

**Wurtzite–zinc-blende polytypism in ZnSe on GaAs(111)A**

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We have studied the wurtzite (W)–zinc-blende (ZB) polytypism in ZnSe films grown on the (111)A-oriented substrates of GaAs. Although the stable structure of bulk ZnSe is ZB, W-structured ZnSe is formed near the interface on the ZB-structured GaAs(111)A substrate. Our first-principles calculations have revealed that the charge state at the ZnSe/GaAs(111)A interface plays a key role in the formation of W-ZnSe. We show that the structural quality of W-ZnSe is significantly improved using a cracked Se source, while ZB-ZnSe is grown using a vicinal GaAs(111)A substrate.

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Polytypism is one of the most fascinating properties in compound semiconductors. Wurtzite (W) and zinc blende (ZB) are the most common polytypes, having a layer stacking of *ABABAB* . . . in the [0001] direction and of *ABCABC* . . . in the [111] direction, respectively (Fig. 1). The W and ZB structures differ only in their third-nearest-neighbor atomic arrangement, and atoms are tetrahedrally and covalently bonded in both structures. Despite the structural similarities between two phases, their electronic structures are different.<sup>1,2</sup> On the other hand, a heterostructure of different polytypes of W and ZB is expected to be free of stress and/or dangling bonds, because the interface between them is almost perfectly lattice matched.<sup>3</sup> Thus, the heterostructure of W and ZB has a great potential in band-structure engineering.<sup>2,4</sup> However, such heterostructures have not yet been successfully fabricated, because of the difficulty in growing single-polytype material without grain boundaries. In addition, the question as to what stabilizes a W or a ZB structure in a given system has not yet been fully answered. Thus, in order to open the way to the fabrication of the W-ZB heterostructures, first, the detailed growth condition under which either a ZB or a W structure is stabilized has to be established.

This paper describes the W-ZB polytypism in ZnSe. Since high-quality bulk ZnSe is difficult to obtain, the nearly lattice-matched substrate of GaAs(001) (lattice mismatch  $\approx 0.27\%$ ) has been most commonly used for ZnSe growth. In the present study, we used the (111)A-oriented GaAs sub-

strate. While the stable structure of bulk ZnSe is ZB, W-structured ZnSe is formed on the (111)A-oriented substrate of GaAs having the ZB structure. We show that the formation of W-ZnSe is closely related with the charge state at the heterovalent interface of ZnSe/GaAs(111)A. In addition, we found that the crystalline quality of W-ZnSe is significantly improved using a cracked-Se source, while ZB-structured ZnSe is successfully grown using a vicinal GaAs(111)A substrate.

The samples were grown using a dual-chamber molecular beam epitaxy (MBE) system. A detailed description of the apparatus and surface cleaning treatments for the GaAs(111)A substrate has been given in our previous paper.<sup>5</sup> After the growth of a few hundred layers of GaAs, the surface showed a  $(2 \times 2)$  reconstruction. The samples were then transferred via ultrahigh-vacuum transfer modules to another MBE chamber for ZnSe growth. Thin ZnSe films were grown at 250 °C on the GaAs(111)A- $(2 \times 2)$  substrate. The beam-equivalent pressures for Zn and Se were  $3.0 \times 10^{-7}$  and  $6.0 \times 10^{-7}$  Torr, respectively. The growth processes of ZnSe were monitored by reflection high-energy electron diffraction (RHEED) in real time. Samples were prepared for cross-sectional transmission electron microscopy (TEM) observation by mechanical thinning to about 5  $\mu\text{m}$  and the ion milling to electron transparency, and were observed on a JEOL JEM-2010 microscope operating at 200 kV.

