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Theoretical investigation on temperature and pressure dependence of structural stability of InP thin layers grown on InP(111)A surface

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ABSTRACT

The growth processes of InP epitaxial layers on InP(111)A P-stabilized surface are theoretically investigated by using our first-principles-based approach which incorporates the growth conditions such as temperature and pressure. Our calculations for adsorption of In and P atoms reveal that the wurtzite structure is feasible at high temperatures with low V/III ratio conditions. On the other hand, at low temperatures with high V/III ratio conditions, the adsorption of P atoms occurs on the surface with In coverage of 0.25, leading to the formation of rotational twins. These results thus imply that the adsorption of P atoms depending on growth conditions plays a role in determining the crystal structure of epitaxial layers on InP(111)A substrates.

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1. Introduction

InP based semiconductors have been intriguing targets in sources and detectors in fiber optic communications and high-speed electronic applications, such as p–n junction light-emitting diodes [1] and one-dimensional polarization-sensitive photodetectors [2]. In particular, modern one-dimensional nanostructures have attracted much attention recently. Representative ones are InP nanowires (NWs) which are grown by various methods such as metal–organic vapor phase epitaxy (MOVPE) [3,4], molecular beam epitaxy [5,6], and laser-assisted catalytic growth [7,8].

InP NWs are generally grown along the [111] direction on InP(111) substrates. However there are several characteristics which have been unsolved at present. One of them is that the plane direction of substrates depends on experimental methods. InP NWs fabricated by selective-area MOVPE (SA-MOVPE) are grown on the InP(111)A substrates [9,10]. On the other hand, InP(111)B substrates are used for InP NWs synthesized by vapor–liquid–solid (VLS) growth [11,12]. Another important issue is the structural stability of InP NWs. The structural stability of InP NWs has been intensively discussed owing to small energy difference between the wurtzite (WZ) and zinc blende (ZB) structures in bulk form [13]. Bhunia et al. have reported that InP NWs fabricated by the VLS growth mechanism have rotational twinning structure which is a mixture of the WZ and ZB layers [11]. Mohan et al. have reported that InP NWs with the pure WZ structure are synthesized by the SA-MOVPE [9]. Kitauchi et al. have recently revealed that the crystal structure of InP NWs grown by the SA-MOVPE depends on growth conditions such as temperature and partial pressure of the supply gas [10]. InP NWs grown for high temperature and low P pressure take the pure WZ structure, whereas those with rotational twins are fabricated for low temperature and high P pressure. Furthermore, these results suggest the formation of the WZ crystal phase even in (111)A planar layers. This fact implies that the growth process of InP layers on InP(111)A surface in itself affects the crystal structure of InP NWs. Despite these experimental findings, temperature and pressure dependence of structural stability of InP layers on InP(111)A surface still remains unclear.

From theoretical viewpoints, we have clarified the relative stability between the WZ and ZB structures in InP NWs. The WZ structure can be stabilized when the contribution of NW side facets to the cohesive energy is prominent, that is, the WZ structure is more stable than the ZB structure for NWs with small diameters [14–16]. However, the structural stability of InP NWs depending on the growth conditions in the SA-MOVPE cannot be explained by only the contribution of NW side facets. In the SA-MOVPE, it is considered that the growth mechanism of InP layers on the surface as well as side facets is quite important for determining their crystal structure. Although Glas et al. have theoretically suggested that the growth processes affect the formation of the WZ structure in NWs [17], little is known about the elemental growth processes of InP layers on InP(111) surface: Knowledge for adsorption and desorption behavior of In and P atoms on InP(111) surfaces is lacking.

In this study, we focus on InP(111)A surface and investigate the growth processes of InP epitaxial layers on InP(111)A P-stabilized surface. In particular, adsorption–desorption behavior on InP(111)A surface is calculated by our first-principles-based approach which incorporates the growth conditions such as temperature and pressure. We demonstrate temperature and pressure dependence of structural stability of InP layers, leading to the formation of rotational twins at low temperature and high V/III ratio conditions.

