Microstructure of CuAu-I-type ordered phase in III-V semiconductor alloys grown on a (001) substrate

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We have investigated via Monte Carlo simulations the microstructure of the CuAu-I ordered phase in III-V semiconductor alloys of $(A_{1-x}B_x)C$ grown on (001) substrates. The Fourier power spectra of atomic configurations in the computer-generated structures could reproduce the features of the electron-diffraction patterns reported previously. Among the three possible variants of the CuAu-I structure, a simulated (001) epilayer contains two variants which have their tetragonal c-axis parallel to the (001) plane. We have found that the CuAu-I ordering occurs even in an off-stoichiometric alloy with $x=0.25$, but a low-deposition rate at a low growth temperature forms a short-range-order state of a Cu_3Au type. [S0163-1829(96)04639-5]

I. INTRODUCTION

For the past decade, several ordered structures have been discovered in various III-V semiconductor alloys grown by epitaxial techniques.[1–4] The formation of the ordered structures has raised an interesting problem in terms of thermodynamics; the ordered phases do not appear in the equilibrium phase diagrams for these alloys in the bulk state.[5–7] Since the ordering affects the electronic properties, such as the band-gap energy and electron mobility,[8–10] understanding the ordering mechanism is important for device processing.

The CuAu-I ($L1_0$) structure, which has a double periodicity along one of the three ⟨100⟩ directions, is one of the major ordered structures reported in the III-V alloys. This structure is usually formed in the epitaxial layers grown on (110) (Refs. 1, 11–15) or (001) substrates.[1,11,16] Studies of the ordering in the (110) epilayers have been carried out by many investigators, and a large amount of data, such as the morphology of ordered domains, have been reported.[1,11–15] Ueda *et al.*[17] succeeded in the controlling of the modulation period along the [001] direction and have established a different trend of the design of artificial superlattices. On the contrary, the CuAu-I ordering in the (001) epilayers has been relatively little explored, and the details of its microstructures remain unclear.

Kuan *et al.*[11] have examined the CuAu-I ordered phase in $Al_{1-x}Ga_xAs$ alloys by means of electron diffraction. They have found that the CuAu-I superlattice reflections appear at $hkl=100$ and 010 positions, but not at $hkl=001$, meaning that only (100) and (010) variants whose c axes are perpendicular to the growth direction exist in the epilayers. For $GaAs_{0.25}Sb_{0.75}$ epilayers, Jen *et al.*[16] also observed a diffraction pattern similar to Kuan's and they speculated the existence of a different ordered phase. We expect a local formation of CuAu-I structure even in the off-stoichiometric alloys. Actually, the development of an ordered structure of a CuPt ($L1_1$) type, the stoichiometric composition of which is $x=0.5$, has been confirmed in epitaxial layers $(A_{1-x}B_x)C$ with $x\neq0.5$.[18,19] In the present paper, we carried out Monte Carlo simulations in order to clarify the microstructure of the CuAu-I ordered phase in the III-V semiconductor alloys grown on (001) substrates.

II. MODEL AND SIMULATION

We carried out Monte Carlo simulations of the CuAu-I ordering in the (001) epitaxial growth, using an Ising-like model.[20] The details of the simulation have been described elsewhere:[21,22] We consider an epilayer of an alloy of $(A_{1-x}B_x)C$, which is growing via the layer-by-layer stacking on an exact (001) substrate. A (001) monolayer, which is a square lattice defined by the [110] and [1$\bar{1}$0] directions, contains 64×64 atoms with planar periodic boundary conditions. After the monolayer is deposited, atoms of A and B elements in the layer exchange their positions with each other for a given time interval $\Delta\tau$, according to the Kawasaki dynamics.[23] The configuration of atoms is frozen-in when the monolayer is covered with a next monolayer. An epilayer made of 64 monolayers is grown by repeating the above procedure. The Fourier transforms of the atomic arrangements thus obtained are compared with the electron-diffraction patterns reported previously.

