Observation of a New Ordered Phase in $Al_xIn_{1-x}As$ Alloy and Relation between Ordering Structure and Surface Reconstruction During Molecular-Beam-Epitaxial Growth

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A new phase with spontaneous atomic ordering on the sublattice is found in $Al_{0.48}In_{0.52}As$ grown on exact (001)InP substrate by molecular-beam epitaxy. The atomic arrangement is a periodic sequence of $\{111\}A$ planes in a unit of $Al_xIn_{1-x}/Al_yIn_{1-y}/Al_zIn_{1-z}$ on the group-III sublattice. The surface reconstruction during growth is (2×3). A CuPt-type ordered phase is observed in crystals grown at higher temperatures, where the reconstruction is (2×1). This correlation with respect to periodicity and direction between the reconstructions and the types of ordered phase unequivocally demonstrates that surface reconstruction plays a central role in ordered structure formation. Band-gap reductions of ~80 and ~30 meV are observed for the new ordered phase and the CuPt-type phase, respectively.

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Ordered phases in which spontaneously ordered atomic structure on group-III or group-V sublattice exists has been observed in a wide range of ternary or quaternary III-V alloy semiconductors [1-8], and has been gathering much attention from various viewpoints such as crystal growth, surface physics, and electronic structures [8-13], and also from a technological perspective [14]. Many different types of ordered phases such as CuAu [1], CuPt [4-8], chalcopyrite [3], and famatinite [2] have been reported. However, the most commonly observed type is CuPt. This paper reports a new type of ordered phase which was found in $Al_{0.48}In_{0.52}As$. This ordered phase is completely different from all the previously reported ones mentioned above. Moreover, this paper demonstrates for the first time a correlation between different ordered phases and different surface reconstructions during $Al_{0.48}In_{0.52}As$ growth, and provides a basis for understanding the formation mechanism of ordered phases. Large band-gap reductions associated with this new type of ordered phase, as well as with the CuPt-type phase, are also reported for the first time.

Epitaxial growth of $Al_xIn_{1-x}As$ ($x \sim 0.48$) was carried out on semi-insulating or S-doped exactly oriented (±0.1°) (001)InP substrates by gas-source molecular-beam epitaxy (GS-MBE). In this composition, $Al_{0.48}In_{0.52}As$ is lattice matched to the InP substrate. Metal solids of indium, gallium, and aluminum were used for group-III sources, and hydrides AsH_3 and PH_3 were used for group-V sources. The cracking temperature for AsH_3 was 1000 °C and the growth chamber pressure was 5×10^{-5} Torr. Each wafer has double epitaxial layers consisting of a top $Al_{0.48}In_{0.52}As$ layer and a $Ga_{0.47}In_{0.53}As$ buffer layer. The $Al_{0.48}In_{0.52}As$ layers with a thickness of 1-1.4 μm were grown on 0.2 μm thick $Ga_xIn_{1-x}As$ ($x \sim 0.47$) buffer layers. $Al_{0.48}In_{0.52}As$ layers were grown at a growth rate of ~1 μm/h with no doping. The growth temperatures for $Al_{0.48}In_{0.52}As$ were 415, 460, 520, and 570 °C. The growth temperature for the $Ga_{0.47}In_{0.53}As$ buffer layer was 520 °C at the beginning of the growth and gradually varied during growth to the respective $Al_{0.48}In_{0.52}As$ growth temperatures. Surface reconstruction was observed *in situ* during growth by reflection high-energy electron diffraction (RHEED) at 20 keV. All the surfaces of the epitaxial layers were mirror smooth.