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2. Computational methods

2.1. First-principles calculation

The total-energy calculations are performed within the generalized gradient approximation (GGA) [18] in the density-functional theory. We use norm-conserving pseudopotentials [19] with partial core correction [20]. The conjugate-gradient minimization technique is used for both the electron-structure calculation and the geometry optimization [21,22]. In the optimized geometries the remaining forces acting on the atoms are less than 3.8×10^{-3} Ry/Å. The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 20.25 Ry, which gives enough convergence of total energy to discuss the relative stability. We take slab models consisting of seven atomic layers with pseudohydrogen atoms [23] and a 10 Å vacuum region. The atoms belonging to bottom bilayer are fixed at their ideal positions. The k points corresponding to 20 points in the irreducible part of the (1×1) surface Brillouin zone are used.

2.2. Phase diagram

Phase diagrams are obtained by considering the adsorption–desorption behavior of In and P atoms, which can be described by comparing the free energy of ideal gas per particle (chemical potential) μ_{gas} to the adsorption energy per atom E_{ad}. The chemical potential of a molecule is expressed as [24,25]

$$\mu_{\text{gas}} = -k_{\text{B}}T\ln\left(\frac{k_{\text{B}}T}{p}\times g\times\zeta_{\text{trans}}\times\zeta_{\text{rot}}\times\zeta_{\text{vib}}\right), \quad (1)$$

where k_{B} is Boltzmann's constant, T is the gas temperature, g is the degree of degeneracy of the electron energy level, and p is the pressure. ζ_{trans}, ζ_{rot}, and ζ_{vib} are the partition functions for translational, rotational, and vibrational motions, respectively. Details of these partition functions are expressed elsewhere [24,25]. We assume In and P as an In atom and a P_2 molecule in gas phase, respectively.

In order to calculate adsorption sites, sample sites of 6×6 mesh are employed for a (2×2) cell. E_{ad} at sample sites is calculated using total-energy electronic-structure calculations within the density-functional theory. Adsorption sites are made a guess from the E_{ad} at sample sites, and then they are found by the calculations with relaxation.

The relative stability between two structures is determined by comparing μ_{gas} to E_{ad}. That is, the structure corresponding to the adsorbed surface is favorable when E_{ad} is less than μ_{gas}, whereas the desorbed surface is stabilized when μ_{gas} is less than E_{ad}.

2.3. Monte Carlo simulation

Stochastic Monte Carlo simulations [26] are performed, complying with following probabilities:

$$P_{\text{ad}}(x) = \frac{\exp[-\Delta\mu(x)/k_{\text{B}}T]}{1+\exp[-\Delta\mu(x)/k_{\text{B}}T]}, \quad (2)$$

$$P_{\text{diff}}(x\rightarrow x') = R\exp[\Delta E(x\rightarrow x')/k_{\text{B}}T], \quad (3)$$

$$P_{\text{de}}(x) = R\exp\{-[E_{\text{de}}(x)-\Delta\mu(x)]/k_{\text{B}}T\}. \quad (4)$$

These probabilities are applied to both atomic species separately. $P_{\text{ad}}(x)$ is the site-correlated adsorption probability, assuming the local-thermal equilibrium approximation. $\Delta\mu(x)$ is the energy difference between $E_{\text{ad}}(x)$ and μ_{gas} at adsorption site x, i.e., $\Delta\mu(x)=E_{\text{ad}}(x)-\mu_{\text{gas}}$. $P_{\text{diff}}(x\rightarrow x')$ is the diffusion probability with the Arrhenius form. R is diffusion pre-factor taken to be $2k_{\text{B}}T/h$ [27], and $\Delta E(x\rightarrow x')$ is the local migration barrier involving the adatom hopping from site x to x'. $\Delta E(x\rightarrow x')$ corresponds to the energy difference between the adsorption energy at site x and that at the saddle point of adsorption energies on the path to site x'. $P_{\text{de}}(x)$ is the desorption probability for an adatom at site x, where $E_{\text{de}}(x)$ is desorption energy at site x ($E_{\text{de}}(x)=-E_{\text{ad}}(x)$). The probability for surmounting the activation energy of $E_{\text{de}}(x)$ ($=R\exp[-E_{\text{de}}(x)/k_{\text{B}}T]$) is reduced (or enhanced) by a weighting function of $\exp[\Delta\mu(x)/k_{\text{B}}T]$ which corresponds to the local-thermal equilibrium desorption probability. In the simulation procedure, we adopt an extensive surface as a growth substrate which is $30{,}000\times30{,}000$ times as large as the (2×2) unit cell. In atoms and P_2 molecules are supplied from gas phase to the surface at an interval of Δt_{gas} per area. Δt_{gas} is derived from Maxwell's law of velocity distribution, which is written by