The pairwise atomic interactions at least up to the second-nearest neighbors are needed to stabilize the ordered structures confirmed experimentally in the III-V semiconductor alloys.[20] Actually, *ab initio* calculations revealed that the second-nearest-neighbor interactions have significant magnitudes.[24] The signs of the parameters are determined naturally by consideration of the ground-state structure. The

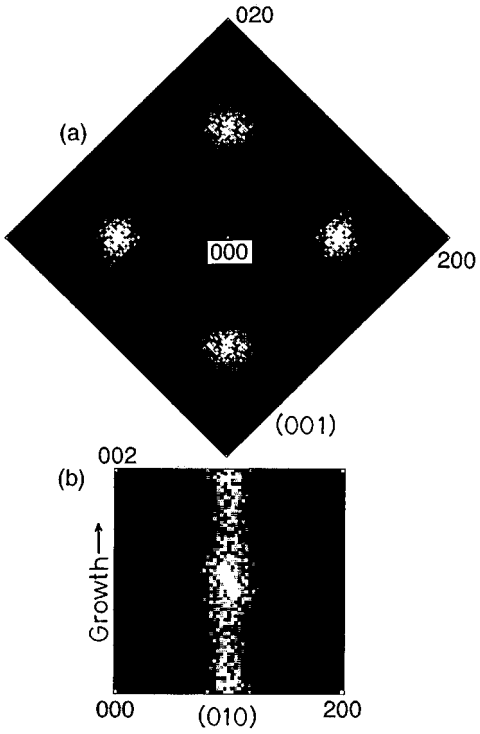

FIG. 1. (a) (001) and (b) (010) Fourier power spectra of atomic arrangement for an epilayer with $x=0.50$. The first-nearest-neighbor interaction of the (001) interplane is $V_{1v}=-0.8|V_{1h}|$, and the time interval is $\Delta\tau=20$ MCS (Monte Carlo step). In addition to the fundamental lattice spots of zinc-blende structure, CuAu-I superstructure reflections appear at $hkl=100$ and 010 positions, but not at the 001 position. A diffuse streak connecting the CuAu-I reflections is located along the growth direction in the (010) spectra.

approximate values are sometimes also determined in the same way. The values have to be consistent with those estimated by *ab initio* calculations. Thus, the range of parameters is limited to comparatively narrow region.

The system prefers unlike-atom pairs (i.e., $A-B$) if the pairwise interaction parameter is negative, or like-atom pairs (i.e., $A-A$ or $B-B$) if it is positive. The (100) and (010) variants of the CuAu-I structure have unlike-atom pairs in the first-nearest neighbor and like-atom pairs in the second-nearest neighbor within the (001) plane. Therefore, the first- and second-nearest-neighbor (1NN and 2NN) interactions in the top surface layer were set to be negative and positive, respectively. Note that the sign of V_{1v}, the interactions with 1NN atoms on the underlying plane, can be either positive or negative, since the numbers of unlike-atom pairs and like-atom ones equal each other. We adopted the values for the parameters so that they would well reproduce the CuAu-I ordering by taking the limitation mentioned above: $V_{1h}<0$, $V'_{1h}=-|V_{1h}|$, $V_{1v}=\pm 0.8|V_{1h}|$, $V_{2h}=0.5|V_{1h}|$, and $V_{2v}=0.3|V_{1h}|$. Growth temperature is $T=|V_{1h}|/k_B$, where k_B is the Boltzmann constant. The V's with a subscript h and v are the (001) intra- and inter-plane interactions, respectively. V_{1h} is of the 1NN pair with a direct linkage via a C atom, and V'_{1h} is of the one without the linkage. The details of the definition of V's were indicated in Fig. 1 of Ref. 22.

III. RESULTS AND DISCUSSION

A. CuAu-I-type ordering in stoichiometric alloy with $x=0.50$

Simulation has been carried out with a negative or a positive value for the 1NN interaction of the (001) interplane, V_{1v}. Fourier power spectra of the atomic arrangements thus obtained exhibit almost the same features as each other regardless of the sign of V_{1v}. Figure 1 shows (a) (001) and (b) (010) patterns for $V_{1v}<0$. Superlattice spots arise at $hkl=\pm 100$ and ± 010 in (a) and $hkl=100$ and 101 in (b), which are indicative of CuAu-I-type ordering. It is noted that 110 and 001 reflections are absent from (a) and (b). This indicates that among the three possible CuAu-I variants the epilayer contains only two variants which have their c axes perpendicular to the [001] direction. Besides the superstructure reflections, a diffuse scattering is located along the growth direction, suggesting the presence of many (001) plane faults. The absence of the (001) variant and the appearance of diffuse streaks have been found experimentally in $Ga_xAl_{1-x}As$ with a CuAu-I order,[11] and our simulations well reproduce the experimental results.