Figure 2(a) shows the high-resolution (HR) TEM image of the ZnSe/GaAs sample. The arrows show the plane of the

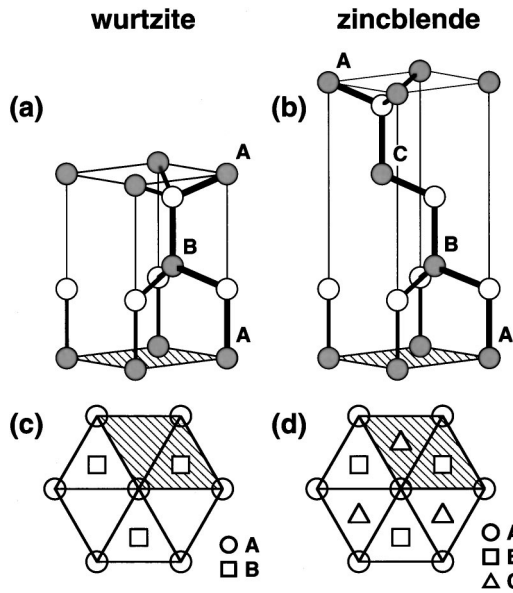


FIG. 1. Three-dimensional perspective views of the primitive hexagonal unit cells of the (a) W and (b) ZB structures. (c) and (d) show the layer stackings of W and ZB along the [0001] and [111] directions, respectively.

interface. The film thickness of ZnSe is about 130 Å. This value is much smaller than the critical thickness for the strain relaxation in this system. The upper half of the ZnSe film is mostly composed of a defect-free layer with a stacking of  $ABC\dots$  inherent to the ZB structure. On the other hand, regions near the interface contain considerable amounts of in-plane stacking faults. Interestingly, the area surrounded by solid lines in Fig. 2(a) shows an  $ABABAB\dots$  stacking sequence intrinsic to the W structure. Such regions were frequently observed near the interface.

The present result for ZnSe/GaAs(111)A stands in marked contrast to the results for (110) and (001) orientations: only ZB-ZnSe is formed on the (001) and (110) surfaces of GaAs. In addition, the W structure in bulk ZnSe is stable only at temperatures above 1425 °C, but is transformed to the ZB structure at lower temperatures.<sup>6</sup> Thus the question should arise why ZnSe forms the W structure on the GaAs(111)A substrate even at a low temperature of 250 °C.

It is known that the W and ZB polytypes can be stabilized depending on the substrate used. For example, while the equilibrium structure of GaN is W, the (001)-oriented substrate of GaAs (Ref. 7) and SiC (Ref. 8) can stabilize ZB-GaN. These results can be explained by considering that a ZB-structured substrate acts as a template for ZB growth. On the other hand, the TEM data shown in Fig. 2(a) clearly evidences that the metastable phase of W-ZnSe is formed on the GaAs(111)A substrate having the different structure of ZB. In the following, a mechanism is proposed for the formation of W-ZnSe.

Since the formation of W-ZnSe is restricted near the interface [Fig. 2(a)], it appears that the ZnSe/GaAs(111)A interface plays a key role in stabilizing W-ZnSe. In order to confirm this, information about the atomic configuration of the interface is indispensable. Here, we note that the surface

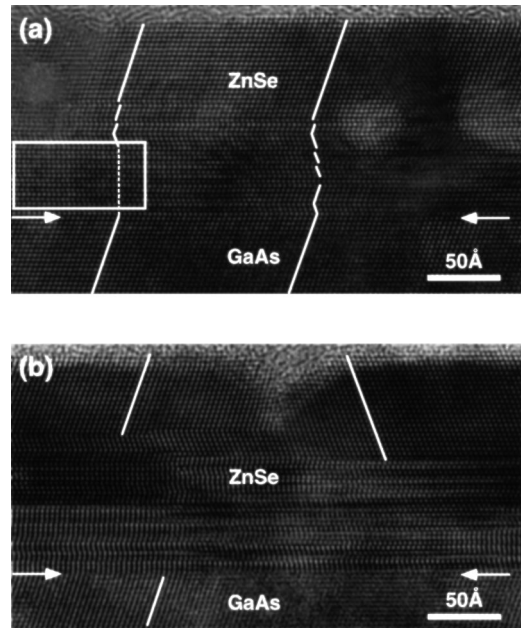


FIG. 2. HRTEM images of the ZnSe film grown on the GaAs(111)A substrate.