Transmission electron diffraction (TED) patterns and lattice images were recorded for edge-on samples in the [110] and $[\bar{1}10]$ zones at 200 kV using an Akashi EM-002B transmission electron microscope (TEM). The specimens were prepared with a dimple grinder and by ion milling, after cleavage and polishing. Photoluminescence (PL) measurements were performed at room temperature with an excitation wavelength of 4880 Å of an argon ion laser. In this study, the PL peak energy is defined to be the band gap energy as in Ref. [4]. Regarding conventions for crystal orientations, to emphasize the *A* and *B* directions, *A* is attached to [111] and $[\bar{1}\bar{1}1]$, as $[111]A$ and $[\bar{1}\bar{1}1]A$, and *B* is attached to $[1\bar{1}1]$ and $[\bar{1}11]$, as $[1\bar{1}1]B$ and $[\bar{1}11]B$, respectively, in this paper. In the present paper, $\langle 111\rangle A$ represents $[111]A$ and/or $[\bar{1}\bar{1}1]A$, and $\langle 1\bar{1}1\rangle B$ represents $[1\bar{1}1]B$ and/or $[\bar{1}11]B$. Conventions for crystal surface orientations are made in the same way.

Figure 1(a) shows a typical $[\bar{1}10]$-zone TED pattern of $Al_{0.48}In_{0.52}As$ grown at 460 °C. In addition to the base matrix spots, strong superstructure reflections are observed at around $[h\pm1/3, k\pm1/3, 1\pm1/3]$ and $[h\mp1/3, k\mp1/3, 1\pm1/3]$ (h,k,l: all even or all odd integers) in the $[111]A$ and $[\bar{1}\bar{1}1]A$ directions. The intensities for the reflections in both directions are nearly equal. The shape of the superstructure reflections is not exactly circular but elongated and tilted, as seen in Fig. 1(a). The positions of the maximum intensity of the superstructure reflection are slightly shifted from the above-mentioned exact positions, i.e., $[h\pm(1-\delta_1)/3, k\pm(1-\delta_2)/3, l\pm(1-\delta_3)/3]$ and $[h\mp(1-\delta_1)/3, k\mp(1-\delta_2)/3, l\pm(1-\delta_3)/3]$, where $\delta_1=\delta_2=5.1\times10^{-3}$, and $\delta_3=8.5\times10^{-2}$. In the [110] zone [Fig. 1(b)], there are no reflections from the superstructures, although only very weak streaks are seen from the base matrix spots. In the [110] zone, the $\langle 1\bar{1}1\rangle B$ variant of the CuPt-type ordered phase was observed in the $Ga_{0.47}In_{0.53}As$ [5] buffer layer in the same specimen.

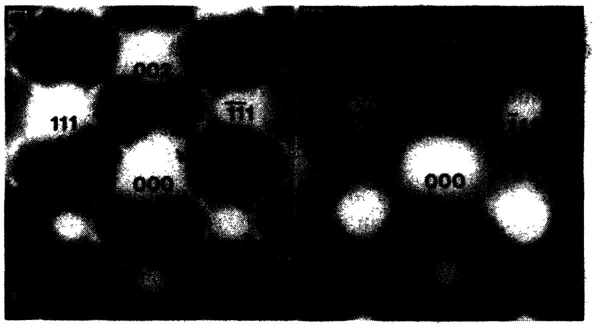

FIG. 1. TED patterns (a) for the $[\bar{1}10]$ zone, and (b) for the $[110]$ zones for $Al_{0.48}In_{0.52}As$ grown on (001) InP at growth temperature of 460 °C. In (a), superstructure reflections are seen at around $[h \pm 1/3, k \pm 1/3, l \pm 1/3]$ and $[h \mp 1/3, k \mp 1/3, l \pm 1/3]$ (h,k,l: all even or all odd integers).

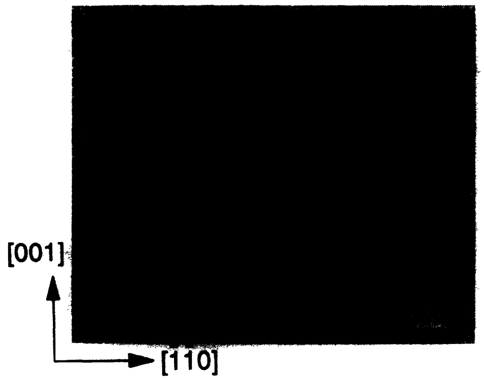

FIG. 2. A typical TEM lattice image in the $[\bar{1}10]$ zone for the same specimen used for Fig. 1. Ordering formation is in the $[\bar{1}\bar{1}1]A$ direction ($TP_{[\bar{1}\bar{1}1]A}$ variant; see text). Arrows indicate the ordering periodicity. The period of the ordering (10.1 Å) is triple that for disordered $Al_{0.48}In_{0.52}As$. Glancing angle observation of this image along the [112] direction helps to more clearly identify the triple-period (TP) ordered phase. Domains of the other variant $TP_{[111]A}$ are not seen clearly in this particular area in the specimen, although they were seen in other places in the specimen as is evident from the almost-equal superstructure intensity [Fig. 1(a)] for both variants of the ordered phase.