The cross-sectional views of atomic configurations which gave Fig. 1 are shown in Fig. 2. Here, open and closed

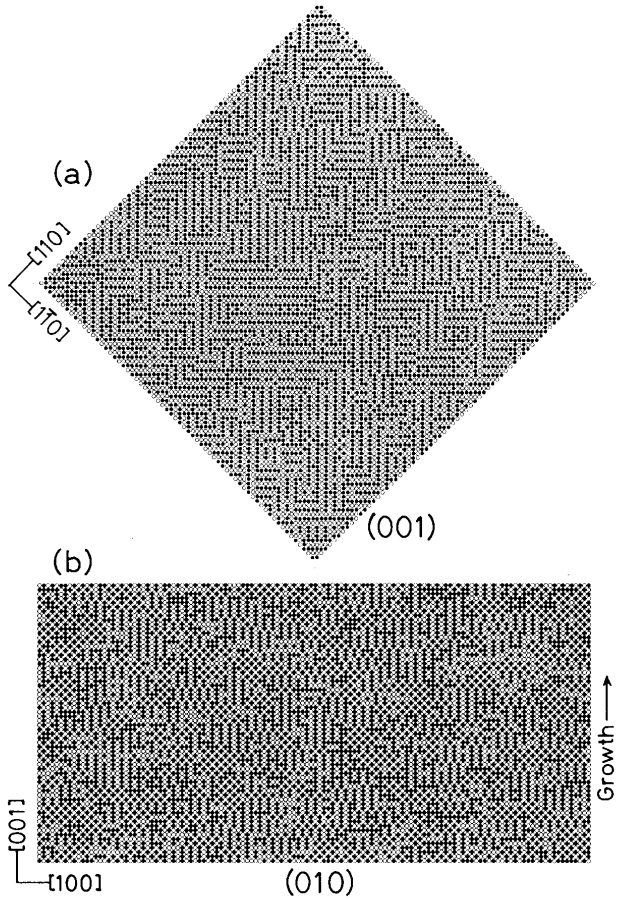

FIG. 2. (a) (001) and (b) (010) cross sections of the atomic arrangement corresponding to the Fourier power spectra of Fig. 1. Two successive planes are superimposed, and open and closed circles indicate A and B atoms, respectively. The major parts of interfaces of CuAu-I ordered phases consist of the (001) plane, and many (001) plane faults exist in the epilayer. The presence of the faults causes the diffuse scattering in Fig. 1(b).

