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Structural and electronic properties of As:Ge_n on Si(001) surface

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The structural and electronic properties of As:Ge_n on Si(001) semi-infinite surface (with n=0∼9) have been analyzed by a self-consistent semi-empirical approach based on the Chadi's total energy model and the charge neutrality condition. The geometry of semi-infinite systems has been treated by the scattering theory method. The geometric and electronic structures are presented and discussed.

1. INTRODUCTION

The effects of surfactants in heteroepitaxial growth have attracted significant attention [1–5]. Due to the lattice mismatch between Si and Ge it is energetically favorable to form islands after only three monolayers of Ge depositing on Si(001) surface. By using arsenic as a surfactant the layer by layer strained growth of up to a thickness of 8∼10 monolayers of Ge on Si(001) surface has been investigated [1,3]. In this process the surface remains terminated by arsenic atoms and Ge atoms will rapidly exchange sites with As atoms during the growth [3,4].

Although the mechanism of surfactants in epitaxial growth has been experimentally studied, no structural and electronic information is available. Very few published work concerning the character of subsurface layers which influences the surface reconstruction is available. In this work the structural and electronic properties of varying thickness Ge layers deposited on arsenic terminated Si(001) surface have been studied in detail by using the self-consistent semi-empirical tight-binding method under the local charge neutrality condition. The purpose of the work is to obtain a better understanding of electronic and structural properties in a microscopic scale during the heteroepitaxial growth.

2. METHODS

Since the complexity of the growth considered, the calculations are restricted to the self consistent semi-empirical tight-binding method, which has been successfully used to study microscopic properties of many heterostructures. The detailed discussion of this method is given in the previous work [6,7], here only a brief description of the method will be given.

In the present work, empirical tight-binding parameters up to second-nearest neighbors are taken into account. These were obtained by fitting the calculated bulk band structures to the corresponding experimental data for Si and Ge by Pandey and Phillips [8]. The interaction parameters between Ge, Si and As given in references [9,10] are used. The tight-binding parameters are scaled by $(d_0/d)^2$, where d_0 and d are the ideal and relaxed bond length, respectively. The distance dependence of parameters U_1 and U_2 in the repulsive term of Chadi's semi-empirical total energy model [11] has also been fully included in the calculations.

The lack of periodicity perpendicular to the surface and the relaxation of the surface can be overcome using the scattering theoretical method, the so-called resolvent Green's function method [12]. In this method, the relaxation of the surface is treated as a two-dimensionally periodic perturbation of an ideal three-dimensionally periodic system. The Green's function contains the full electronic information of the semi-infinite surface system in the framework of tight-binding method. The relaxation of the surface will also be taken into account and the optimal structures of the surface have been determined by minimizing the total energy based on the Chadi's total energy model. It is carried out by calculating Hellmann-Feynman forces on all relaxed atoms and by relaxing atoms until the forces are small than 10^{-3}eV/Å (for more

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detail please see references [6,7]).

3. RESULTS

Due to the 4.2% lattice mismatch between Si and Ge, it is energetically favorable for Ge epitaxially growing on Si(001) surface to form unstrained islands after only three monolayer coverage. Tromp and co-workers have adopted arsenic as a surfactant, until 8~10 ML Ge layer-by-layer growth on Si(001) surface has been observed [3–5]. The As atoms adsorbed on Si(001) will break the Si-Si dimers and saturated dangling bonds and change the reconstruction of the clean surface from 1×2 to 2×1, or from 2×1 to 1×2. The exchange of 1×2 to 2×1 can be seen from the top view given in Fig. 1. The case of As on Ge(001) is similar. Therefore, the system of Ge deposited on an arsenic terminated Si(001) surface is treated with a 2×1 symmetry.

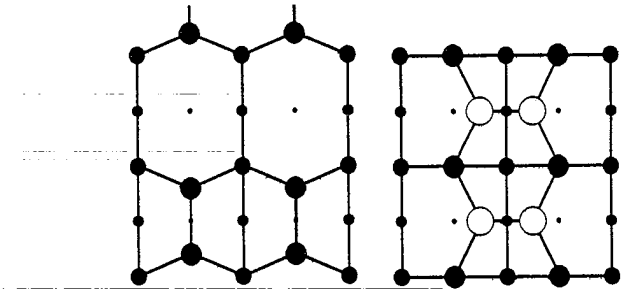

FIG. 1. Top view of As:Ge_n/Si(001) model. Shaded atoms represent Ge or Si atoms. Atoms in the top four layers are indicated by circles of decreasing sizes. (a) 1×2 model without As; (b) 2×1 model with As.

