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X-ray crystallographic study of the optically active semiconductor $(\mathrm{Ga}_x\mathrm{In}_{1-x})_2\mathrm{Se}_3$

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Crystal structures of two kinds of optically active semiconductors $(\mathrm{Ga}_{0.60}\mathrm{In}_{0.40})_2\mathrm{Se}_3$ and $(\mathrm{Ga}_{0.40}\mathrm{In}_{0.60})_2\mathrm{Se}_3$, both of which are defect wurtzite structures but show different reduced c_w/a_w ratios, have been studied using powder X-ray diffraction and Rietveld analysis. The final reliability factors are as follows: $R_{wp}=10.00\%$, $S=2.4234$, $R_F=4.19\%$ for $(\mathrm{Ga}_{0.60}\mathrm{In}_{0.40})_2\mathrm{Se}_3$ and $R_{wp}=10.48\%$, $S=2.4324$, $R_F=2.78\%$ for $(\mathrm{Ga}_{0.40}\mathrm{In}_{0.60})_2\mathrm{Se}_3$. The structure of $(\mathrm{Ga}_{0.60}\mathrm{In}_{0.40})_2\mathrm{Se}_3$ with $c_w/a_w=1.633$ is called the ideal defect wurtzite structure; the bond lengths are nearly the same and the bond angles are almost to be the ideal bond angle of tetrahedral bonding 109.47°. Meanwhile, the structure of $(\mathrm{Ga}_{0.40}\mathrm{In}_{0.60})_2\mathrm{Se}_3$ with $c_w/a_w=1.565$ is called the layered defect wurtzite structure; the nearest $(001)_{\text{group III}}$ and $(001)_{\mathrm{Se}}$ layers are waved and very close to each other as if they merged into one atomic layer. The average bond length along the c axis is 5.89% longer than that between the atoms in the merged $(001)_{\text{group III}}$ and $(001)_{\mathrm{Se}}$ layers; the average bond angle whose one side is the bond along the c axis is 13.11% smaller than 109.47°. Based on these structural results, the anomalous dependence of the optical band gap on composition is discussed from the view of bonding nature. The additional ionic bonding between the merged (001) layers in the layered defect wurtzite structure makes the c parameter smaller but the band gap larger than those of the ideal defect wurtzite structure although the ionic bonding nature is dominant for the both defect wurtzite structures.

I. INTRODUCTION

We have been interested in the crystal structures and the optical properties of $\mathrm{III}_2\mathrm{VI}_3$ compound semiconductors in recent years. The structure of $(\mathrm{Ga}_x\mathrm{In}_{1-x})_2\mathrm{Se}_3$ ($x=0.00$–0.70) has been found to be a defect wurtzite-type with either a $P6_1$ or $P6_5$ space group, in which the structural vacancies and the group-III atoms are ordered in screw form along the c axis[1–4] (see Fig. 1). We have demonstrated that the single crystals possess pure optical activity along the c axis and the maximum rotatory power comes up to 210°/mm for visible light.[5–7] One of the most interesting results is that the lattice constant and the optical band gap do not obey Vegard's law.[6] Our previous results have shown there exist two composition regions. One is In-rich region with composition x from 0 to 0.45. The c_w/a_w ratio is almost 1.565 and the band gap linearly increases from 1.70 to 2.06 eV with increasing composition x, where c_w and a_w are reduced lattice constants from the proposed defect wurtzite structure to the normal wurtzite structure. Another is a Ga-rich region with composition x from 0.45 to 0.70. The c_w/a_w ratio is nearly 1.633 and the band gap abruptly decreases to 1.81 eV with increasing composition x. Therefore, both types of $(\mathrm{Ga}_x\mathrm{In}_{1-x})_2\mathrm{Se}_3$ process the same basic crystal structures and show pure optical activity along the c axis. Their electronic structures, however, are obviously different to each other.

For the purpose of elucidating the structural difference between two types of $(\mathrm{Ga}_x\mathrm{In}_{1-x})_2\mathrm{Se}_3$, it is necessary to get more detailed information, such as bond length and angle. In this paper we first refine the crystal structures of the Ga-rich and In-rich $(\mathrm{Ga}_x\mathrm{In}_{1-x})_2\mathrm{Se}_3$ using powder X-ray diffraction and Rietveld analysis. Based on the results, the structural differences and the anomalous dependence of the optical band gap on the composition are discussed from the view of bonding nature.