$$\Delta t_{\text{gas}} = \sqrt{2\pi mk_{\text{B}}T/p}, \quad (5)$$

where m is the mass of an In atom or a P_2 molecule. Trials of adsorption judged from Eq. (2) are iterated during the simulation. Events for adatoms on the surface comply with the following equations:

$$K_{\text{diff}}(x\rightarrow x_i) = \frac{P_{\text{diff}}(x\rightarrow x_i)}{\sum_j P_{\text{diff}}\left(x\rightarrow x_j\right)+P_{\text{de}}(x)}, \quad (6)$$

$$K_{\text{de}}(x) = \frac{P_{\text{de}}(x)}{\sum_j P_{\text{diff}}\left(x\rightarrow x_j\right)+P_{\text{de}}(x)}, \quad (7)$$

$$\Delta t = \frac{1}{\sum_j P_{\text{diff}}\left(x\rightarrow x_j\right)+P_{\text{de}}(x)}. \quad (8)$$

$K_{\text{diff}}(x\rightarrow x_i)$ is the relative diffusion probability from site x to x_i and $K_{\text{de}}(x)$ is the relative desorption probability at site x. Events for adatoms occur at an interval of Δt.

3. Results and discussion

Fig. 1 shows schematics of the adsorption of In and P atoms with the WZ and ZB structures on ideal InP(111)A surface. While each lattice site of P atoms is located above that of topmost In atoms, there are two types of lattice sites for In atoms, each of which corresponding to *ABAB*⋯ (WZ) or *ABCABC*⋯ (ZB) stacking sequence. In this study, we apply these adsorption sites on the reconstructed InP(111)A surface. Fig. 2 shows the lattice sites of In atoms for the WZ and ZB structures on the (2×2) surface with P trimer [28]. Focusing on these adsorption sites, we discuss adsorption–desorption behavior of In and P atoms under growth conditions. On the basis of experimental results, we here consider two types of growth conditions: high temperature and low V/III ratio (660 °C and V/III = 18, condition (i) hereafter) and low temperature and high V/III ratio (600 °C and V/III = 55, condition (ii) hereafter) [10].

Fig. 3(a) and (b) shows contour plots of adsorption energies for In and P atoms, respectively. The values of contour plots are measured from the values of chemical potentials μ_{gas} under the growth condition (ii) which are -2.5 and -1.2 eV for In and P, respectively.

There are four adsorption sites for an In atom labeled 1, 2, 3, and 4 in Fig. 3(a). Three of them (sites 1, 2, and 3) are symmetrically equivalent and correspond to the adsorption sites for the ZB structure, and the other (site 4) corresponds to the adsorption site for the WZ structure. The adsorption energy difference among the adsorption sites for the WZ and ZB structure is negligible (0.06 eV). The positive values of adsorption energy (0.60 and 0.66 eV) indicate that the adsorption hardly occurs under typical growth conditions [9,10]. The calculated adsorption probability (see Eq. (2)) of an In atom under the growth condition (ii) is found to be less than 0.03%.

However, even if the adsorption probability is 0.03%, the adsorption occurs three times out of 10,000 times. Although it takes relatively long time until the adsorption, the small adsorption probability on the (2×2)-P trimer surface is particularly unproblematic. This is due to stabilization of the P trimer surface, i.e., the P trimer hardly desorbs under typical growth conditions. Our Monte Carlo (MC) simulations for

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