structure of the GaAs(111)A-( $2\times 2$ ) substrate is the Ga-vacancy-buckling structure,<sup>9,10</sup> in which 0.25 ML of Ga atom is missing at the outermost layer. While Zn atoms are hardly adsorbed on the GaAs(111)A-( $2\times 2$ ) surface at 250 °C, Se atoms are stably adsorbed forming the adsorption structure containing 0.25 ML of Ga vacancies.<sup>11</sup> These results suggest that the ZnSe growth starts with the formation of Ga-Se bonds, leaving the Ga-vacancy site unoccupied. Thus, we can propose one of the simplest structure model for the ZnSe/GaAs(111)A interface as shown in Fig. 3(a), which contains 0.25 ML of Ga vacancy at the interface. While more complicated interface models extending several atomic layers can be proposed, we restricted our discussion to the

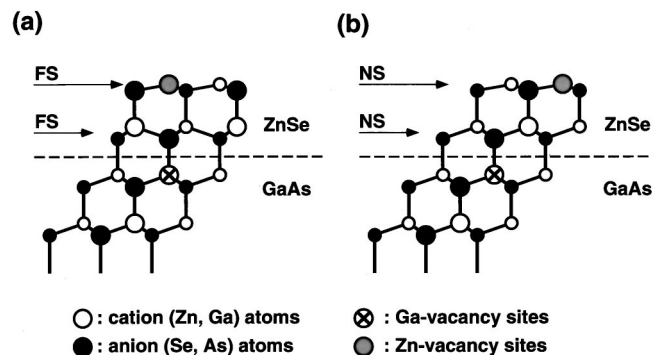


FIG. 3. Models employed for the first-principles density-functional calculations. (a) ZB-ZnSe/GaAs(111)A. (b) W-ZnSe/GaAs(111)A. NS and FS denote normally- and faultily-stacking layers, respectively. Two circle sizes denote atoms in different vertical planes. The back side of the slab is terminated with four fictitious H atoms (0.75 nuclear and 0.75 electronic charges) that eliminate artificial dangling bonds and prevent it from coupling with the front side.

above model. The reason is that we could not find any characteristic contrast at the interface in the HRTEM image shown in Fig. 2(a).

In order to study the role of the interface on the formation of W-ZnSe, we performed first-principles density-functional calculations<sup>12–14</sup> with the generalized gradient approximation.<sup>15</sup> The wave functions were expanded in plane waves with a kinetic-energy cutoff of 25.0 Ry. A slab geometry was used for the simple calculation, which has the supercell consisting of 2 bilayers (BL) of the GaAs substrate, of 2 BL of the ZnSe overlayer, and of a vacuum region corresponding to 3 BL in thickness.<sup>16</sup> We assumed that the front side of the slab has the  $(2 \times 2)$  vacancy-buckling geometry, because of the following reasons. The growing ZnSe(111)A surface shows a  $(2 \times 2)$ RHEED pattern at 2 BL thickness, the intensity distribution of which is quite similar to those for the Ga-vacancy-buckling structure of GaAs(111)A- $(2 \times 2)$ . In addition, it has been predicted that the vacancy-induced  $(2 \times 2)$  reconstruction of the (111)A surface is energetically favorable for II-VI compounds.<sup>10</sup>

The calculations were performed for two models; W-ZnSe/GaAs [Fig. 3(a)] and ZB-ZnSe/GaAs [Fig. 3(b)]. Comparing total energies between the two models, we found that the W-ZnSe model has an energy lower by 36 meV per  $(2 \times 2)$  unit cell relative to the ZB-ZnSe model. On the other hand, the calculations for the ZB- and W-ZnSe layers on ZB-ZnSe(111)A showed that ZB-ZnSe is stable by 41 meV/ $(2 \times 2)$  unit cell with respect to W-ZnSe. Also we confirmed that ZB-ZnSe is slightly more stable (5 meV/atom) than W-ZnSe in bulk, in good agreement with the result in Ref. 3. These calculated results clearly show that W-ZnSe is stabilized on the GaAs(111)A substrate, being consistent with the experimental results.