II. EXPERIMENT

Specimens $(\mathrm{Ga}_{0.60}\mathrm{In}_{0.40})_2\mathrm{Se}_3$ and $(\mathrm{Ga}_{0.40}\mathrm{In}_{0.60})_2\mathrm{Se}_3$ are selected as representatives of the two composition regions. They have obviously different reduced c_w/a_w ratios and

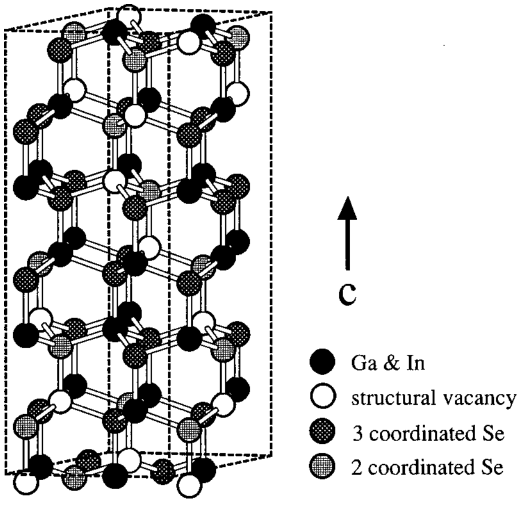

FIG. 1. Crystal structure model of $(\mathrm{Ga}_{0.60}\mathrm{In}_{0.40})_2\mathrm{Se}_3$ with the space group of $P6_1$. It is based on a defect wurtzite structure, in which the structural vacancies on $\frac{1}{3}$ of the cation sites are ordered in a screw arrangement along the c axis. There exist two kinds of Se atoms: the two-coordinated Se atom and the three-coordinated Se atom. The former is bonded with two group-III atoms and the later is bonded with three group-III atoms.

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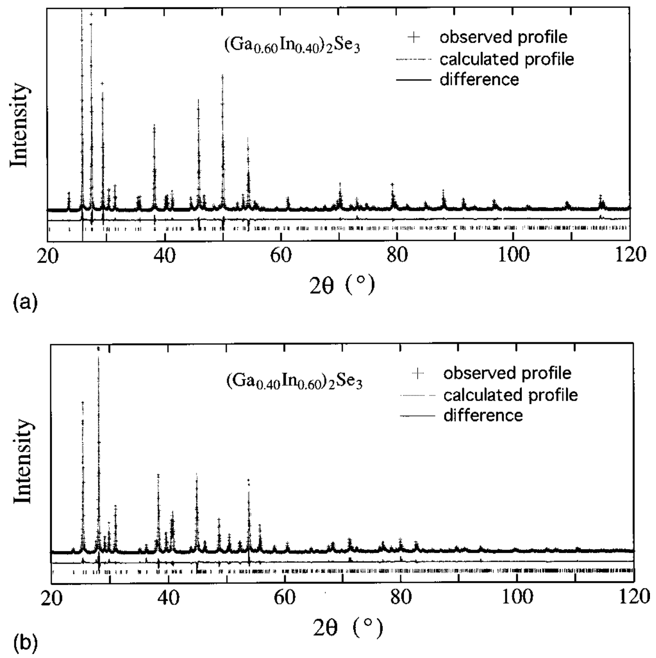

FIG. 2. Measured powder X-ray diffraction profiles (cross-shaped dots) and final Rietveld refinement profiles of $(Ga_{0.60}In_{0.40})_2Se_3$ and $(Ga_{0.40}In_{0.60})_2Se_3$. The difference curves and reflection markers at the bottom.

band gaps but show less difference in compositions. Specimens are synthesized from Ga_2Se_3 and In_2Se_3 (Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan). Grains of Ga_2Se_3 (purity: 3*N*; melting point: 1278 K) and In_2Se_3 (purity: 5*N*; melting point: 1153 K) are melted at 1343 K in evacuated and sealed silica tubes. After complete mixing, the specimens are held at 973 K for two weeks and then the specimens are cooled in air. Compositions of the specimens were confirmed to be $(Ga_{0.60}In_{0.40})_2Se_3$ and $(Ga_{0.40}In_{0.60})_2Se_3$ using energy dispersive X-ray spectroscopy. Powder X-ray diffraction profiles are collected within an angular range of 2θ from 20° to 100° in steps of 0.02° by a Bragg-Brentano type θ-2θ diffractometer equipped with a curved graphite monochromator using Cu $K\alpha$. Data collection is performed at room temperature. Silicon powder (NIST SRM 640b) is used as the internal *d*-spacing standard to justify the instrument. RIETAN98 and FAT-RIETAN SYSTEM (Ref. 8) is used for Rietveld refinement of the crystal structures.

