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Numerical calculation with empirical interatomic potential for formation mechanism of CuAu-I type ordered structure in InGaAs/(110)InP

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Abstract

In an InGaAs/(110)InP, a CuAu-I type ordered structure is formed during growth with a propagation of two-monolayer steps (2-MLSs). The numerical calculation with an empirical interatomic potential has suggested that the ordered InGaAs clusters are stabilized at kink edges of the 2-MLSs. We confirmed that In and Ga adatoms preferentially occupy the upper and lower sites at a kink of 2-MLS, respectively. This explains that the CuAu-I type ordered structure which is made of alternately stacked In- and Ga-rich (110) planes is formed by propagation of the 2-MLS with kinks. Our Monte Carlo simulation using the ordering model showed that the ordered structure is actually formed at the growth temperature (~ 700 K).

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Keywords: Empirical interatomic potential calculation; CuAu-I type ordered structure; Ordering mechanism; Migration potential; Semiconductor alloy

1. Introduction

InGaAs and InP have a zinc-blende structure composed of two *fcc* sublattices: One *fcc* sublattice is occupied by group-III atoms and the other by group-V atoms. It is known that a CuAu-I type ordered structure is formed in an InGaAs epilayer grown on a vicinal (110)InP substrate in spite that there is no stable region of an ordered phase in the equilibrium phase diagram for bulk. The ordered structure has a double periodicity along [001] and [110] directions by alternately preferential-occupancies of In and Ga atoms as shown in Fig. 1. Since the existence of ordered structure enhances the electron

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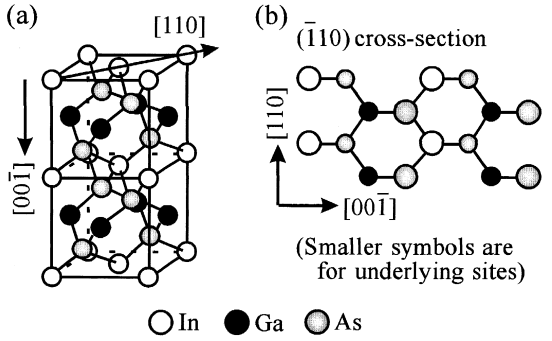


Fig. 1. CuAu-I type ordered structure in an InGaAs alloy: (a) schematic drawing of three dimensions, (b) ($\bar{1}$10) cross-section.

mobility [1], understanding of the ordering mechanism is important for device designing.

Ueda et al. [2] found that the two-monolayer steps (2-MLSs) on the growth surface play an important role in the ordering process of CuAu-I. Alternately stacked In- and Ga-rich (110) planes are formed by propagation of the 2-MLSs, if In and Ga atoms are preferentially adsorbed at different stair-levels of the 2-MLS edge, respectively. In order to clarify the formation mechanism of the ordered structure, we studied the migration potentials for adatoms and the stable atomic arrangement in the adatom-cluster on the substrate surface with a 2-MLS by numerical calculation with an empirical interatomic potential [3,4]. Monte Carlo simulation by using the energy parameters estimated from the empirical interatomic potential was also carried out to examine the possibility of ordering at the practical growth temperature ($\sim$ 700 K).

2. Methods

Numerical calculations with an empirical interatomic potential were carried out for the system of vicinal (110)InP substrate. For comparison with experimental results, we take the following assumptions: (a) A 2-MLS exists on the substrate surface, (b) Phospor (P) atoms on the substrate surface have been replaced completely with arsenic (As) atoms after thermal treatment under As atmosphere and the InP substrate is then covered with a monolayer of InAs.

In the system, each atom is susceptible to the force F_i and moves to its equilibrium position. F_i is given by:

$$F_i = \sum_j \frac{\partial V_{ij}}{\partial r_{ij}}, \tag{1}$$

where r_{ij} is the distance between the atoms and V_{ij} is the universal empirical interatomic potential [4], the absolute value of which is written:

$$V_{ij} = A\exp\left\{-\beta\left(r_{ij} - R_i\right)^{\gamma}\right\}\left\{\exp\left(-\theta r_{ij}\right) - \frac{B_0}{Z_i^o}\exp\left(-\lambda r_{ij}\right)G(\eta)\right\}. \tag{2}$$

Here, R_i is the minimum distance between neighbors. The potential parameters A, B_0, η, λ, α, β, γ and θ listed in Table 1 were determined from the cohesive energies, bulk moduli, shear stiffness and the relative stabilities among particular structures