According to a simple bond-charge picture, there exist extra charges at the ZnSe/GaAs interface having Ga vacancies (Fig. 3). On the other hand, a charge-balanced interface can be formed when the Ga-missing site is buried by Zn atoms, because the number of Zn-As bonds equals that of the Ga-Se bonds [three bonds per  $(2 \times 2)$  unit]. Thus, if the extra charge at the interface plays a key role in the formation of W-ZnSe, it could be confirmed by the calculations for the model including a Zn atom embedded in the Ga-missing site. The results showed that W-ZnSe on the charge balanced interface is less stable than ZB-ZnSe by 91 meV per  $(2 \times 2)$  unit cell, suggesting that W-ZnSe is formed closely relating with the charge state at the heterovalent interface of ZnSe/GaAs(111)A.

While other II-VI semiconductors, such as CdS, CdSe, and ZnS, are known to be prepared in either form of W or ZB,<sup>3</sup> there have been only a few reports about the formation of W-ZnSe: previous transmission electron diffraction (TED) studies have suggested that W-ZnSe can be formed on the cubic-structured substrates of Ge(111) (Ref. 17) and NaCl(111),<sup>18</sup> although it is not clear whether the TED data were obtained from W-ZnSe or ZB-ZnSe with in-plane stacking faults. Here, it is interesting to point out that both ZnSe/Ge(111) and ZnSe/NaCl(111) systems have the heterovalent interface. Thus, it is reasonable to consider that the interface charge state has a significant effect also on these

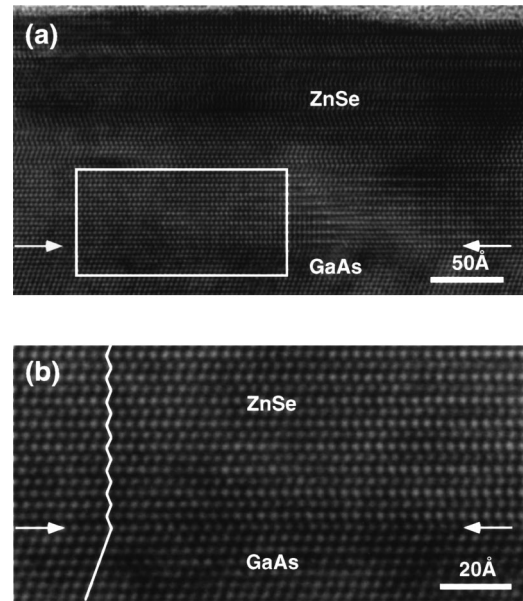


FIG. 4. (a) HRTEM image of the ZnSe film grown on the GaAs(111)A substrate using the cracked-Se source. (b) The magnified image of (a).

two systems, but without details about their interface structure a quantitative discussion is difficult at this stage.

As seen in Fig. 2(a), as the effect of the interface is weakened with increasing film thickness, the structure of the ZnSe film changes from W to ZB. Thus, unless the formation of ZB-ZnSe starts at the same plane, a high density of defects will be generated in the film. Indeed, as shown in Fig. 2(b), regions with a crystal orientation rotated  $180^\circ$  with respect to the substrate are frequently observed. Although the surfaces of both regions are flat, the anti-phase boundary between them manifests itself as a depression, giving rise to the growth-front roughening.