This reconfirms that the identification of the $[\bar{1}10]$ zone in Fig. 1(a) is correct.

A TEM bright-field lattice image for the same specimen for Fig. 1(a) is shown in Fig. 2. Contrast coming from the $[-1/3, -1/3, 1/3]$ superstructure is seen, e.g., around the indicated arrows. The period of the ordered structure is 10.1 Å. This is *triple* that (3.37 Å) of the disordered $Al_{0.48}In_{0.52}As$. Thus, the new ordered phase is sometimes referred to as a "triple-period (TP)" ordered phase hereafter. The variant of the ordered phase with the $[\bar{1}\bar{1}1]A$ direction is referred to as $TP_{[\bar{1}\bar{1}1]A}$, and that for $[111]A$, as $TP_{[111]A}$. The domain size of $TP_{[\bar{1}\bar{1}1]A}$ is very small (several tens of Å) (Fig. 2). Many similar microdomains are also seen in this figure. The existence of these microdomains is believed to be contributing to the distorted features such as the elongation, tilt, and shift from the exact $1/3\langle 111\rangle A$ positions of the superstructure reflections mentioned above. Similar features in TED patterns have been observed [15,16] and analyzed [16,17] for CuPt-type ordered phase. The TED patterns [Figs. 1(a) and 1(b)] and a lattice image (Fig. 2) indicate the existence of a new ordered phase which has a sequence of group-III $(111)A$ or $(\bar{1}\bar{1}1)A$ planes $\ldots/XYZ/XYZ/XYZ/XYZ/\ldots$ along the $[111]A$ or $[\bar{1}\bar{1}1]A$ directions, respectively, where $X = Al_xIn_{1-x}$, $Y = Al_yIn_{1-y}$, $Z = Al_zIn_{1-z}$, as shown in Fig. 3.

Table I summarizes relations among surface reconstructions observed by RHEED during the AlInAs growth, the ordered structures, and ordering directions in the epitaxial layers, as a function of growth temperature. The reflection intensities for RHEED and TED are also shown qualitatively. As shown in this table, the (2×3) structure was observed for growth temperatures of 415 and 460 °C, corresponding to the triple-period ordered phase found in the present study. On the other hand, for growth temperatures of 520 and 570 °C, the surface reconstruction was (2×1). Correspondingly, a CuPt-type (double period) ordered phase was observed by TEM. Thus, it is recognized that, at least within the investigated temperature range, *there is one-to-one correspondence between different surface reconstructions and different types of ordered structure.*

The period of TP-type ordered structure in the [110] direction on the (001) plane (d_{110}^{TP}) is also triple that for disordered $Al_{0.48}In_{0.52}As$ (i.e., $d_{110}^{\mathrm{TP}} = 3d_{110}$, where d_{110} is the period in the [110] direction for disordered $Al_{0.48}In_{0.52}As$). On the other hand, the (2×3) structure on the growing surface also has triple periodicity in the [110] direction ($d_{110}^{(2\times 3)} = 3d_{110}$). Thus, the *direction* for ×3 *and* the ×3 *period* for the (2×3) structure during growth *coincide* with the direction for ×3 and the period in which TP-type ordered structure takes on the (001) plane in the epilayer, respectively. This indicates quite clearly that the TP-type ordered phase resulted from the (2×3) surface reconstruction. As shown in Table I, the TP-type

