Экспериментальное исследование и *ab initio* расчеты моделей Si(111)(2/3)√3×(2/3)√3-Mg

М.В. Рыжкова [1] ✉, Л.В. Бондаренко [1], Д.А. Цуканов [1, 2]

[1] Институт автоматики и процессов управления ДВО РАН, г. Владивосток, Россия;
[2] Дальневосточный федеральный университет, г. Владивосток, Россия
✉ lavric@iacp.dvo.ru

Аннотация. В настоящей работе с использованием VASP и AIRSS проведено моделирование возможных структур Si(111)(2/3)√3×(2/3)√3-Mg. Для исследования структурных моделей поверхности Si(111)(2/3)√3×(2/3)√3-Mg были использованы расчеты *ab initio* методом теории функционала плотности (DFT) с использованием псевдопотенциалов. Ряд моделей был проанализирован в ячейке поверхности 2×2. В исследовании выявлена наиболее энергетически выгодная структура в конфигурации 2×2 – модель «7-3_random», содержащая 1,75 монослоя (МС) магния и 0,75 МС кремния. Результаты расчетов хорошо согласуются с экспериментом (наблюдения поверхности методами ДМЭ и СТМ).

Ключевые слова: силицид магния, поверхность кремния, сверхтонкие пленки, теория функционала плотности, сверхвысокий вакуум, структура поверхности, моделирование структуры поверхности, поверхностная энергия

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Introduction

A considerable number of studies have focused on the investigation of magnesium silicide Mg_2Si on the Si(111) surface [1–4] due to its technological importance. However, atomic scale ultrathin films of Mg_2Si have not been explored theoretically and experimentally in detail, for example, a structural model of Si(111)(2/3)√3×(2/3)√3-Mg (thereafter (2/3)√3-Mg) surface structure has been proposed in [2], but comprehensive structure calculations was not performed. Here, in this study, we present the atomic model of the (2/3)√3-Mg reconstruction, in particular, atomic structure and composition were calculated used ab-initio calculations. The accuracy of the model was compared with experimental data. It should be noted that the periodicity of the structure obtained in diffraction experiments does not always reflect the real periodicity observed by the scanning tunneling microscopy. For example, in the case of the surface 3×1-Mg periodicity observed on the low-energy electron diffraction pattern, which reflects the arrangement of silicon atoms on the reconstructed surface, while scanning tunneling microscopy observations clearly show the 3×2 periodicity, which also takes into account the arrangement of silicon and magnesium atoms.

Materials and Methods

The Mg/Si(111) sample was prepared in the Omicron MULTIPROBE ultrahigh vacuum system (UHV) equipped with scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). The base pressure in UHV system was in the order of 1×10^{-10} Torr. The atomically clean Si(111)7×7 sample was first annealed in situ at 600 °C for several hours and finally was flashed to 1280 °C. Mg atoms were deposited from a Ta tube. The (2/3)√3-Mg surface phase was prepared by deposition of ~2 monolayers (ML) of Mg onto the Si(111)7×7 surface at 50–100 °C. Mg deposition rate was calibrated using well known Mg/Si(111) reconstructions: Si(111)3×2-Mg (1/6 ML of Mg) [5], Si(111)6×6-MgPb (1 ML of Mg) [6] and Si(111)4×4-MgPb (0.6 ML of Mg) surface phases [6].

The calculation was conducted using a plane-wave basis set and correlation functional projector-augmented wave pseudopotentials (PAW-PBE) with generalized gradient approximation (GGA) for the exchange-correlation energy. VASP ab initio program package was used for this study. Wave functions were performed using energy cutoff 250 eV. The geometry was optimized until the total energy was converged to 10^{-6} eV and the atomic forces reduced to 10^{-2} eV/Å. For Γ– point the 7×7×1 grid was used.