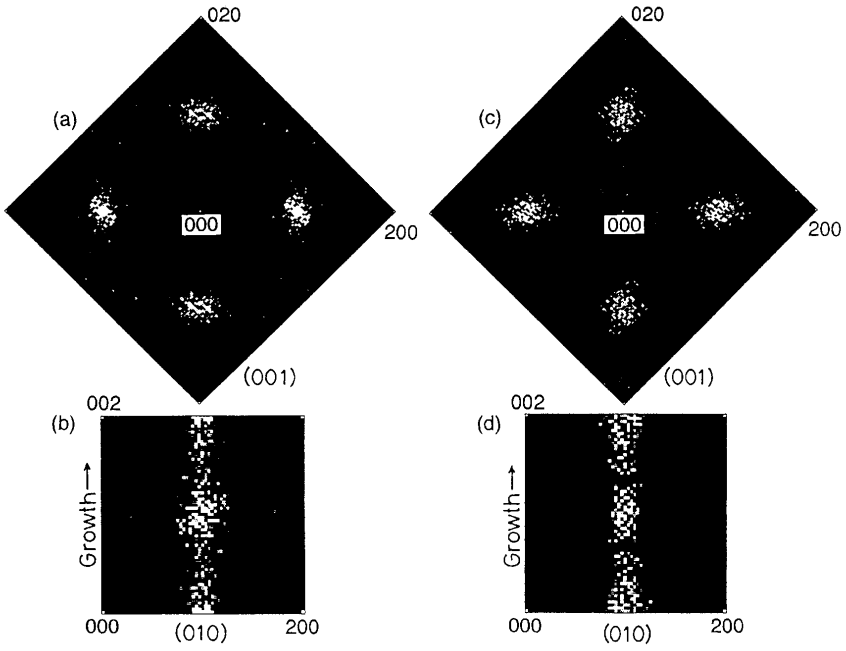

FIG. 3. Fourier power spectra for $x=0.25$ obtained with short-time intervals $\Delta\tau=20$ MCS. (a), (b) $V_{1v}=-0.8|V_{1h}|<0$ and (c), (d) $V_{1v}=0.8|V_{1h}|>0$. The feature of both spectra is almost the same and the superstructure reflections arise at the 100 and 010 positions, suggesting that the CuAu-I ordering progresses even in the off-stoichiometric alloys.

circles denote A and B atoms, respectively. The ordered structures with a double periodicity along the [100] or [010] direction are found in the (001) cross section (a), showing the appearance of CuAu-I variants. There are two different types of atomic arrangements in the (010) cross section (b): a chessboard pattern and a vertically striped pattern along [100]. The former and the latter are the atomic arrangements of (010) and (100) variants, respectively. The ordered phase develops to platelike structures perpendicular to the growth direction, and numerous (001) plane faults are involved in the alloy. [The ordered domains and plane faults in Fig. 2(b) are seen well by viewing the page obliquely along the [001] direction.] It is clearly seen that the streak along the growth direction in the (010) spectrum is caused from the (001) plane faults.

This microstructure formation process can be interpreted in terms of the pairwise atomic interactions. During the (001) epitaxial growth, V_{1v} does not contribute to the formation of the ordered structure; thus, the ordering along the growth direction is due to the 2NN interaction, V_{2v}. The absolute value of V_{2v} adopted in the present simulation is much smaller than the growth temperature. Thus, thermal fluctuation may easily disturb the ordering along the growth direction, and many plane faults arise between the (001) planes.

B. New ordered phase in $(A_{0.75}B_{0.25})C$ alloys

Figures 3 and 4 demonstrate Fourier power spectra of atom configurations obtained for (a), (b) $V_{1v}<0$ and (c), (d) $V_{1v}>0$. The time interval $\Delta\tau$ in Figs. 3 and 4 are a 20 and 1000 MCS (Monte Carlo step), respectively. The increase in $\Delta\tau$ corresponds to an increase in the frequency of atomic diffusion on a surface during the epilayer formation. The features of the spectra of Fig. 3 are almost similar to those of Fig. 1, and this is consistent with the results of transmission electron microscope (TEM) observations for $Ga_{0.75}Al_{0.25}As$ (Ref. 11) and $GaAs_{0.25}Sb_{0.75}$.[16] For the $(A_{0.75}B_{0.25})C$ alloy, the ground state is a Cu_3Au ordered phase. However, (100) and (010) variants of CuAu-I can develop even in an epilayer with $x=0.25$, which is far from the stoichiometric composition $x=0.5$.

In the case of the larger $\Delta\tau$ (1000 MCS) which corresponds to the lower-deposition rate, the superlattice spots change their shape and new reflections appear in the spectra. The 100 and 010 reflections extend along the [010] and [100] directions, respectively, in the (001) pattern for $V_{1v}<0$ in Fig. 4(a). On the other hand, they elongate toward the fundamental lattice spots for $V_{1v}>0$ in Fig. 4(c). According to the diffraction theory, the elongation of superlattice spots in (a) and (c) suggests the existence of platelike ordered domains and/or antiphase boundaries. Since the oval-shaped reflections similar to those in (a) have been observed experimentally,[16] the value of V_{1v} should be negative in the CuAu-I ordering of III–V semiconductor alloys. Although the parameters except for V_{1v} are determined by considering only the ground-state structure, our simulations successfully reproduce the features of diffraction pattern, such as the appearance of diffuse streaks and the shape of superlattice spots. This suggests that our model is quite useful in discussing the ordering mechanism and the phase state in the epitaxial layers and in predicting the values of the pairwise atomic interactions. In addition to these spots in Figs. 4(a) and 4(c), some ring patterns exist in the reciprocal-lattice space and their intensity increases with the progress of ordering, suggesting the formation of a secondary phase.

