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Relations between compositional modulation and atomic ordering degree in thin films of ternary III–V semiconductor alloys*

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This paper derives the expressions for the ordering degree and the modulation factor of A and B atoms in $A_xB_{1-x}C$ epilayers of ternary III–V semiconductor alloys. Using these expressions, it identifies quantitatively the alternating atom-enhanced planes, compositional modulations, atomic ordering degree on the group-III sublattices and the fine structure of NMR spectra.

Keywords: atomic ordering degree, enhanced factor, ternary III–V semiconductor alloy, thin film
PACC: 6890, 6860, 6116N

Various epitaxial techniques have been utilized for growing thin films of ternary III–V semiconductor alloys $A_xB_{1-x}C$, including $Ga_xIn_{1-x}P$ and $Al_xGa_{1-x}As$ epilayers, because of its usefulness in optoelectronics and electronic devices.

All experiments, including transmission electron microscopy (TEM),[1−3] atomic force microscopy,[4,5] electron diffraction,[2] x-ray diffraction (XRD)[2,6,7] and nuclear magnetic resonance (NMR)[8,9] demonstrated that in $A_xB_{1-x}C$ epilayers A and B atoms on their group III sublattices often show spontaneously partially ordered structure because of surface-induced effects.[10,11] In partially ordered domains of $A_xB_{1-x}C$ epilayers, as shown in Fig.1, the existence of alternating A- and B-enhanced planes on the group-III sublattices along (111) (CuPt-type) has been observed.[2,6] It also has been both experimentally and theoretically verified that the ordering of A and B atoms on their group III sublattices in $A_xB_{1-x}C$ epilayers decreases the bandgaps[12,13] and has an obvious influence on the material's electronic structure, phase transitions, thermodynamic stability, optical, magnetic, mechanical and transport properties.[13−20] A and B atoms on their group-III sublattices in $A_xB_{1-x}C$ epilayers, grown by different conditions and techniques, may show different types of ordering, including CuPt-, CuAu- and clustering-type, along different directions.[9]

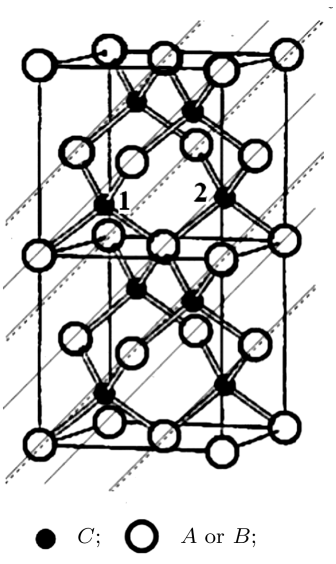


Fig.1. Schematic diagram of a $A_xB_{1-x}C$ epilayer with A- and B-enhanced planes in the group-III sublattices along the (111) direction.

In this paper, we study the relations between compositional modulation and atomic ordering degree in the thin films of ternary III–V semiconductor alloys.

In XRD,[6] we have introduced enhanced factor

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ε ($0 \leq \varepsilon \leq 0.5$). If A and B atoms in a $A_xB_{1-x}C$ epilayer are distributed randomly on their group-III sublattices, there is $\varepsilon = 0$. And then, $(0.5 + \varepsilon)$ represents the ordering degree for A and B atoms in the $A_xB_{1-x}C$ epilayer, that is, represents the probability of A atom on the A-enhanced plane and B atom on the B-enhanced plane, respectively.

We can take

$$S = 2\varepsilon, \tag{1}$$

where S is called the order parameter.

It is well known that the partially ordered structure of A and B atoms leads to the compositional modulation in the $A_xB_{1-x}C$ epilayer, i.e.

$$A_xB_{1-x}C \xrightarrow{\text{compositional modulation}} (A_{x+y}B_{1-x-y}C)_1(A_{x-y}B_{1-x+y}C)_2. \tag{2}$$

We have indicated that the modulation factor y can be determined by the composition x and enhanced factor ε[6] as follows:

$$y = \begin{cases} x(0.5-\varepsilon) = x(0.5 - S/2), & x \leq 0.5, \\ (1-x)(0.5-\varepsilon) = (1-x)(0.5-S/2), & x \geq 0.5. \end{cases} \tag{3}$$

From Eq.(3), when $0.5+\varepsilon = 1$ (i.e. $S = 1$), $y = 0$. It correctly indicates that when the $A_xB_{1-x}C$ epilayer shows perfectly ordered structure (i.e. A atoms are situated on A-enhanced plane and B atoms on B-enhanced plane), then, the compositional modulation automatically disappears. Figure 1 represents the schematic diagram of an $A_xB_{1-x}C$ epilayer with A- and B-enhanced planes in the group-III sublattices along (111) direction.