The (2/3)√3-Mg surface structure has been simulated using the slab with periodicity of Si(111)2×2. The slab consists of 6 Si layers and vacuum region with more than 20 Å to prevent interaction between surfaces in two adjacent cells. The dangling bonds of the bottom silicon layer have been saturated by hydrogen atoms. Two bottom layers and hydrogen atoms were fixed and the rest atoms in slab were allowed to move freely.

For structure search calculation the ab initio random structure search (AIRSS) was used. Energy convergence was 10^{-5} eV and 5×5×1 *k*-points grid was set for this case. Since the (2/3)√3 cell disrupts the periodicity of the silicon substrate, a 2×2 unit cell was used taking into account that 2×2 cell contains 3 subcells of (2/3)√3 cell.

The formation energy was calculated following this formula:

$$E_{form/1\times1} = \frac{E_{tot} - E_{slab} - n_{\mathrm{Si}}\mu_{\mathrm{Si}} - n_{\mathrm{Mg}}\mu_{\mathrm{Mg}}}{N},$$

where E_{tot} is total energy of calculated model, E_{slab} is energy of relaxed slab without silicon atoms in surface phase (usually 3 atoms), n_{Si} and n_{Mg} are numbers of Si and Mg atoms, respectively. μ_{Si} and μ_{Mg} are the chemical potentials for the Si and Mg, respectively, taken from bulk phases of these elements. N is a number of 1×1 cells in the given structure ($N = 4$ for 2×2, $N = 6$ for 3×2, $N = 3$ for 3×1 and $N = 49$ for 7×7 cell).

All calculations were performed using the resources of the Shared use center of Far-Eastern Computational Resource [7].

Results and Discussion

Figure 1, *a* shows the STM pattern obtained from the (2\3)√3-Mg surface at room temperature. It is evident that the surface has a 2×2 periodicity with one protrusion per cell (highlighted in white). Figure 1, *b* shows the Fourier transform of such a surface, with the 2×2 and (2\3)√3 spots observed in picture. Figure 1, *c* shows the LEED pattern of the same surface, with only the (2\3)√3 spots remaining. This resembles the situation with the 3×2-Mg surface phase, which also demonstrated different periodicities in the LEED and STM experimental pictures.

Initially, we considered the model of (2\3)√3-Mg surface presented in the article [2] and calculated its structure in the process of relaxation. It was shown that this model lost the periodicity of (2/3)√3 and leaving only the 2×2 periodicity. However, this model demonstrated a high formation energy (−0.153 eV/1×1) compared to other calculated models (Table).

We have modified this structure called as "model 9-3" (increased the Mg coverage to 2.25 ML: 9 atoms in a 2×2 cell, while the number of Si atoms remained the same (3 Si atoms or 0.75 ML of Si)). After calculations the formation energy for this structure decreased to −0.619 eV/1×1 (Table), while maintaining only the periodicity of (2/3)√3. It is worth noting that "model 9−3" best fits the parameters of the bulk magnesium silicide Mg_2Si structure: interatomic distances 4.48Å for Si-Si and Mg-Mg bonds.

Using AIRSS method, the most favorable structures were calculated for magnesium coverage of 1.75 ML (7 Mg and 3 Si atoms per 2×2 cell, called as "7−3_random" model), 2 ML (8 Mg and 3 Si atoms, "8−3" model) and 2.25 ML (9 Mg and 3 Si atoms, "9−3_random" model), as well as 2 ML (8 Mg and 2 Si atoms) and 2.25 ML (9 Mg and 1 Si atoms, "9−1" model).