Table 1
Potential parameters for InAs, GaAs, InP, GaGa, InIn, AsAs and GaIn

	InAs	GaAs	InP	GaGa	InIn	AsAs	GaIn
A [eV]	−709.0028	2477.8329	−338.1097	7005.5649	−722.2010	4634.8038	−811.52950
B_0	1.9778563	0.2494045	3.0151112	0.0044236	11.560933	0.0810363	6.522109
θ [Å^{-1}]	1.79440	2.77083	1.68907	3.83929	2.052298	3.16044	2.135383
λ [Å^{-1}]	2.35475	1.75326	2.70879	0.81707	3.399920	1.54759	3.264590
α	−0.3684513	0.46489	−0.7325367	0.6788446	−0.555713	0.6311375	−0.472887
β	12.02834	18.51165	11.94511	21.87022	14.20514	18.39756	16.349808
γ	3.20203	3.28387	3.16617	3.43356	3.335810	3.32921	3.320481
η	0.137927	0.755422	0.176048				

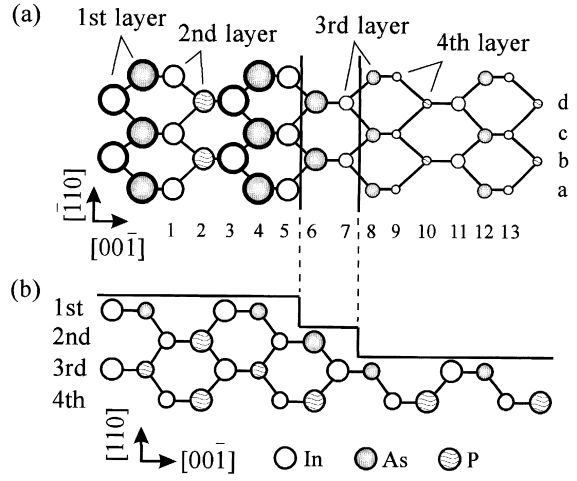


Fig. 2. Schematic drawing of the calculated system with a 2-MLS: (a) over-viewed, (b) side-viewed. P atoms on the top surface of (110)InP are completely replaced by As atoms to form InAs monolayer.

obtained by first-principle calculations and experiments [4,5]. The effective coordination number Z_i is given by:

$$Z_i = \sum_j \exp\left\{-\beta\left(r_{ij}-R_i\right)^{\gamma}\right\}. \quad (3)$$

The bond bending term $G(\eta)$ is written:

$$G(\eta) = 1 + \sum_{k(\neq i,j)} \left\{\cos\left(\eta\Delta\theta_{jik}\right) - 1\right\}, \quad (4)$$

$$\Delta\theta_{jik} = \theta_{jik} - \theta_i,$$

where θ_{jik} is the angle between bonds ij and ik, θ_i is the equilibrium angle between nearest-neighbor bonds for the regular structure (i.e., 109.47° for zinc-blende structure). The system energy E is given by [3]:

$$E = \sum_{ij} \frac{1}{2} V_{ij} + C|\Delta Z|. \quad (5)$$

Here, the first term in the right hand side indicates the cohesive energy estimated by universal empirical interatomic potential V_{ij}, and the second is the correction term due to the charge redistribution in the dangling bonds. This energy term is defined as a function of the number of electrons ΔZ remaining in the cation dangling bonds. The coefficient has values of $C = 0.40$ and 0.45 eV for Ga and In adatoms, respectively [3].

3. Results and discussion

3.1. Migration potentials for In and Ga adatoms

In this section, we report the results of calculation of migration potentials and discuss about the preferably adsorbed sites for In and Ga adatoms near the 2-MLSs. Fig. 2 illustrates the system with a 2-MLS under consideration. In the schematic drawing, symbols ‘‘a’’ to ‘‘d’’ and ‘‘1’’ to ‘‘13’’ denote the ordinates and the abscissas of atom sites in the system, respectively. Migration potentials were obtained by calculating the system energies E given by Eq. (5) when an adatom is attached to particular positions on the surface. Fig. 3(a) and (b) show the migration potentials for In and Ga adatoms calculated for the system, respectively, where we let the lowest system energy be zero. The present calcula-