In the present calculations the 2×1 reconstruction is considered, in which all As atoms, Ge atoms and atoms in top two Si layers are relaxed. The optimal structures of these systems have been obtained by calculating the Hellmann-Feynman force acting on each relaxed atom. For all considered systems the optimal results using different initial geometry all lead to the same configuration with As atoms forming symmetric dimers. Each surface As atom is thus threefold coordinated and bonded to two atoms in the subsurface layer which is fourfold coordinated (Fig. 1 (b)).

Table I lists the obtained results for As:Ge_n on Si(001) semi-infinite surface with n varying from 0 to 9. For As/Si(001) 2×1, the As-As dimer bond length is found to be 2.52Å which is in good agreement with results of *ab initio* calculations 2.52Å by Krüger and Pollmann [13] and 2.55Å by Uhrberg *et al* [14]. The subsurface atoms move towards each other and the backward bond length between As and the subsurface Si is found to be 2.39Å which is close to the value 2.42Å by Krüger and Pollmann [13] and 2.44Å by Uhrberg [14]. For As:Ge_n/Si(001) with n ranging from 1 to 9, our results show that As-As dimer bond length is 2.51~2.50Å and approaches a constant value at about two monolayers of Ge deposition. The atomic displacement of the second layer in the direction parallel to the surface is found to be 0.15~0.16Å and the backward bond length of As-Ge tends to a constant, 2.36Å, with n varying from 1 to 9. Table II gives structural parameters obtained for As:Ge_9 on Si(001) 2×1 surface. The optimal structures show that there exist parallel displacements 0.03Å in the sixth layer below the surface. It might be explained by the long range extension of surface strain during the dimer formation. The relaxation of the Ge/Si interface is found to be very small and the distance between the Ge and Si interface layer is about 1.40Å (see Table I).

The surface structure of As:Ge_n/Si(001) 2×1 is found to be very similar to that of As/Si(001) 2×1, except in the expansion of Ge heterolayers in the direction perpendicular to the surface. The Ge layers growing on Si surface will be compressed parallel to the surface to match the Si lattice constant. In order to relieve the strain, the Ge layers will expand in the perpendicular direction. The distance of the expanded Ge layer determined by the method of minimizing the elastic energy given in the article [15] is 1.455Å. In the present work by calculating the Hellmann-Feynman forces on each Ge atoms, the distance of Ge layers for variours n have been obtained and listed in Table I. The average distance of Ge layers changes between 1.45~1.47Å for different thickness of Ge layer. It is in agreement with that obtained by minimization of elastic energy [15].

The change in electronic structures during the growth is shown in fig. 2. The figure shows the density of states of the surface layer for As:Ge_n/Si(001) 2×1 surface with n=0 to 9 at the Γ-point. The state labeled by A consists mainly of the p_z orbital and a part of s orbital of arsenic,

TABLE I. Structural parameters for As:Ge$_n$ on Si(001) 2×1 semi-infinite surface, in Å. Δx and Δz represent the atomic displacements from the corresponding position of ideal bulk Si, the index 1 and 2 indicates the first and second layer, respectively. As-As is the dimer bond length, As-Si and As-Ge the corresponding backbond length, respectively. $d_{n,m}$(Ge) is the distance between the n-th and m-th Ge layer, $\bar{d}$(Ge) the average distance between Ge layers and d(Ge-Si) the distance of Ge and Si interface layer.

n	0	1	2	3	4	5	6	7	8	9
Δx_1	0.65	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67
Δz_1	0.01	0.10	0.22	0.33	0.45	0.58	0.70	0.79	0.90	1.02
$\Delta x_1'$	-0.65	-0.67	-0.67	-0.67	-0.67	-0.67	-0.67	-0.67	-0.67	-0.67
$\Delta z_1'$	0.01	0.10	0.22	0.33	0.45	0.58	0.70	0.79	0.90	1.02
Δx_2	0.13	0.15	0.15	0.15	0.16	0.16	0.16	0.16	0.16	0.16
Δz_2	-0.02	0.02	0.13	0.25	0.37	0.49	0.61	0.71	0.82	0.93
$\Delta x_2'$	-0.13	-0.15	-0.15	-0.15	-0.16	-0.16	-0.16	-0.16	-0.16	-0.16
$\Delta z_2'$	-0.02	0.02	0.13	0.25	0.37	0.49	0.61	0.71	0.82	0.93
As-As	2.52	2.51	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
As-Ge		2.36	2.36	2.36	2.36	2.36	2.36	2.36	2.36	2.36
As-Si	2.39									
$d_{2,3}$(Ge)			1.45	1.45	1.45	1.45	1.45	1.45	1.45	1.45
$d_{3,4}$(Ge)				1.48	1.48	1.48	1.48	1.48	1.48	1.48
$d_{4,5}$(Ge)					1.47	1.48	1.47	1.47	1.47	1.47
$d_{5,6}$(Ge)						1.47	1.48	1.48	1.48	1.48
$d_{6,7}$(Ge)							1.47	1.47	1.47	1.47
$d_{7,8}$(Ge)								1.47	1.48	1.48
$d_{8,9}$(Ge)									1.47	1.47
$d_{9,10}$(Ge)										1.47
$\bar{d}$(Ge)			1.45	1.46	1.47	1.47	1.47	1.47	1.47	1.47
d(Ge-Si)		1.38	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40