III. RESULTS

The two collected X-ray diffraction profiles can be indexed by the aforementioned defect wurtzite structure. It is noted, however, that their intensity profiles are obviously different to each other. Figures 2(a) and 2(b) show observed, calculated powder X-ray diffraction profiles and difference curves for $(Ga_{0.60}In_{0.40})_2Se_3$ and $(Ga_{0.40}In_{0.60})_2Se_3$ after the Rietveld analysis. Tables I and II show the refined crystal data. The final reliability factors are as follows: $R_{wp} = 10.00\%$, $S = 2.4234$, $R_F = 4.19\%$ for $(Ga_{0.60}In_{0.40})_2Se_3$ and $R_{wp} = 10.48\%$, $S = 2.4324$, $R_F = 2.78\%$ for $(Ga_{0.40}In_{0.60})_2Se_3$, where the compositions of the sites $M1$ and $M2$ are assumed to be the same as the nominal one and the temperature factors of Se2 and Se3, as well as those of $M1$ and $M2$, are constrained to be the same.

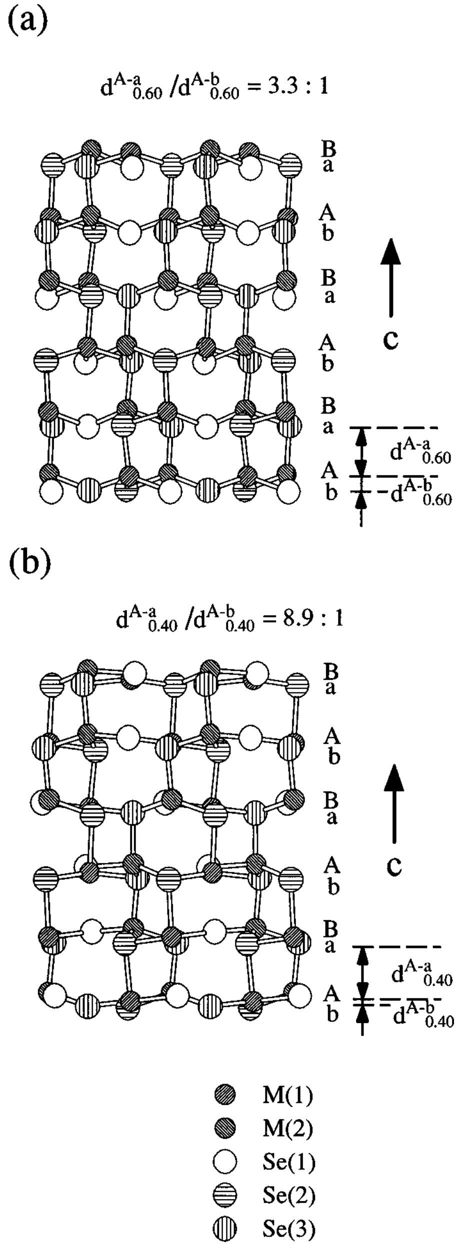

FIG. 3. The [010] projections of the atomic arrangements of (a) $(Ga_{0.60}In_{0.40})_2Se_3$ and (b) $(Ga_{0.40}In_{0.60})_2Se_3$ from simulated results of the final Rietveld refinement. *A*, *B* and *a*, *b* denote atomic positions of the closed packed $(001)_{\text{group III}}$ and $(001)_{\text{Se}}$ layers on the basis of wurtzite structure, and $d_{0.60}^{A-a}$, $d_{0.60}^{A-b}$, $d_{0.40}^{A-a}$, and $d_{0.40}^{A-b}$ denote the distances between the $(001)_{\text{group III}}$ and $(001)_{\text{Se}}$ layers.