So far as we know, no TEM work on the $GaAs_{0.25}Sb_{0.75}$ microstructure, such as dark-field images and high-resolution

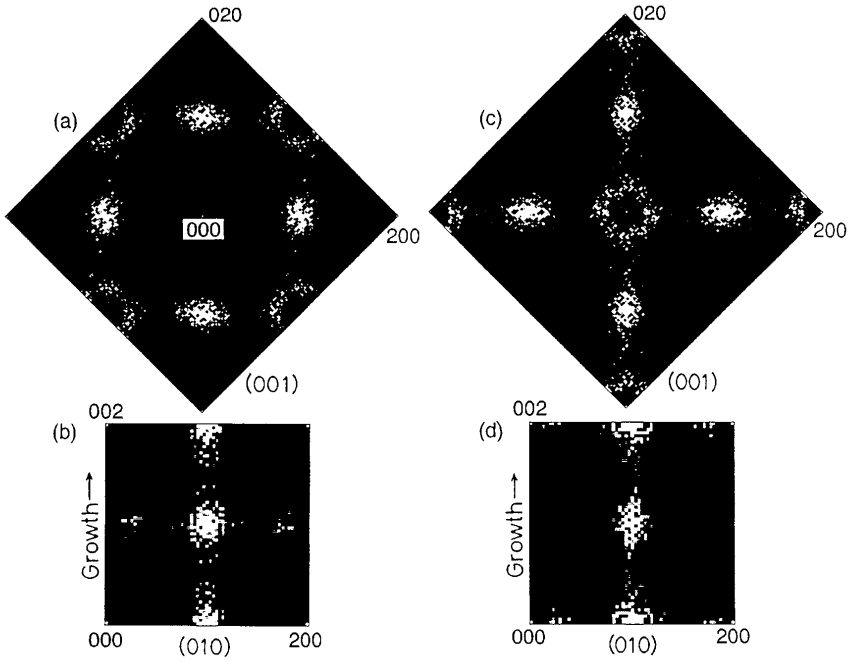

FIG. 4. Fourier power spectra for $x=0.25$ obtained with long-time intervals $\Delta\tau=1000$ MCS. (a), (b) $V_{1v}<0$ and (c), (d) $V_{1v}>0$. Note that the superlattice spots become an ellipse in shape. The elongated spots of (a) are found in the actual diffraction pattern of a $GaAs_{0.25}Sb_{0.75}$ epitaxial layer (Ref. 16). In addition to the reflection, some ring patterns appear in the spectra.

images, has been reported. In order to clarify the atomic arrangement for $x=0.25$, (001) projections of the epilayer corresponding to the spectra in Fig. 4 are shown in Fig. 5. The projections in Figs. 5(a) and 5(b) are quite different from each other. In the case of $V_{1v}<0$ [Fig. 5(a)], it is clearly seen that a double periodicity along the [100] or [010] direction occurs homogeneously throughout the crystal. In addition, another atomic arrangement is recognized in some regions, some of which are encircled. This structure has a double periodicity along the [100] and [110] directions, and its ordered domains are small. The short-range ordering (SRO) of the fine domains causes the ring pattern in Fig. 4(a). In contrast to the homogeneity of Fig. 5(a), the regions of ordered phase are embedded in A atom-rich matrix in Fig. 5(b). The mixture of the ordered and the A-rich regions is responsible for the ring-pattern reflections around the fundamental reflections shown in Fig. 4(b).

