Atomic Structures of a Monolayer of AlAs, GaAs, and InAs on Si(111)

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We study atomic structures of a monolayer of AlAs, GaAs, and InAs on a Si(111) substrate from first-principles. The surface with the stacking sequence of ...SiSiMAsSiAs is energetically more stable than the surface with the stacking sequence of ...SiSiSiAsMAs, where M is Al, Ga, or In. The atomic structure of the three top layers of the low-energy surfaces are quite robust, irrespective of M, and the atomic structure of the AlAsSiAs terminated surface and that of the GaAsSiAs terminated surface are very similar. For the high-energy AsMAs terminated surfaces, the broken local tetrahedral symmetry plays an important role in the atomic structures. The calculated atomic structures of InAs on the Si(111) substrate depart most from the structure of crystalline Si.

I. INTRODUCTION

Semiconductors such as AlAs, GaAs, and InAs on Si substrates have long been the subject of semiconductor research because of the high mobility of electrons, the possibility of band gap engineering, and new device applications resulting from superlattice modulations. Recently, various semiconductor quantum dot structures have been formed on Si substrates [1]. The quantum dot properties are strongly influenced by the strain arising from the lattice mismatch, and GaAs [2] and InAs [3–5] quantum dot structures have been fabricated on Si(100) substrates by using molecular beam epitaxy (MBE) and metalorganic vapor phase epitaxy (MOVPE). On Si(111) substrates, InAs nanowires [6–8], InAs quantum dots [3, 4], and InGaAs qunatum dots [9] have been grown. Actually, Si(100) and Si(111) substrates are technologically important because a single-crystalline Si ingot can be easily cut in its crystallographic directions. However, the physical properties of the substrates are dramatically different because dangling bonds are very different, and they can be utilized to achieve desired device properties, such as a nanometer scale pattern on a vicinal Si(111) surface [10]. To understand the physical properties and the microscopic growth mechanisms, it is desirable to know the atomic structures of such systems. To obtain information on the atomic structures, an X-ray standing wave (XSW) technique has been employed [11], and first-principles studies have been carried out.

For example, GaAs [12–17] or As [18–20] incorporated on the top layers of a Si substrate have been analyzed theoretically. In particular, the first monolayer of GaAs on a Si(111) substrate has been studied by using the XSW technique [21,22] and from first-principles [12,13]. Such studies are very helpful in understanding the physical properties of important surfaces microscopically and in utilizing III-V semiconductors for controlling and manipulating the Si(111) surface. However, first-principles studies on AlAs or InAs on a Si(111) substrate have been absent as far as the authors know. In this research, we investigated the atomic structural properties of MAs (M = Al, Ga, and In) monolayers on a Si(111) substrate from first-principles. Our calculations enable us to understand heteroepitaxial growth of various III-V semiconductors on Si(111) substrates in perspective, whereas previous works are mainly focused on GaAs heteroepitaxial growth. For simplicity, we only analyze (1 × 1) surfaces and the detailed geometry. By analyzing the bond lengths of a few top layers of the surfaces, we obtain important microscopic information relevant to understanding the physical properties of the surfaces for different stacking sequences, the AsMAs termination and the MAsSiAs termination in Figs. 1(a) - (b). We determine the more stable stacking sequence between the two stacking sequences considered in this paper and find that the size of an M atom influences the corresponding surface atomic structures strongly.

II. CALCULATION

We calculate the total energies and the atomic structures of both the AsMAs and the MAsSiAs terminated surfaces. The structures are studied in a centrosymmet-
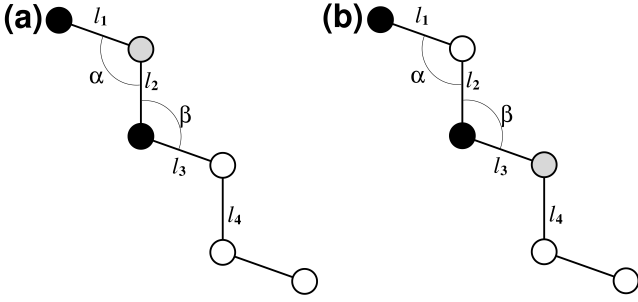
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Fig. 1. (a) Atom positions in the (111) plane for the As-MAs terminated surface and (b) the MAsSiAs terminated surface. Six atoms from the top layer are shown in the figure. The centrosymmetric surface supercell contains six Si atoms, four As atoms, and two M atoms, and only half of twelve atoms are shown. The black and the white circles represent As and Si atoms, respectively. The gray circles represent M atoms, where M is Al, Ga, or In. l_1, l_2, l_3, and l_4 are bond lengths among surface atoms, and α and β are bond angles among surface atoms.