Table

Parameters of models for (2/3)√3-Mg/Si(111) surface

Model	Energy, eV/1×1	Si-Si, Å	Mg-Mg, Å
(2/3)√3-Mg [2]	−0.153	4	4.9
9-3	−0.619	4.4	4.4
9−3_random	−0.703	3.5−4.5	3−3.7
8−3	−0.772	4.8−5.1	3.1−4.7
7−3_random	−0.822	4.3−4.6	3.9−4.5
8−2	−0.604	4.6	3.1−4.6
9−1	−0.467	–	3−3.3
Si(111)3×2-Mg	−0.53	–	–
3×1-Mg	−0.527	–	–
Si(111)7×7	−0.356	–	–
Mg_2Si [10]	–	4.48	4.48

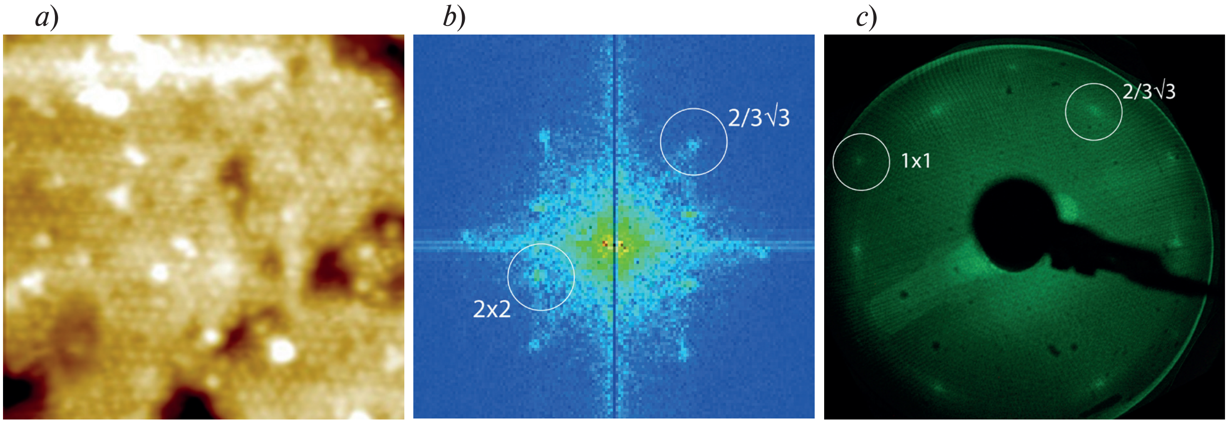

Fig. 1. STM picture (20×20 nm^2) obtained from the (2/3)√3-Mg/Si(111) (*a*), Fourier transform of STM pattern with the 2×2 and (2/3)√3 spots (one of the spots is marked with a white circle for each type) (*b*), LEED pattern from the (2/3)√3-Mg/Si(111) surface, beam energy E_p = 36 eV (*c*)