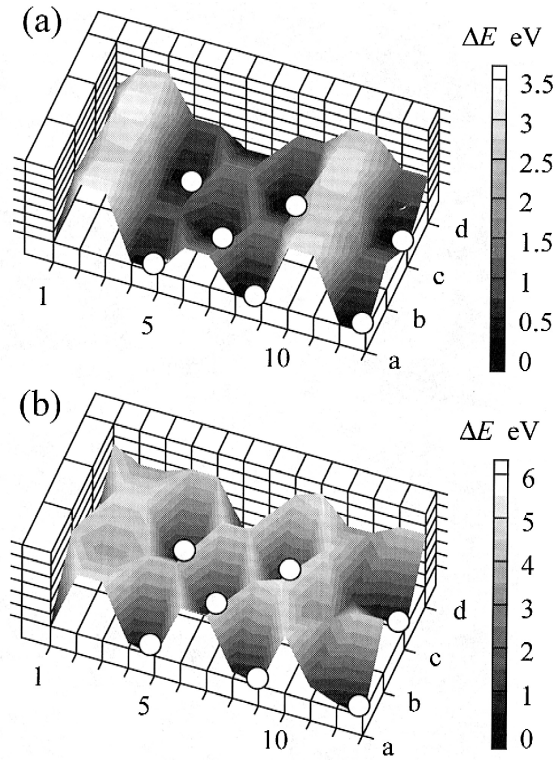


Fig. 3. Migration potentials: (a) for In, (b) for Ga. ΔE indicates a change of system energy due to the In or Ga migration. White circles denote the stable sites for In or Ga adatoms. Ordinates ‘‘a’’ to ‘‘d’’ and abscissas ‘‘1’’ to ‘‘13’’ are the same ones as in Fig. 2.

tion indicates that all the regular sites for group-III atoms on the step and terrace are stable ones for In and Ga adatoms. These migration potentials suggest that adatoms on the terrace are stable at their positions and do not migrate toward the step edge, though the actual crystal growth is promoted by a step-flow growth mode. Then, an additional factor to attract adatoms to the step must be invoked in order to account for the step-flow growth mode. We here assume the presence of kinks (Fig. 4) since in general an atomic step has kinks which usually provide preferable sites for adatoms. Fig. 5(a) and (b) show the migration potentials for In and Ga adatoms calculated for the system with a kink, respectively. In Fig. 5(a) and (b), the potentials have lower values at upper and lower kink sites denoted by white circles. The results indicate that during growth In and Ga adatoms migrate to the kink sites on the surface to be adsorbed, and that the crystal growth is then promoted by the step-flow growth mode. However, the present result still suggests that the potential at the site on the upper stair-level has almost the same value as that on the lowest stair-level. The first pair of In and Ga adatoms are not expected to have a tendency to occupy particular sites. This seems as if

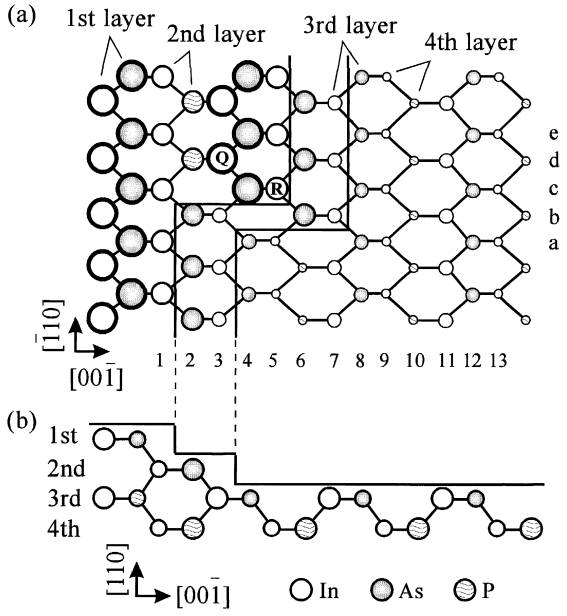


Fig. 4. Schematic drawing of the calculated system with a 2-MLS and a kink: (a) over-viewed, (b) side-viewed.