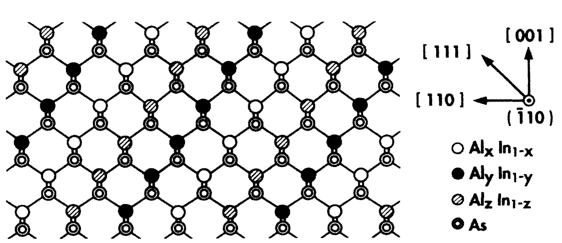

FIG. 3. Model for the triple-period (TP) ordered phase ($TP_{[111]A}$ variant; see text) in $Al_{0.48}In_{0.52}As$, as projected in the $[\bar{1}10]$ direction. The ordered structure in its ideal form has a repeated arrangement of a unit of $Al_xIn_{1-x}/Al_yIn_{1-y}/Al_zIn_{1-z}$ in the $[111]A$ direction on the group-III sublattice, where $(x+y+z)/3 = 0.48$, $0 \leq x,y,z \leq 1$, $x \neq y \neq z$, or $x = y \neq z$. The compositions (x,y,z) are not determined at present. There is another variant ($TP_{[\bar{1}\bar{1}1]A}$) with the same atomic arrangement with the $[\bar{1}\bar{1}1]A$ ordering direction.

TABLE I. Growth temperature dependence of surface reconstruction, ordered-phase structure, and its ordering direction for $Al_{0.48}In_{0.52}As$ grown on exact (001) InP by GS-MBE. "TP" represents the new triple-period ordered phase found in the present study.

T_g (°C)	Surface reconstruction	Ordered structure and ordering direction in epilayers [111]A	[$\bar{1}\bar{1}1$]A	[$1\bar{1}1$]B	[$\bar{1}11$]B
415	2×3 (medium)[a]	TP(strong)	TP(strong)	None	None
460	2×3 (medium)	TP(strong)	TP(strong)	None	None
520	2×1 (weak)	None	None	CuPt(weak)	CuPt(weak)
570	2×1 (weak)	None	None	CuPt(weak)	CuPt(weak)

[a] "Medium" intensity is compared to the "strong" intensity for the (2×4) structure for P-stabilized (001) InP surface.

ordering directions are A directions (i.e., $\langle 111\rangle A$). This asymmetry in the TP-type-ordering-variant appearance, meaning the appearance of $TP_{[111]A}$ and $TP_{[\bar{1}\bar{1}1]A}$ variants and *no* appearance of $TP_{[1\bar{1}1]B}$ and $TP_{[\bar{1}11]B}$, is believed to be a consequence of the asymmetry of the (2×3) structure, with regard to the As-atom arrangements in the [$\bar{1}$10] and [110] directions during growth.

Table I also shows that the CuPt-type ordering directions in $Al_{0.48}In_{0.52}As$ are B directions (i.e., [$1\bar{1}1$]B and [$\bar{1}11$]B), and there is no ordering in the A directions. With regard to the variant appearances, the previous observations of CuPt-type ordering in AlInAs [7] are consistent with this present observation. The previously described formation model [9,10] for CuPt-type ordered phase in III-III-V type alloys, which emphasized the necessity of a monolayer group-V coverage 2× structure due to dimer and dangling bond arrays, is consistent with the present observations: (1) the correlation between the existence of a 2×1 structure and the existence of a CuPt-type ordering in AlInAs, and, in detail, (2) the coincidence between the 2× direction and the 2× periodicity of (2×1) structure, and the ordering direction and the periodicity of a CuPt-type ordered structure on the (001) plane in the epilayer (i.e., $d_{\bar{1}10}^{(2\times1)}=2d_{\bar{1}10}$ and $d_{\bar{1}10}^{\mathrm{CuPt}}=2d_{\bar{1}10}$). These appearance asymmetries between the A and B variants for TP-type and CuPt-type ordered phase are thought to have similar origins, i.e., the asymmetries of the surface reconstructions in the [110] and [$\bar{1}$10] directions during growth under the growth conditions which give rise to the respective ordered phases. Murgatroyd, Norman, and Booker noticed that the 2× periodicity and its direction of the (2×4) reconstruction coincides with the 2× periodicity and the direction of the CuPt-type ordering on the (001) surface in the GaAsSb epilayer, which is a III-V-V type alloy. They suggested the importance of the surface reconstruction for ordered-phase formation [8]. However, regarding the coincidence, it occurred only for one case, i.e., (2×4) versus the CuPt-type ordering. Thus, it could be a fortuitous coincidence. LeGoues *et al.* reported a correlation between CuPt ordered-phase formation and (2×1) reconstruction for SiGe alloy [18]. However, the use of a Sb-surfactant-mediated SiGe growth to correlate nonexistence of the ordered phase with the non-2×1 surface reconstruction made it difficult to exclude a possibility of Sb incorporation and subsequent diffusion-enhanced disordering of once formed ordered phase. In the present $Al_{0.48}In_{0.52}As$ case, the coincidences were observed consistently for different ordered structures with different ordering periodicities and different ordering directions for four growth temperatures. These consistently observed coincidences serve as convincing evidence for essential roles of surface reconstruction during growth in ordered-phase formation. This owes much to the present discovery of the new TP-type ordered phase with the new periodicity and the new ordering direction.