The results of the Rietveld analysis reveal each structure is distinguished from the other by the interplanar distances between the close-packed planes perpendicular to the *c* axis. Figures 3(a) and 3(b) show the [010] projections of $(Ga_{0.60}In_{0.40})_2Se_3$ and $(Ga_{0.40}In_{0.60})_2Se_3$, respectively. In case of $(Ga_{0.60}In_{0.40})_2Se_3$, the structural vacancies and group-III atoms are ordered in screw form along the *c* axis and all atomic positions are similar to those of the ideal wurtzite structure. Two kinds of the (001) layers made of group-III atoms and Se atoms are very planar and arranged alternately with a sequence of *AaBb* along the *c* axis if we ignore the existence of structural vacancy, where *A*, *B* and *a*, *b* denote atomic positions of the group-III and Se layers on the basis

TABLE I. Fractional coordinates and isotropic atomic displacement parameters (B) for $(\mathrm{Ga}_{0.60}\mathrm{In}_{0.40})_2\mathrm{Se}_3\,(Z=2)$. Space group: $P6_1$ (NO. 169), $a=0.6843(5)$ nm, $c=1.935(1)$ nm, and $V=0.7849(9)$ nm^3. $R_{wp}=10.00\%$, $R_p=7.81\%$, $R_e=4.13\%$, $R_F=4.19\%$, $S=2.4234$.

Atom	Site	Symmetry	x	y	z	B (nm^2)
Se1	6a	1	0.305(2)	0.325(3)	0.1223(3)	0.023(2)
Se2	6a	1	−0.029(1)	0.622(2)	0.1275(2)	0.016(1)
Se3	6a	1	0.689(2)	0.023(2)	0.1260(3)	0.016(1)
$M1$	6a	1	−0.006(2)	0.674(3)	−0.0053(2)	0.0094(8)
$M2$	6a	1	0.652(2)	0.003(2)	0.00000	0.0094(8)

TABLE II. Fractional coordinates and isotropic atomic displacement parameters (B) for $(\mathrm{Ga}_{0.40}\mathrm{In}_{0.60})_2\mathrm{Se}_3\,(Z=2)$. Space group: $P6_1$ (NO. 169), $a=0.6985(9)$ nm, $c=1.899(2)$ nm, and $V=0.8026(17)$ nm^3. $R_{wp}=10.48\%$, $R_p=7.95\%$, $R_e=4.31\%$, $R_F=2.78\%$ $S=2.4324$.

Atom	Site	Symmetry	x	y	z	B (nm^2)
Se1	6a	1	0.303(1)	0.354(1)	0.1578(3)	0.004(1)
Se2	6a	1	−0.025(2)	0.623(1)	0.1267(3)	0.023(1)
Se3	6a	1	0.722(1)	0.039(1)	0.1308(3)	0.023(1)
$M1$	6a	1	−0.001(1)	0.668(1)	−0.0229(3)	0.0095(5)
$M2$	6a	1	0.6875(9)	0.0005(10)	0.00000	0.0095(5)

TABLE III. Bond lengths l and bond angles ∅ for $(\mathrm{Ga}_{0.60}\mathrm{In}_{0.40})_2\mathrm{Se}_3$ based on the tetrahedral bonding structure. The symmetry codes are as follows (i) $-y, x-y, \frac{1}{3}+z$. (ii) $-x+y, -x, \frac{2}{3}+z$. (iii) $-x, -y, \frac{1}{2}+z$. (iv) $y, -x+y, \frac{5}{6}+z$.