of the p_z orbital and a part of s orbital of arsenic, corresponding to the occupied dangling bond state. The state labeled by B is mainly from the p_z orbital of arsenic and p_z orbital of the subsurface atoms, corresponding to the As backward bond state to the underlying atoms. The C state in fig.1 denotes the dimer bond state originating from p_y orbitals of As atoms. For the dimer of the clean Si or Ge(001) 2×1 surface there is an occupied and an unoccupied dangling bond. It is energetically favorable to saturate the dangling bond of the surface. Since As has one more valence electron than that of Si and Ge, the dangling bond of the dimerized As will be filled. It is shown that the state induced by As remains almost unshifted during the Ge deposition. For systems with 1 to 9 monolayers of Ge deposited on the As terminated Si(001) surface, the surface state, the backward bond state and the dimer bond state remain almost unchanged. This similarity of electronic structures of the surface state can be explained in terms of the passivation of the surface by the arsenic monolayer.

I. CONCLUSIONS

The As:Ge$_n$/Si(001) 2×1 semi-infinite surface has been studied by the self-consistent semi-empirical tight-binding method combined with the local charge neutrality condition and the Chadi's

TABLE II. Structural parameters for As:Ge_9 on Si(001) 2×1 semi-infinite surface, in Å. Δx and Δz represent the atomic displacements to corresponding the position of ideal Si.

Layer	Δx	Δz	$\Delta x'$	$\Delta z'$
1	0.67	1.02	-0.67	1.02
2	0.16	0.93	-0.16	0.93
3	0.00	0.69	0.00	0.99
4	0.00	0.60	0.00	0.83
5	-0.06	0.60	0.06	0.60
6	-0.03	0.48	0.03	0.48
7	0.00	0.34	0.00	0.40
8	0.00	0.23	0.00	0.27
9	0.01	0.13	-0.01	0.13
10	0.00	0.02	-0.00	0.02
11	0.00	-0.01	0.00	-0.02
12	0.00	0.00	0.00	-0.01

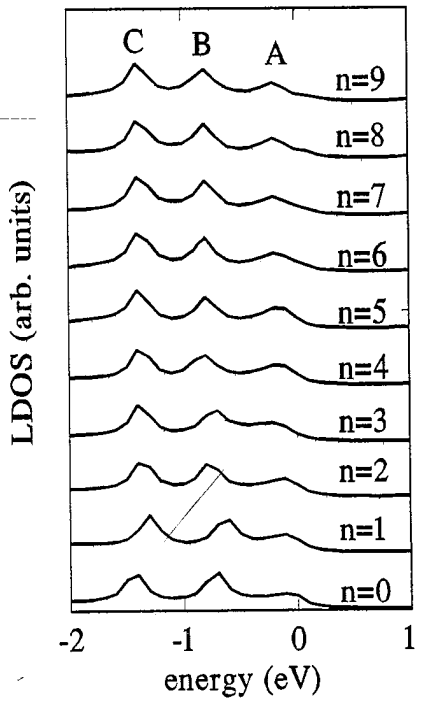

FIG. 2. Surface layer density of states of As:Ge_n/Si(001) 2×1 with $n = 0$ to 9 and clean Si(001) 2×1 surface. The state labeled by A corresponds to the dangling bond surface state, B to the backbond state and C to the dimer bond state.

total energy model. For the As:Ge_n/Si(001) 2×1 surface with n=1 to 9 our calculations show that the geometry of the top two surface layers remains almost unchanged and is similar to that of As/Si(001) 2×1 surface. It is found that for all cases As atoms at the surface form the symmetric dimer and the atomic displacement of the subsurface in the direction parallel to the surface induced by the dimer formation is large and not negligible. The reason is that the subsurface atoms move towards dimerized As to search for a bulklike atomic environment. The relaxation of the Ge/Si interface is very small. The average distance of deposited Ge layers determined by Hellmann-Feynman forces is about 1.47Å. The electronic structures of As:Ge_n/Si(001) 2×1 surface with n=1 to 9 are all similar, which means that a stable surface can be formed by having an arsenic layer on the surface.

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