Figure 6 displays cross-sectional views for $V_{1v}<0$ corresponding to Fig. 5(a). One can see that the CuAu-I ordered phase is included in the epilayer and the major parts of their

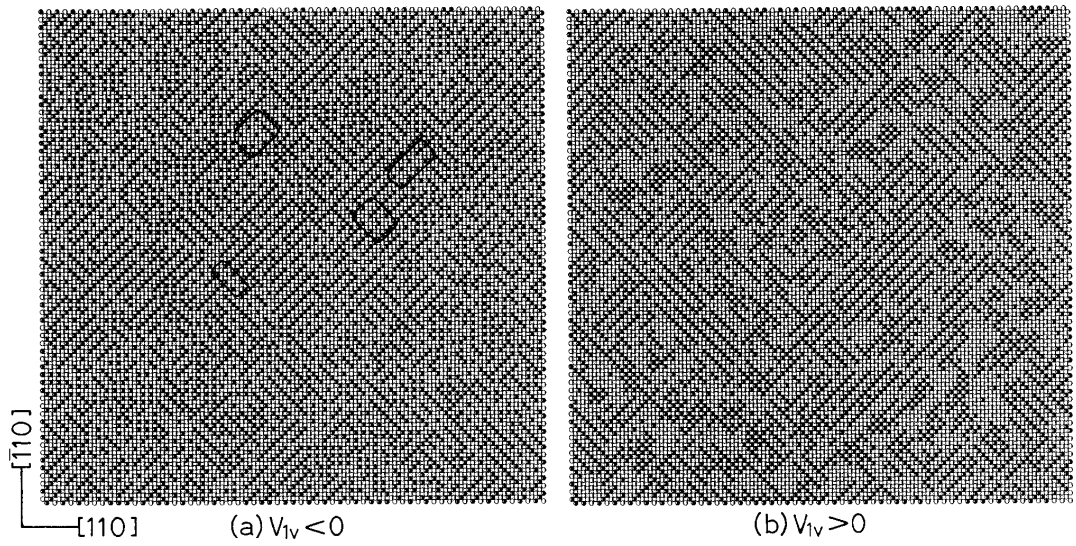

FIG. 5. (001) projections of the epilayer with $x=0.25$. (a) $V_{1v}<0$ and (b) $V_{1v}>0$. Open, closed, and half-closed circles indicate that the atomic columns are A atom-rich, B atom-rich, and an equal mixture of A and B atoms, respectively. The ordered regions are distributed uniformly in (a), while the ordered regions and the like-atom clusters coexist in (b).

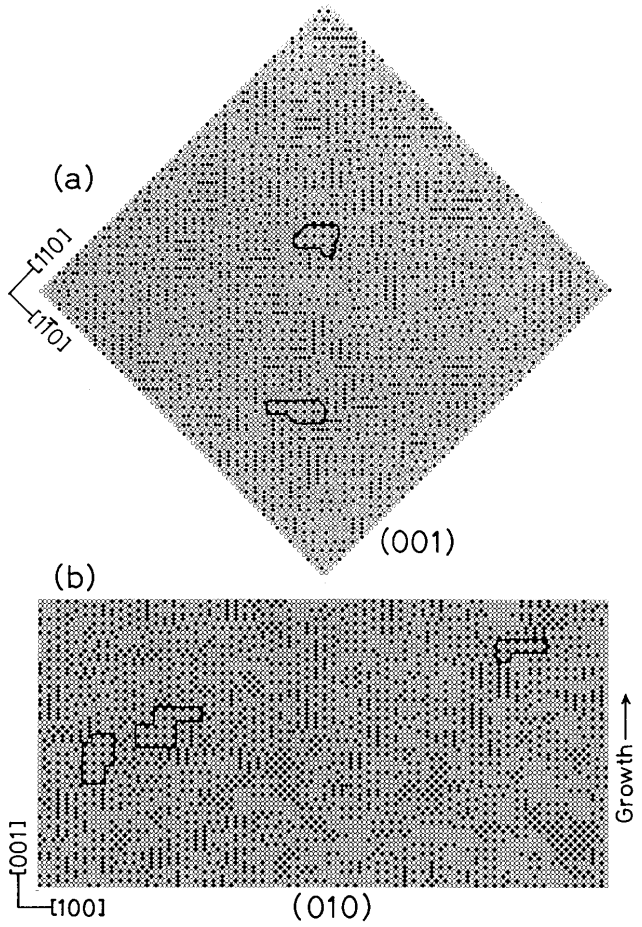

FIG. 6. Cross-sectional views of the atomic arrangements corresponding to Fig. 5(a). The CuAu-I structure with the (100) and (010) variants can exist in the epilayer with $x=0.25$. In addition to this, a Cu_3Au-type ordered phase surrounded by a line is observed.