	l (nm)		∅ (°)
$\mathrm{Se}1^{\mathrm{iii}}-M1^{\mathrm{iii}}$	0.2438(12)	$M1^{\mathrm{ii}}\text{-}\mathrm{Se}1^{\mathrm{iii}}\text{-}M2^{\mathrm{ii}}$	105.89(46)
$\mathrm{Se}1^{\mathrm{iii}}\text{-}M2^{\mathrm{ii}}$	0.2451(20)		
$\mathrm{Se}2^{\mathrm{i}}\text{-}M1^{\mathrm{iii}}$	0.2556(14)	$M1^{\mathrm{iii}}\text{-}\mathrm{Se}2^{\mathrm{i}}\text{-}M1^{\mathrm{i}}$	98.93(48)
$\mathrm{Se}2^{\mathrm{i}}\text{-}M1^{\mathrm{i}}$	0.2589(06)	$M1^{\mathrm{i}}\text{-}\mathrm{Se}2^{\mathrm{i}}\text{-}M2^{\mathrm{iii}}$	106.90(39)
$\mathrm{Se}2^{\mathrm{i}}\text{-}M2^{\mathrm{iii}}$	0.2441(12)	$M2^{\mathrm{iii}}\text{-}\mathrm{Se}2^{\mathrm{i}}\text{-}M1^{\mathrm{i}}$	105.62(58)
$\mathrm{Se}3^{\mathrm{ii}}\text{-}M1^{\mathrm{iv}}$	0.2524(15)	$M1^{\mathrm{iv}}\text{-}\mathrm{Se}3^{\mathrm{ii}}\text{-}M2^{\mathrm{ii}}$	101.22(56)
$\mathrm{Se}3^{\mathrm{ii}}\text{-}M2^{\mathrm{ii}}$	0.2447(06)	$M2^{\mathrm{ii}}\text{-}\mathrm{Se}3^{\mathrm{ii}}\text{-}M2^{\mathrm{iv}}$	107.29(37)
$\mathrm{Se}3^{\mathrm{ii}}\text{-}M2^{\mathrm{iv}}$	0.2540(13)	$M2^{\mathrm{iv}}\text{-}\mathrm{Se}3^{\mathrm{ii}}\text{-}M1^{\mathrm{ii}}$	103.42(53)

TABLE IV. Bond lengths l and bond angles ∅ for $(\mathrm{Ga}_{0.40}\mathrm{In}_{0.60})_2\mathrm{Se}_3$ when assuming the structure is based on the tetrahedral bonding one. The parts enclosed by {}* are deviated from covalent ones. The symmetry codes are as follows (i) $-y, x-y, \frac{1}{3}+z$. (ii) $-x+y, -x, \frac{2}{3}+z$. (iii) $-x, -y, \frac{1}{2}+z$. (iv) $y, -x+y, \frac{5}{6}+z$.

	l (nm)		∅ (°)
$\mathrm{Se}1^{\mathrm{iii}}\text{-}M1^{\mathrm{ii}}$	0.2594(12)	$M1^{\mathrm{ii}}\text{-}\mathrm{Se}1^{\mathrm{iii}}\text{-}M2^{\mathrm{ii}}$	109.10(30)
$\mathrm{Se}1^{\mathrm{iii}}\text{-}M2^{\mathrm{ii}}$	0.2530(09)		
$\mathrm{Se}2^{\mathrm{i}}\text{-}M1^{\mathrm{iii}}$	0.2597(12)	$\{M1^{\mathrm{iii}}\text{-}\mathrm{Se}2^{\mathrm{i}}\text{-}M1^{\mathrm{i}}\}^*$	92.03(28)
$\{\mathrm{Se}2^{\mathrm{i}}\text{-}M1^{\mathrm{i}}\}^*$	0.2855(07)	$M1^{\mathrm{i}}\text{-}\mathrm{Se}2^{\mathrm{i}}\text{-}M2^{\mathrm{iii}}$	107.91(35)
$\mathrm{Se}2^{\mathrm{i}}\text{-}M2^{\mathrm{iii}}$	0.2396(11)	$M2^{\mathrm{iii}}\text{-}\mathrm{Se}2^{\mathrm{i}}\text{-}M1^{\mathrm{i}}$	103.95(31)
$\mathrm{Se}3^{\mathrm{ii}}\text{-}M1^{\mathrm{iv}}$	0.2609(12)	$\{M1^{\mathrm{iv}}\text{-}\mathrm{Se}3^{\mathrm{ii}}\text{-}M2^{\mathrm{ii}}\}^*$	92.40(27)
$\{\mathrm{Se}3^{\mathrm{ii}}\text{-}M2^{\mathrm{i}}\}^{*\mathrm{i}}$	0.2497(06)	$M2^{\mathrm{ii}}\text{-}\mathrm{Se}3^{\mathrm{ii}}\text{-}M2^{\mathrm{iv}}$	102.45(36)
$\mathrm{Se}3^{\mathrm{ii}}\text{-}M2^{\mathrm{iv}}$	0.2437(11)	$M2^{\mathrm{iv}}\text{-}\mathrm{Se}3^{\mathrm{ii}}\text{-}M1^{\mathrm{ii}}$	107.21(36)