ric surface supercell containing six Si atoms, four As atoms, and two M atoms. The thickness of the vacuum region is approximately 10 Å. The calculations are performed using the *ab-initio* total-energy and molecular-dynamics program VASP (Vienna *ab-initio* simulation program) developed at the Institute für Materialphysic of the Universitat Wien, by using the projector-augmented-wave (PAW) approach [23]. We adopt the generalized gradient approximation (GGA) implemented by Perdew, Burke, and Ernzerhof (PBE) [24] for the exchange-correlation energy functional. We employ a plane-wave basis set with a cutoff energy of 300 eV. For the surface supercell, the Brillouin zone is sampled on a regular mesh of (15×15) **k**-points. In the irreducible part of the Brillouin zone, there are 27 **k**-points. We determine the lattice constant of the surface supercell from the lattice constant of the crystalline Si. The surfaces are relaxed until the maximum of the remaining forces on atoms is less than 0.015 eV/Å. To determine the lateral dimension of the surface supercell and to check the computational accuracy, we calculate the lattice constants of bulk crystalline Si, AlAs, GaAs, and InAs (5.47 Å, 5.73 Å, 5.75 Å, and 6.19 Å, respectively), which agree with the experimental data in the literature [25] to within 3%. We also calculate the cohesive energies of the same materials (4.55 eV, 3.69 eV, 3.16 eV, and 2.89 eV, respectively), which agree with the experimental data in the literature [26] to within 7%.

III. RESULTS AND DISCUSSION

Figures 1(a) - (b) show the atom positions in the (111) plane for two different stacking sequences. We confirm that a surface with the MAsSiAs termination has considerably lower total energy than a surface with the As-

Table 1. Comparison of the experimental positions of surface atoms with the theoretically calculated positions for two different stacking sequences. See Fig. 1 and the text for an explanation of the stacking sequences. The angstrom unit is used for the positions of atoms relative to crystalline Si(111) planes.

Atom	XSW[a] (M = Ga)	Theory[b] (M = Ga)	present (M = Ga)	present (M = Al)	present (M = In)
AsMAs termination
As	0.36	0.26	0.63	0.50	1.14
M	0.08	0.41	0.56	0.48	0.63
As	-0.02	0.11	0.20	0.20	0.16
Si		-0.08	-0.04	-0.03	-0.04
Si		-0.03	-0.02	-0.02	-0.02
Si		0.0	0.0	0.0	0.01
MAsSiAs termination
As	0.36	0.27	0.49	0.53	0.92
Si		0.07	0.24	0.28	0.67
As	-0.02	0.10	0.24	0.28	0.70
M	0.08	-0.01	0.06	0.10	0.23
Si		-0.02	0.0	0.0	-0.01
Si		0.0	0.0	0.0	0.0

[a]The experimental values are based on the X-ray standing-wave technique in Refs. 21 and 22.
[b]The calculated positions are from Ref. 12.

MAs termination, consistent with the GaAs results of Northrup [12]. On the low-energy surfaces, the top layers are M-As-Si-As, where atoms represented by M reside in the fourth layer from the top and Si atoms occupy positions in the second layer.

In Table 1, the calculated positions of the atoms are relative to those which Si atoms would have in an unrelaxed surface, as measured in the XSW techuique. The experimental data and the theoretical calculations in the literature for the top layers of GaAs on a Si(111) substrate are tabulated. Our calculations from first-principles for top four layers of MAs (M = Al, Ga, and In) on a Si(111) substrate for two different stacking sequences are also tabulated.

For the case of GaAs, the total energy of the surface with the GaAsSiAs termination is lower by about 0.49 eV/(surface atom) than that of the surface with the AsGaAs termination. The corresponding value is 0.57 eV/(surface atom) in Northrup's report [12]. For the case of InAs, the total energy of the surface with the InAsSiAs termination is lower by about 0.32 eV/(surface atom) than that of the surface with the AsInAs termination. Similarly, the total energy of the AlAsSiAs terminated surface is lower by about 0.41 eV/(surface atom) than that of the AsAlAs terminated surface. It is noteworthy that the covalent atomic radii are about 1.25 Å for both a Ga atom and an Al atom, but that the total energy differences between the stacking sequences are distinct.

Table 2. Calculated bond lengths and bond angles at the surfaces for two different stacking sequences. See Fig. 1 and the caption for Fig. 1 for the explanation of l_1, l_2, l_3, l_4, α, and β.