interfaces are parallel to (001) planes. The presence of the CuAu-I structure reveals that the off-stoichiometric alloys have a tendency to form heterogeneous regions with *a high degree of order* rather than homogeneous regions with *a low degree of order* throughout the epilayer. Besides the CuAu-I, the Cu_3Au-type structure is recognized in the alloy. The Cu_3Au ordered regions, some of which are contoured, are dispersed in the epilayer, causing the ring pattern around $hkl=110$ and 001 positions in Figs. 4(a) and 4(b). The ring pattern has not been recognized in the actual diffraction pattern.[16] Although the Cu_3Au structure is the ground state of $(A_{0.75}B_{0.25})C$ alloy, the CuAu-I configuration may become stable at a finite temperature. The experimental growth conditions may be above the critical temperature of Cu_3Au formation, so that SRO of Cu_3Au is formed in the matrix of CuAu-I. In other words, our result suggests that the low-deposition rate at a low growth temperature gives rise to the formation of Cu_3Au ordered phase.

As mentioned above, Jen *et al.*[16] have expected that an ordered structure, which is composed of alternating (100) planes of pure Sb atoms and of 0.5As and 0.5Sb atoms, is formed in a $GaAs_{0.25}Sb_{0.75}$ alloy. This structure is essentially of CuAu-I with *a low degree of order*. (The proposed structure may be different from the Cu_3Au type, because the 110 reflection that the Cu_3Au structure should give is not seen in their diffraction pattern.[16]) In the present simulation, we do not find the atomic arrangement proposed by Jen *et al.*, but have observed the local formation of CuAu-I with *a high degree of order* in the off-stoichiometric alloy.

C. Effect of surface reconstruction on ordering

The different types of atomic configurations, depending on the sample preparation, have been observed in $GaAs_xSb_{1-x}$ epilayers grown on a (001) substrate: CuAu-I- and CuPt-type structures.[18,25] Why does the atomic arrangement differ in the same alloy system? In the case of $GaAs_xSb_{1-x}$ alloys, the CuPt structure was found in the specimens obtained by molecular-beam epitaxy,[18,25] and the existence of a 2×4 reconstructed structure was confirmed by *in situ* reflection high-energy electron diffraction.[18] On the other hand, the CuAu-I structure was observed only in the samples grown by organometallic vapor phase epitaxy. Unfortunately, the surface state was not examined in this case, but we believe that the reconstructed structure is different from that of the molecular-beam epitaxy-grown specimens.

Gomyo and co-workers[26,27] have investigated surface reconstructions, ordered-phase structures, and ordering direction in epilayers as a function of growth temperature, and found that there is one-to-one correspondence between the surface reconstruction and the type of ordered structures. From *ab initio* calculations, the reconstruction has been pointed out to change the values of the pairwise atomic interactions.[24] In our crystal model, therefore, the difference in values for parameters in the simulations of CuAu-I and CuPt ordering[28,29] reflects the difference in surface reconstruction. In future investigations, the effective interactions of the III-V semiconductor alloys during epitaxial growth should be estimated by using *ab initio* calculations or electron counting methods. Our simulations give an invaluable suggestion for the effective interaction parameters on the reconstructed surface.

IV. SUMMARY

The formation of a CuAu-I-type ordered phase during (001) epitaxial growth of III-V semiconductor alloys $(A_{1-x}B_x)C$ has been investigated by Monte Carlo simulations based on an Ising-like crystal-growth model. The results of Fourier power spectra and cross-sectional views of atomic arrangements clearly reveal that in the (001) epilayer two CuAu-I variants whose c axes lie on the growth plane are formed, containing numerous (001) plane faults. The CuAu-I ordered structure can develop even in an off-stoichiometric alloy with $x=0.25$. Our calculations suggested that the large mobility of surface atoms leads to a SRO of Cu_3Au.

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