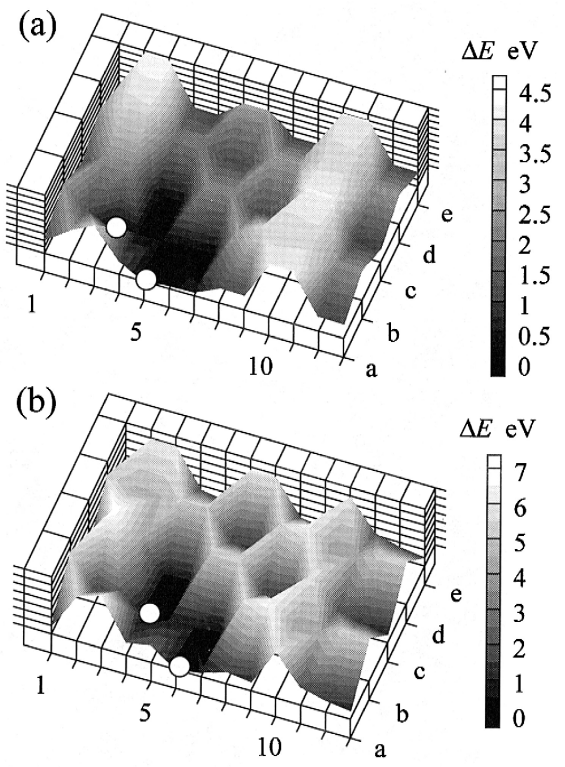
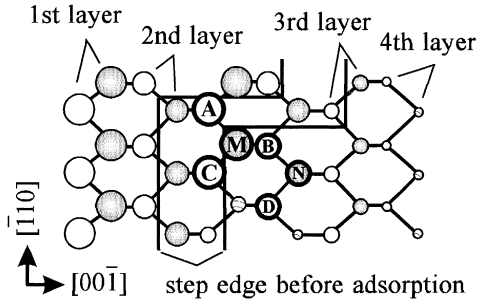


Fig. 5. Migration potentials: (a) for In, (b) for Ga. White circles denote the stable sites for In or Ga adatoms. Ordinates ''a'' to ''e'' and abscissas ''1'' to ''13'' are the same ones as in Fig. 4.

the present model could not explain the formation of the ordered structure. But, the second pair of In and Ga adatoms have different potential energy from the first one since the atom species at Q and R sites for the first pair of adatoms are different from those for the second one.

3.2. Stable atomic configuration of In and Ga atom-pair adsorbed at kink edge

We further examined the stable atomic configuration in In and Ga atom-pairs adsorbed at kink sites of 2-MLS. Fig. 6 illustrates the calculated system. Here, we have assumed that the atomic ratio of the group-III atoms adsorbed at the 2-MLS edge is always In:Ga = 1:1. The assumption is acceptable as a first approximation since our transmission electron microscopy (TEM) analysis did not indicate the presence of clustering region in the InGaAs/(110)InP. If



	A	B	C	D
Case 1	In	Ga	In	Ga
Case 2	In	Ga	Ga	In
Case 3	Ga	In	In	Ga
Case 4	Ga	In	Ga	In

Fig. 6. Schematic drawing of the calculated system with an InGaAs cluster adsorbed at a kink edge (over-viewed).

A–B sites were occupied by In–In (Ga–Ga) pair, C–D sites should be occupied by Ga–Ga (In–In) pair and thereafter like-atom pairs should come alternately in order to maintain the composition in each four-atom cluster. On the assumption above mentioned, a pair of In and Ga adatoms first occupy A and B sites. The configuration of the In and Ga atom-pair is frozen after As atoms cover the adatoms. Subsequently, another pair of In and Ga atoms occupy C and D sites. In the process, the In and Ga atom-pair can exchange their positions during growth before they are covered with As atoms. This is because the diffusion coefficient is large on the surface but very small within the bulk III–V semiconductor (e.g., the self-diffusion coefficient [6] of Ga in GaAs at 673 K is 7.63×10^{-31} cm^2/s). The calculated results show that the system energy of ''Case 1'' is smaller by 45 meV than that of ''Case 2''. The system energy of ''Case 3'' is smaller by 83 meV than that of ''Case 4''. These results indicate that In and Ga prefer C and D sites, respectively, irrespective of the atomic configuration at A and B sites: In and Ga adatoms preferably occupied the upper and lower stair-level sites of kink edge, respectively, and then In- and Ga-rich planes are alternately stacked along [110].