TABLE V. Average values (av) and standard deviation of the bond lengths l and the bond angles $\varnothing$ for $(Ga_{0.60}In_{0.40})_2Se_3$ and $(Ga_{0.40}In_{0.60})_2Se_3$. The average values for the bond lengths or the bond angles between the $(001)_{\text{group III}}$ and $(001)_{\text{Se}}$ layers are denoted by $\text{av}_{(001)}$; the others for the bond lengths along the c axis or the bond angles, whose one side is the bond along the c axis, are denoted by $\text{av}_{[001]}$.

	$(Ga_{0.60}In_{0.40})_2Se_3$		$(Ga_{0.40}In_{0.60})_2Se_3$	
	l (nm)	$\varnothing$ (°)	l (nm)	$\varnothing$ (°)
av	0.2498(61)	104.18(314)	0.2564(141)	102.15(716)
$\text{av}_{(001)}$	0.2492(54)	105.82(151)	0.2527(91)	106.12(280)
$\text{av}_{[001]}$	0.2518(100)	100.08(162)	0.2676(253)	92.22(26)
$\lvert\text{av}_{[001]}-\text{av}_{(001)}\rvert/\text{av}_{(001)}$	1.06%	5.43%	5.89%	13.11%

of wurtzite structure, respectively. Hereafter, these two layers are defined as the $(001)_{\text{group III}}$ layer and the $(001)_{\text{Se}}$ layer. The distances of $d_{0.60}^{A-a}$ and $d_{0.60}^{A-b}$ between the $(001)_{\text{group III}}$ and the $(001)_{\text{Se}}$ layers are 0.2476 and 0.0749 nm. Thus the $d_{0.60}^{A-a}/d_{0.60}^{A-b}$ ratio is 3.3:1, which is very close to ratio 3:1 of the ideal wurtzite.

On the other hand, in case of $(Ga_{0.40}In_{0.60})_2Se_3$, the structural vacancies and group-III atoms are also ordered in screw form, and the $(001)_{\text{group III}}$ and the $(001)_{\text{Se}}$ layers are also arranged alternately with the same sequence of $AaBb$ along the c axis. However, both the layers are waved and the nearest $(001)_{\text{group III}}$ and $(001)_{\text{Se}}$ layers are very close to each other. The distances of $d_{0.40}^{A-a}$ and $d_{0.40}^{A-b}$ between the $(001)_{\text{group III}}$ and $(001)_{\text{Se}}$ layers is 0.2846 and 0.0319 nm, respectively, and the $d_{0.40}^{A-a}/d_{0.40}^{A-b}$ ratio becomes 8.9:1. In other words, it seems as if the group-III and Se layers merge into one atomic layer. Consequently, the $AaBb$ stacking is changed to $\alpha\beta$ stacking as the same sequence of h-BN structure, where α and β denote atomic positions of the merged layers, and the merged aB and bA correspond to α and β, respectively.