In order to improve the structural quality of ZnSe, first, we tried to suppress the formation of ZB-ZnSe. This was achieved by using a cracked-Se source. Shown in Fig. 4(a) is the TEM image for the sample grown using the Se source cracked at  $1000^\circ\text{C}$ . In this image, the ZB structure is not observed. Furthermore, the crystalline quality of W-ZnSe near the interface is considerably improved [Fig. 4(b)] as compared to that in Fig. 2(a).

It is well known that Se sublimates as polyatomic molecules of  $\text{Se}_n$  ( $n = 1, 2, 3, 5, 6, 7,$  and  $8$ ), with the relative concentrations of each species determined by the evaporation reaction temperature. While the molecular beam from the conventional cell (without cracking) is mainly composed of Se and  $\text{Se}_2$ , with the ratio<sup>19</sup> of  $\sim 1$ , we obtained the Se/ $\text{Se}_2$  ratio of  $\sim 9$ , when the Se source cracked at  $1000^\circ\text{C}$  was used. Since Se molecules have to be dissociated before being incorporated into the growing film, it is likely that the surface processes of growing ZnSe is significantly altered by using Se, which might result in the successive evolution of the hexagonal-stacking sequence.

An alternative method to improve the structural quality of ZnSe is to directly grow the ZB-ZnSe films on the GaAs substrate by suppressing the formation of W-ZnSe at the



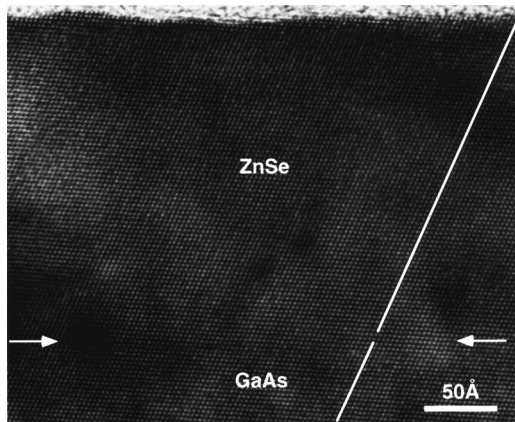


FIG. 5. HRTEM image of the ZnSe film grown on the vicinal GaAs(111)A substrate.

beginning of the growth. For this purpose, we used vicinal GaAs(111)A substrates. The substrates were oriented  $4^\circ$  toward the [011] direction, giving a mean separation of  $\sim 47$  Å between steps. Figure 5 shows the TEM image, in which only ZB-structured ZnSe is observed. Similar results were obtained when the substrate surface was tilted along the opposite direction of [100] (not shown). These results can be explained as follows. On the vicinal surface, since the distance from arriving atoms and molecules to step edge becomes smaller, the nucleation at step edges should be more favorable. Although details about the atomic configurations of the step edges are unknown, it is certain that the step edge

sites are better coordinated than the lattice sites on the flat terraces. Thus it appears that ZnSe nucleated at the step edges on the vicinal substrate easily receive the ZB structure of GaAs which overcomes the effect of the interface on the formation of W-ZnSe.

In conclusion, we present the evidence that either W- or ZB-structured ZnSe can be grown on the (111)A-oriented substrate of GaAs. On the vicinal GaAs(111)A substrate ZnSe grows with the ZB structure, while W-structured ZnSe is formed using the cracked Se source. We have found that the charge state at the heterovalent interface of ZnSe/GaAs(111)A plays an important role in the formation of W-ZnSe. Thus, these findings will offer us a good opportunity to fabricate heterostructures of different polytypes of W and ZB also for systems other than ZnSe/GaAs. In addition, it is interesting to note that ZnSe, a promising material for applications in blue-green laser diodes,<sup>20</sup> forms the W structure. Since the valence band does not degenerate in hexagonal materials as in strained-layer superlattices, the laser threshold of W-ZnSe should be lower than that of ZB-ZnSe.<sup>21</sup> Hence, the use of W-ZnSe is expected to improve the performances of the ZnSe-based light-emitting devices.

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