3.3. Monte Carlo simulation

A Monte Carlo simulation using the energy differences ΔE associated with the exchange of In and Ga atom-pair adsorbed at a kink sites on the growth surface was carried out in order to examine if the values ΔE are large enough to form actually the ordered structure in InGaAs at high temperature ($\sim$ 700 K). Fig. 7 shows a schematic drawing of the modeled growth surface with a 2-MLS and a kink. The simulation method is as follows: (1) In and Ga adatoms migrate to the kink sites and at first distribute randomly at A and B site in Fig. 7. (2) The atoms of In and Ga exchange their positions with a following probability [7]:

$$P(\Delta E, T) = \frac{1}{2}\left\{1 - \tanh\left(\frac{\Delta E}{2k_{\mathrm{B}}T}\right)\right\}, \qquad (6)$$

where k_{B} is Boltzmann's constant and T the growth temperature. The energy difference ΔE due to the exchange is estimated by the empirical interatomic potential calculation. Here, we assumed that the values of ΔE for A and B sites depend upon only the configuration at the first-nearest-neighboring *fcc* sublattice sites. These sites are denoted by cross-hatched circles in Fig. 7. Trials are repeated 50 times which seems large enough for the configuration of the atom-pair to reach almost the thermal equilibrium state. (3) Atoms of As are adsorbed at M and N

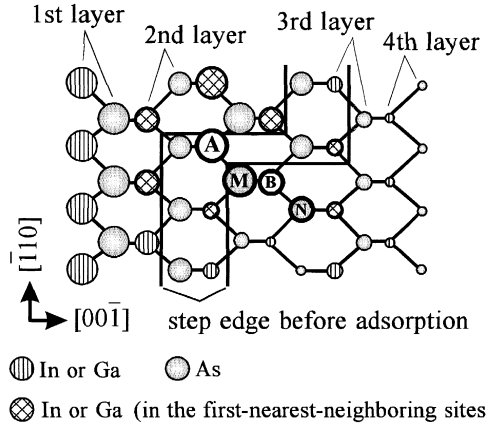


Fig. 7. Schematic drawing of the modeled growth surface with a 2-MLS and a kink (over-viewed).

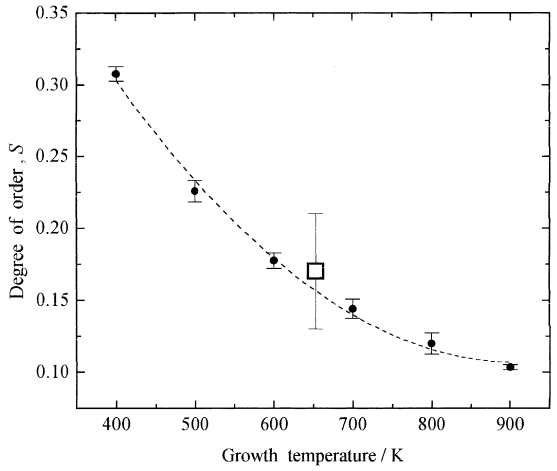


Fig. 8. Variation in the degree of order S with the growth temperature. Closed circles; calculated. Open square; experimental.

sites and the atom configuration of In and Ga at A and B sites is then fixed. The kink proceeds by one atomic step toward $[1\bar{1}0]$.

By repetition of the procedure, an epitaxial layer is grown with the propagation of a kink and a 2-MLS. In this study, the epitaxial layer has a size of $32 \times 32 \times 32$ unit cells with a periodic boundary condition along the directions parallel to (110). The degree of order S is given by:

$$S = \frac{\gamma_{\mathrm{In}} - x_{\mathrm{A}}}{1 - x_{\mathrm{A}}}, \tag{7}$$

where γ_{In} is the occupancy ratio of In atoms at the sites corresponding to the upper stair-levels of 2-MLSs and x_{A} the composition of In (0.5 in the present). Fig. 8 shows the degree of order S obtained as a function of growth temperature T. One can see that the degree of order S at 700 K has a non-vanishing value, that is, the ordered structure is formed at the growth temperature ($\sim$ 700 K). The calculated value of S for 653 K ($\sim$ 0.15) is comparable to the experimental value ($0.1 \sim 0.2$) estimated by TEM [8].

4. Conclusions

We studied the formation mechanism of a CuAu-I type ordered InGaAs grown on the vicinal (110)InP substrate with 2-MLSs. The calculation of the migration potentials for In and Ga on the substrate surface shows that In and Ga adatoms migrate toward the kink sites of 2-MLSs. At a kink edge, In and Ga adatoms tend to occupy the sites on the upper and lower stair-levels, respectively. The result indicates that In- and Ga-rich planes are formed alternately along [110] by propagation of 2-MLSs with kinks and a CuAu-I type ordered structure then appears. Our Monte Carlo simulation shows that the CuAu-I type ordered structure can be formed in the InGaAs at the growth temperature ($\sim$ 700 K).

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