The observed reflection intensities for $CuPt_{[1\bar{1}1]B}$ and $CuPt_{[\bar{1}11]B}$ variants in $Al_{0.48}In_{0.52}As$ were approximately equal in the present study. This equality in intensity was observed at both growth temperatures of 520 and 570 °C. This observation is consistent with the use of exact (001)InP substrates, which have no misorientation component towards the $\langle 1\bar{1}1\rangle B$ direction [4]. The equal superstructure reflection intensities from $TP_{[111]A}$ and $TP_{[\bar{1}\bar{1}1]A}$, as shown in Fig. 1(a), also suggest that a similar variant selection mechanism [4,9,10] is working for the new TP-type phase formation. Equality in intensity was also observed at 415 °C.

The (2×1) surface reconstruction observed in the growth temperatures of 520 and 570 °C is considered to be a structure in which the surface is fully covered with monolayer As which consists of As dimer arrays and dangling bond arrays. On the other hand, the (2×3) structure exists for 415 and 460 °C, and the (2×1) structure exists at higher temperatures of 520 and 570 °C. Generally, lower temperatures tend to make the surface a

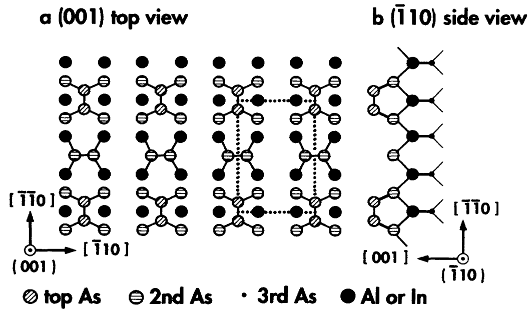

FIG. 4. A possible model for the (2×3) surface reconstruction on As-stabilized (001) $Al_{0.48}In_{0.52}As$. The top two atomic layers are made of As atoms. Dotted line shows a unit cell.

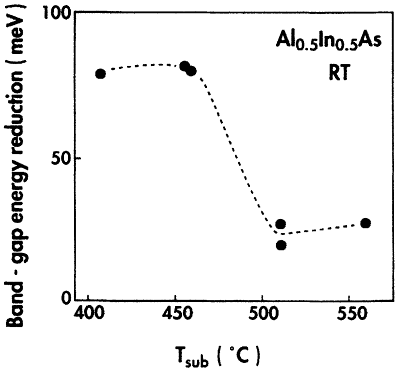

FIG. 5. Band-gap reduction for $Al_{0.48}In_{0.52}As$, which is measured at room temperature, as a function of growth temperature. The dashed line is an eye guide. The "standard" band gap is taken as 1.475 eV for disordered $Al_{0.48}In_{0.52}As$.

more As-rich structure [19]. It is highly probable that the (2×3) structure on the present $Al_{0.48}In_{0.52}As$ surface is due to a surface doubly covered with As, as shown in Figs. 4(a) and 4(b).