Such structural differences can be evaluated by their bond lengths and angles in details. Tables III and IV show the bond lengths and angles for $(Ga_{0.60}In_{0.40})_2Se_3$ and $(Ga_{0.40}In_{0.60})_2Se_3$, respectively, which are evaluated on the basis of tetrahedral bonding structure. The two-coordinated Se atoms are denoted by Se1 and the three-coordinated Se atoms are denoted by Se2 and Se3. The bonds of $\text{Se2}^{\text{i}}\text{-}M1^{\text{i}}$ and $\text{Se3}^{\text{ii}}\text{-}M2^{\text{ii}}$ are nearly along the c axis and the others are between the atoms in the nearest $(001)_{\text{group III}}$ and $(001)_{\text{Se}}$ layers. The average bond lengths between the group-III and Se atoms in $(Ga_{0.60}In_{0.40})_2Se_3$ and $(Ga_{0.40}In_{0.60})_2Se_3$ are 0.2498 and 0.2564 nm, which is in agreement with the estimated tetrahedral bonding distances applying the atomic radius of Ga, In, and Se atoms by Pearson.[9] Table V shows the averages and the standard deviations of the bond lengths and angles for $(Ga_{0.60}In_{0.40})_2Se_3$ and $(Ga_{0.40}In_{0.60})_2Se_3$. The structure of $(Ga_{0.60}In_{0.40})_2Se_3$ is conformed to be based on the tetrahedral bonding structure; the bond lengths are nearly the same and the bond angles are close to the angle of the ideal tetrahedral bonding structure. In case of $(Ga_{0.40}In_{0.60})_2Se_3$, however, the standard deviations of the bond lengths and angles are more than twice the values for $(Ga_{0.60}In_{0.40})_2Se_3$. This implies the existence of two kinds of bonds: one is between the atoms in the nearest $(001)_{\text{group III}}$ and $(001)_{\text{Se}}$ layers and the other is along the c axis. The former bonds show almost same bond lengths and their bond angles are very close to the ideal angle of 109.47°. The later bonds show that the lengths $(\text{Se2}^{\text{i}}\text{-}M1^{\text{i}},\text{Se3}^{\text{ii}}\text{-}M2^{\text{ii}})$ and the angles $(M1^{\text{iii}}\text{-Se2}^{\text{i}}\text{-}M1^{\text{i}},M1^{\text{iv}}\text{-Se3}^{\text{ii}}\text{-}M2^{\text{ii}})$, whose one side is the

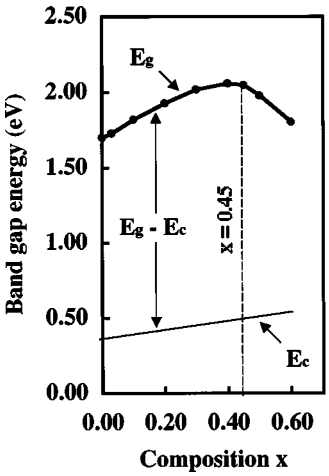

FIG. 4. Schematic diagram shows the dependence of optical band-gap energy on composition in $(Ga_xIn_{1-x})_2Se_3$. E_g and E_c denoted the measured band-gap energy along the c axis and the estimated covalent band energy. The difference between E_g and E_c is considered to be almost contributed by ionic bonding nature.

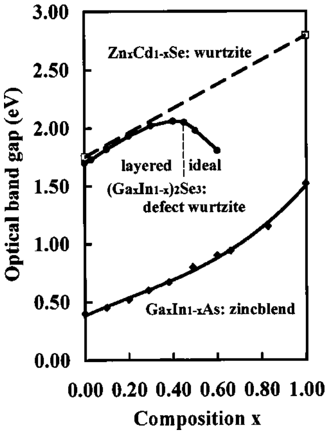

FIG. 5. Comparison of the optical band gaps among the III-V, III_2VI_3, and II-VI compound semiconductors: $Ga_xIn_{1-x}As$, $(Ga_xIn_{1-x})_2Se_3$, and $Zn_xCd_{1-x}Se$ (Refs. 6, 10–12). The band gaps of ZnSe and CdSe are measured along the c axis of wurtzite structure the same as that of $(Ga_xIn_{1-x})_2Se_3$. The dish line denoted the estimated band gap of $Zn_xCd_{1-x}Se$ from the values of ZnSe and CdSe by applying Vegard's law.

bond along the *c* axis, are obviously deviated from the tetrahedral bonding characteristics. The average bond length along the *c* axis is about 6% longer than that between the atoms in the merged (001) layers; the average bond angle ($M1^{\mathrm{iii}}$-Se2^{i}-$M1^{\mathrm{i}}$,$M1^{\mathrm{iv}}$-Se3^{ii}-$M2^{\mathrm{ii}}$) is 13% smaller than the ideal angle of 109.47°.

From the above results, the structure in the Ga-rich region is called the ideal defect wurtzite structure. Meanwhile, the structure in the In-rich region is called the layered defect wurtzite structure, which is obviously deviated from the tetrahedral bonding structure and which shows some structural characteristics of the layered compound such as *h*-BN.

IV. DISCUSSION

In the refinement, the compositions and temperature factors for $M1$ and $M2$, as well as the temperature factors for Se3 and Se3, are fixed to be the same. Essentially, such parameters should be refined independently. We actually tried it but could not obtain significant differences among these parameters due to poor diffraction quality. It is enough, however, to characterize the structural difference between the ideal and layered defect wurtzite structures. Further refinements, including partial ordering of metal atoms in the sites $M1$ and $M2$ and individual temperature factors are still necessary by improving data quality of x-ray diffraction.