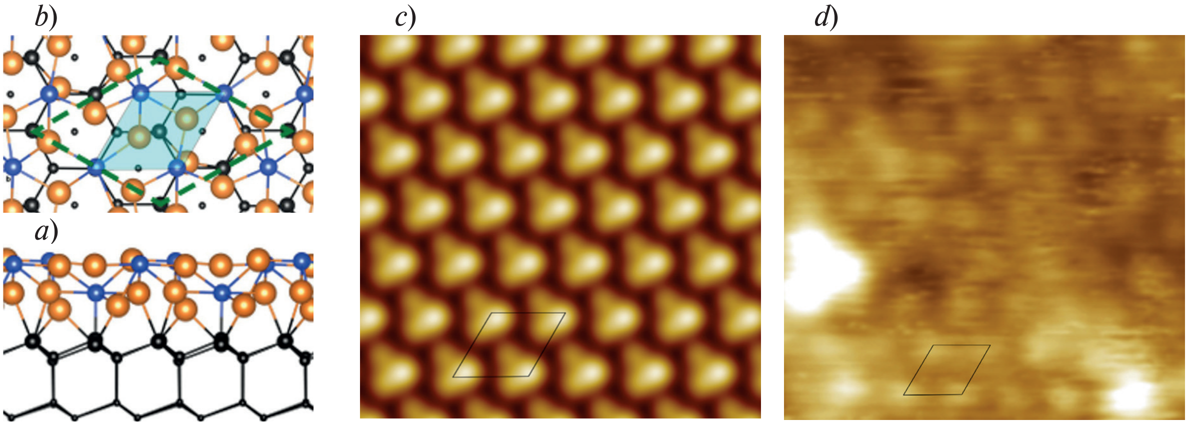

Fig. 2. Model "7-3_random" of (2/3)√3-Mg/Si(111) surface structure (Mg atoms seen as orange balls, Si atoms in Mg_2Si structure seen as blue, Si atoms in Si(111) structure seen as black, 2×2 cell is marked with a green rhombus and (2/3)√3 cell is marked with a light blue rhombus), top view and side view (*a*, *b*). Simulated STM picture of (2/3)√3-Mg/Si(111) surface (*c*). Experimental STM picture (6×6 nm^2) obtained from the (2/3)√3-Mg/Si(111) surface (2×2 cell is marked with a black rhombus) (*d*)

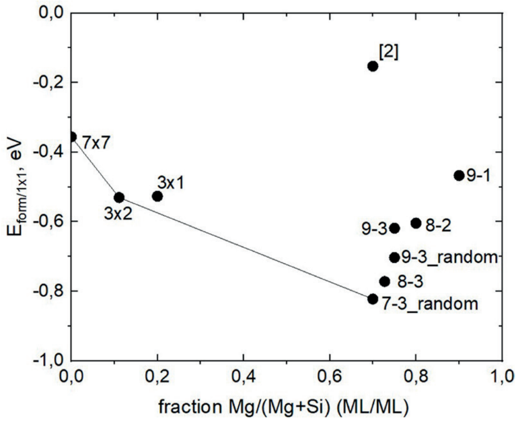

Fig.3. The formation energy versus fraction of magnesium

Thus, we found the model with the lowest formation energy (−0.822 eV/1×1) and structure consisting of 1.75 ML of Mg and 0.75 ML of Si atoms, model "7−3_random". In Fig 2, *a*, *b* its atomic structure is shown, top view and side view, moreover, in Fig. 2, *c* the simulated STM image shows an excellent match with surface structure observed experimentally by STM (Fig. 2, *d*).

Let us note that all calculated models have only a 2×2 periodicity; the (2/3)√3 periodicity is preserved only for silicon atoms with 3 Si atoms in structure. Considering models of magnesium silicide it is visible that 3 Si atoms in the slab surface prefer symmetric places T_4, H_3 and T_1, which ensures a (2/3)√3 periodicity.

Fig. 3 shows the results of calculations of the formation energy depending on the amount of Mg atoms placed in the Mg_2Si/Si(111) surface structure. This plot also contains reference points that relate to the calculations of the Si(111)3×2-Mg, Si(111)3×1-Mg and Si(111)7×7 surface reconstructions. The latter structures we have also calculated based on the models of alkaline earth adsorbates presented for 3×2 and 3×1 in the article [8] while surface structure of Si(111)7×7 was calculated related to standard DAS model [9]. It is seen that the most favorable structure for Mg_2Si/Si(111) ultrathin layer is “7–3_random” model that has 1.75 ML of Mg and 0.75 ML of Si with 2×2 periodicity that is confirmed by STM observation.

Conclusion

We have performed ab initio calculation and experimental study to investigate Si(111) (2/3)√3×(2/3)√3-Mg surface structure models. The most favorable structure with the lowest formation energy (–0.822 eV/1×1) is the “7–3_random” model that consist of 1.75 ML of Mg and 0.75 ML of Si atoms with 2×2 periodicity. The results of ab initio calculations are well confirmed by experimental methods used in this work (STM and LEED observations).

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THE AUTHORS

RYZHKOVA Maria V.
lavric@iacp.dvo.ru
ORCID: 0000-0001-8990-7140

TSUKANOV Dmitry A.
tsukanov@iacp.dvo.ru
ORCID: 0000-0002-8900-3480

BONDARENKO Leonid V.
bondarenko@iacp.dvo.ru
ORCID: 0000-0002-2660-3622

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