$Ga_{0.5}In_{0.5}P$ with a CuPt-type ordering is known to show a band-gap reduction [4]. In Fig. 5, the room-temperature band-gap difference between a band-gap value of 1.475 eV for disordered $Al_{0.48}In_{0.52}As$ and a band-gap for $Al_{0.48}In_{0.52}As$ grown by GS-MBE, is plotted as a function of growth temperature. The disordered $Al_{0.48}In_{0.52}As$ was grown in our laboratory at growth temperature of 650–700 °C by metalorganic vapor phase epitaxy [20]. The band gap reduction takes a large value of ~80 meV when growth temperature is 415 and 460 °C, where the TP-type ordered phase is well formed. The band gap decreases to ~30 meV when growth temperature increases to 520–570 °C, where CuPt-type phase is weakly formed. Band-gap reductions were also recently reported for GaInAs and InAsSb with CuPt-type ordered phase [21, 22]. The present observation of band-gap reduction in $Al_{0.48}In_{0.52}As$ with CuPt-type ordered phase provides a new example in which the CuPt-type ordering reduces band gap. The band-gap reduction for the TP-type ordered phase found in this study is the first case in which band-gap reduction is observed for an ordered phase with a structure *other than* a CuPt-type structure.

The findings described in the present paper will become a basis for further understanding of the ordered phase formation mechanism, and, in turn, will promote understanding of epitaxial growth processes on surfaces of III-V binary compounds and their alloys. Because $Al_xIn_{1-x}As$ is a very important material for long-wavelength optoelectronic and high frequency devices [20], the new ordered phase found in the present study and its associated optoelectronic properties may add a new degree of freedom for designing these and coming new devices. Thus, the new ordered structure is also expected to become important from a technological point of view.

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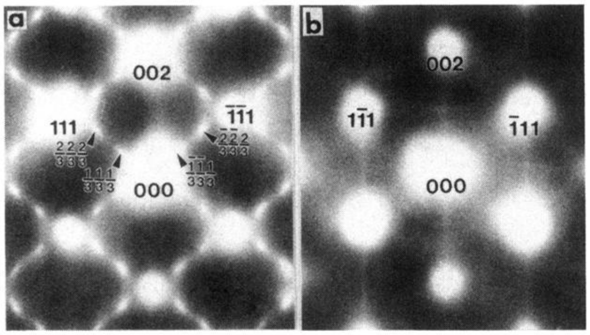

FIG. 1. TED patterns (a) for the $[\bar{1}10]$ zone, and (b) for the [110] zones for $Al_{0.48}In_{0.52}As$ grown on (001) InP at growth temperature of 460 °C. In (a), superstructure reflections are seen at around $[h \pm 1/3, k \pm 1/3, l \pm 1/3]$ and $[h \mp 1/3, k \mp 1/3, l \pm 1/3]$ (h, k, l: all even or all odd integers).

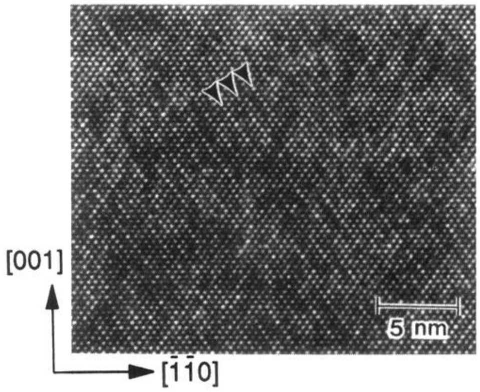

FIG. 2. A typical TEM lattice image in the $[\bar{1}10]$ zone for the same specimen used for Fig. 1. Ordering formation is in the $[\bar{1}\bar{1}1]A$ direction ($\mathrm{TP}_{[\bar{1}\bar{1}1]A}$ variant; see text). Arrows indicate the ordering periodicity. The period of the ordering (10.1 Å) is triple that for disordered $\mathrm{Al}_{0.48}\mathrm{In}_{0.52}\mathrm{As}$. Glancing angle observation of this image along the [112] direction helps to more clearly identify the triple-period (TP) ordered phase. Domains of the other variant $\mathrm{TP}_{[111]A}$ are not seen clearly in this particular area in the specimen, although they were seen in other places in the specimen as is evident from the almost-equal superstructure intensity [Fig. 1(a)] for both variants of the ordered phase.