The bonding nature of the ideal and layered defect wurtzite structures are obviously different to each other. In the ideal defect wurtzite structure, the bond lengths and angles are almost equal, so that each bond possesses uniform covalent and ionic components. In the layered defect wurtzite structure, however, the bond lengths along the *c* axis are obviously longer than those between the atoms in the merged (001) layers. In addition, the bond angles whose one side is the bond along the *c* axis are deviated far from 109.47° and almost equal to 90°. Consequently, the bonds are not uniform any longer and the bonds in the merged (001) layers become much stronger than those along the *c* axis. Moreover, the *c* parameter of the layered defect wurtzite structure is much smaller than that of the ideal one, although the layered defect wurtzite structure appears in an In-rich region. These facts imply that overall bondings in the layered defect wurtzite structure become much stronger than those in the ideal one. It is suggested that extra ionic bondings act in the merged (001) layers and make the *c* parameter of the layered defect wurtzite much smaller than that of the ideal one.

Such consideration can also explain the anomalous dependence of the optical band gap on composition *x*. Figure 4 shows the relationship between the measured optical band gap E_g and composition *x* together with the estimated covalent band energy E_c. Since the purely covalent materials Ge and α-Sn, as the same periodic elements of Ga, Se, and In, are well known to possess the band gaps of 0.66 and 0.08 eV, respectively, the E_c is estimated from the band-gap data by applying Vegard's law. It is found that with the increasing of composition *x* from 0.00 to 0.60, E_c only increases from 0.37 to 0.55 eV; these values are much smaller than the band-gap energy E_g. This means that the band-gap energy E_g is almost originated from the ionic bonding nature and the ionic bonding nature is dominant for both the defect wurtzite structures. In the In-rich region with composition *x* from 0.00 to 0.45, the difference ΔE between E_g and E_c is much larger than E_c, although E_c increases a little with the increasing Ga content. In the Ga-rich region with composition *x* from 0.45 to 0.70, the ΔE abruptly decreases although E_c continues to become larger with increasing Ga content. This indicates that the abrupt decrease of the ΔE in the Ga-rich regions is due to the loss of the extra ionic bonding. Therefore, ionic bonding is dominant in both the defect wurtzite structures and the additional ionic binding acts between the merged (001) layer in the layered defect wurtzite.

These results also can be confirmed by making a comparison of the band gaps among the III-V, $\mathrm{III_2VI_3}$, and II-VI compound semiconductors. Figure 5 shows the band gaps of $(\mathrm{Ga}_x\mathrm{In}_{1-x})\mathrm{As}$, $(\mathrm{Zn}_x\mathrm{Cd}_{1-x})\mathrm{Se}$, and $(\mathrm{Ga}_x\mathrm{In}_{1-x})_2\mathrm{Se}_3$ as the representatives with the same periodic elements of Ga, Zn, As, and Se or Cd and In. The band gap of the $\mathrm{III_2VI_3}$ with either the layered or ideal wurtzite structure is much closer to the value of the wurtzite-type II-VI compound rather than that of the zincblend-type III-V compound. This seems reasonable because the ionicity of the anion in $\mathrm{III_2VI_3}$ is the same as that of II-VI and the ionicity is responsible for the band gap of compound semiconductors. In other words, $\mathrm{III_2VI_3}$ compound semiconductors can be regarded as one of the relatives of II-VI compounds. Furthermore, the band gap of the layered defect wurtzite structures is almost equal to the value of the II-VI compounds; meanwhile the band gap of the ideal defect wurtzite structure tends to be far from that. This remarkable difference is originated from the extra ionic bonding in the layered defect wurtzite structure as stated above. Therefore, the structural difference between the layered and ideal defect wurtzite structures can be distinguished from the viewpoint of electronic structure although their space groups and basic structures are the same. The structural feature of the layered defect wurzite is a unique one: it is a layered one but still holds sp^3-like bonds. Such a feature comes from the ordered arrangement of structural vacancies in the defect wurtzite, and is never realized in the usual wurtzite structure or *h*-BN-type structure.

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