	M = Ga	M = Al	M = In
AsMAs termination			
l_1	2.39	2.38	2.58
l_2	2.73	2.65	2.84
l_3	2.46	2.46	2.44
l_4	2.35	2.35	2.35
α	111.11	109.93	120.23
β	114.70	114.61	113.92
MAsSiAs termination			
l_1	2.47	2.47	2.46
l_2	2.36	2.36	2.33
l_3	2.44	2.44	2.57
l_4	2.43	2.46	2.60
α	115.08	115.08	115.05
β	113.56	113.60	119.51

On the other hand, the covalent atomic radius of an In atom is about 1.50 Å, which is much larger than that of a Si atom, 1.17 Å. Therefore, the atomic structures of the surface with the AsInAs termination and that with the InAsSiAs termination are expected to be very different from that of a pure Si(111) surface. Indeed, the calculated position of an As atom at the top layer is 1.14 Å for the AsInAs terminated surface and 0.92 Å for the InAsSiAs terminated surface. The corresponding values for other surfaces lie between 0.49 Å and 0.63 Å in our calculations. This means that an In atom pushes out its nearest neighbor atoms much more than other atoms to accommodate larger covalent bonds between the In atom and its nearest neighbor atoms.

To investigate the atomic arrangement more closely, we tabulate in Table 2 the bond lengths and the bond angles for surface atoms at the four top layers. From the calculated lattice constants, we determine ideal bond lengths of 2.48 Å, 2.49 Å, and 2.68 Å for crystalline AlAs, GaAs, and InAs, respectively. For the MAsSiAs terminated surfaces, l_1, l_2, and α do not vary much. That is, the three top AsSiAs layers are quite robust, irrespective of M. However, depending on M, l_3, l_4, and β vary significantly to accommodate covalent bonds of different sizes. Indeed, the calculated atomic structures of the GaAsSiAs terminated surface and the AlAsSiAs terminated surface are strikingly similar, which is consistent with the similar covalent atomic radii being about 1.25 Å. For the AsMAs terminated surfaces, l_3, l_4, and β do not vary much. That is, depending on M, the three top AsMAs layers determine the surface atomic structures. Compared to the MAsSiAs terminated surfaces, the overall M dependences of bond lengths and bond angles are larger for the AsMAs terminated surfaces. It

is interesting that there is noticeable difference in the atomic structures of the AsGaAs terminated surface and the AsAlAs terminated surface. An M atom in the As-MAs termination does not have a tetrahedral symmetry because an As atom at the top layer has a dangling bond. Therefore, the difference in l_1 and l_2 and deviation of α from the tetrahedral angle reflect the broken local tetrahedral symmetry about the M atom. The symmetry is broken most for the AsInAs terminated surface and least for the AsAlAs terminated surface.

So far, we have only addressed (1×1) surfaces, while larger surface supercells such as (2×2) surfaces are more realistic. There are two points on the larger surface supercells to be addressed. One is the possibility of reconstruction. The As-terminated Si(111) surface is known to be very close to the ideal (1×1) surface due to the higher valency of the As atoms [19, 20, 27, 28]. Similarly, our calculated surfaces are not likely to be stabilized by dangling-bond reduction, and the surfaces are likely to be close to the ideal (1×1) surfaces in typical growth conditions. The other is the possibility of a lower energy structure due to mixtures of the calculated surfaces being formed. Indeed, (2×2) surface calculations for mixtures of the GaAsSiAs and the SiAsGaAs terminated surfaces confirm that the (1×1) GaAsSiAs terminated surface has almost the minimum total energy and that the atomic structure is quite similar to that of the minimum total energy surface among the mixtures [12]. We expect a similar trend for mixtures with different M atoms, and we believe that our analyses of the energetics and the atomic structures are intact.

In summary, we have studied the atomic structures of a monolayer of AlAs, GaAs, and InAs on a Si(111) substrate from first-principles. The surface with the MAsSiAs termination is energetically more stable than the counterpart surface with the AsMAs termination. The atomic structure of the three top layers of the low-energy surfaces are quite robust, irrespective of M, and the atomic structure of the AlAsSiAs terminated surface and that of the GaAsSiAs terminated surface are very similar. For the high-energy AsMAs terminated surfaces, the local tetrahedral symmetry is broken most for the AsInAs terminated surface and least for the AsAlAs terminated surface. In any case, the large covalent radius of an In atom is consistent with the calculated atomic structures with a large change from the atomic positions of the bulk crystalline Si.

IV. CONCLUSIONS

We clarify the energetics and the atomic structures of a monolayer of AlAs, GaAs, and InAs on a Si(111) substrate by analyzing the total energies and the atomic geometries of the surfaces. We believe that our findings will be useful in understanding III-V semiconductors on Si(111) substrates and shed light on ways to

improve the physical properties of semiconductor heterostructures and quantum dots made of III-V semiconductors on Si(111) substrates.

ACKNOWLEDGMENTS

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