As shown in the compositional modulation Eq.(2) and Fig.1, a C atom can bond with the most neighbouring A and B atoms according to the following five types: (1) a C atom bonds with four A atoms, including $(A)_1^3(A)_2^1$ and $(A)_1^1(A)_2^3$; (2) a C atom bonds with three A and one B atoms, including $(A)_1^3(B)_2^1$, $(B)_1^1(A)_2^3$, $3(B)_1^1(A)_1^2(A)_2^1$ and $3(A)_1^1(A)_2^2(B)_2^1$; (3) a C atom bonds with two A and two B atoms, including $3(A)_1^1(B)_1^2(A)_2^1$, $3(A)_1^2(B)_1^1(B)_2^1$, $3(A)_1^1(A)_2^1(B)_2^2$ and $3(B)_1^1(B)_2^1(A)_2^2$; (4) a C atom bonds with one A and three B atoms, including $(A)_1^1(B)_2^3$, $(B)_1^3(A)_2^1$, $3(A)_1^1(B)_1^2(B)_2^1$ and $3(B)_1^1(A)_2^1(B)_2^2$; (5) a C atom bonds with four B atoms, including $(B)_1^3(B)_2^1$ and $(B)_1^1(B)_2^3$; where the superscript denotes the number of atoms and the subscript denotes the part 1 or part 2 in the compositional modulation equation (2). Suppose the relative intensities of five spectra, given by the above mentioned five types, are proportional to the products of compositions of A and B atoms in compositional modulation equation (2), and then, the relative intensities I'_n ($n = 4, 3, 2, 1, 0$) of five spectra, showing the ordering degree of A and B atoms in the $A_xB_{1-x}C$ epilayer, can be directly derived from the above mentioned five bonding types:

$$\begin{aligned}
I'_4 &= [(x+y)_1^3(x-y)_2 + (x-y)_2^3(x+y)_1], \\
I'_3 &= (x+y)_1^3(1-x+y)_2 + (1-x-y)_1(x-y)_2^3 \\
&\quad +3[(1-x-y)_1(x+y)_1^2(x-y)_2 \\
&\quad +(1-x+y)_2(x-y)_2^2(x+y)_1], \\
I'_2 &= 3[(x+y)_1(1-x-y)_1^2(x-y)_2 \\
&\quad +(x+y)_1(x-y)_2(1-x+y)_2^2 \\
&\quad +(1-x+y)_2(x-y)_2^2(1-x-y)_1 \\
&\quad +(x+y)_1^2(1-x-y)_1(1-x+y)_2], \\
I'_1 &= (x+y)_1(1-x+y)_2^3 + (x-y)_2(1-x-y)_1^3 \\
&\quad +3[(x+y)_1(1-x-y)_1^2(1-x+y)_2 \\
&\quad +(x-y)_2(1-x+y)_2^2(1-x-y)_1], \\
I'_0 &= (1-x-y)_1^3(1-x+y)_2 \\
&\quad +(1-x-y)_1(1-x+y)_2^3.
\end{aligned}$$

They can be simplified as

$$\begin{aligned}
I_n &= I'_n/2 \\
&= \binom{4}{n}\left[x^n(1-x)^{4-n} + (-1)^{n+1}y^4\right].
\end{aligned} \tag{4}$$

Equations (3) and (4) indicate that the relative intensities of five spectra are dependent on the composition x and enhanced factor ε.

Tycko *et al*[8] have measured the fine structure of the spectra of $Ga_{0.515}In_{0.485}P$ epilayers by ^{31}P NMR, obtained with magic angle spinning, and have calculated the areas under these spectra. Revising the mis-

take in calculating the area $A_2^{\dagger}$, made by Tycko *et al*,[8] we can also obtain Eq.(4).

The partially ordered structure of the $Ga_xIn_{1-x}P$ ($x \sim 0.5$) epilayer even though with a larger bandgap $E_g = 1.89\,eV$ also has been directly observed in terms of both selected-area electron diffraction pattern and imaging in TEM.[2] Therefore, the samples of $Ga_{0.515}In_{0.485}P$ epilayers with bandgaps from 1.81 to 1.88 eV, made by Tycko *et al*,[8] might have the ordered structure from higher to low. Suppose $Ga_{0.515}In_{0.485}P$ epilayers show higher ($E_g = 1.81\,eV$, $x = 0.515$, $\varepsilon = 0.35$, $S = 0.7$ and $y = 0.0728$) and low ($E_g = 1.88\,eV$, $x = 0.515$, $\varepsilon = 0.1$, $S = 0.2$ and $y = 0.19$) ordered structures, then the intensity ratio of these five spectra, given by Eq.(4), are equal to $1 : 4.25 : 6.77 : 4.79 : 1.27$ and $1 : 4.47 : 6.79 : 5.02 : 1.28$, respectively. The above calculations are in good agreement with the experimental results.[8] The incorrect relationship $S = 2y$, used by Tycko *et al*,[8] certainly led to the largest compositional modulation and led to the largest deviation from the experimental results,[8] when a $Ga_xIn_{1-x}P$ epilayer has a higher ordered structure.

Degen *et al*[9] have measured the relative intensities I_0 andI_4 of NMR spectra in $Al_{0.297}Ga_{0.703}As$ epilayer, grown by metal organic vapour phase epitaxy, and have derived the expressions for three types of ordering, including CuPt-, CuAu- and clustering-types. Degen *et al*[9] also wrongly used S/2 to substitute y and it should be revised as $y = x(0.5 - S/2)$. Then, we obtain

$$(I_0/I_4)_{\text{cal.}}^{\text{CuAu}} = \left\{[(1-x)^2 - y^2]/(x^2 - y^2)\right\}^2. \quad (5)$$

Under conditions of $x = 0.297$, $\varepsilon = 0.25$, $S = 0.50$ and $y = x(0.5 - S/2) = 0.074$, we have

$$(I_0/I_4)_{\text{cal.}}^{\text{CuAu}} = \left\{[(1-x)^2 - y^2]/(x^2 - y^2)\right\}^2 = 34.9.$$

And, it is in good agreement with the experimental value $(I_0/I_4)_{\text{exp}} = 35$ (see Ref.[9]).

It means that Al- and Ga-atoms on the group-III sublattices in $Al_{0.297}Ga_{0.703}As$ epilayer show CuAu-type ordering along (001) direction with enhanced factor $\varepsilon = 0.25$, modulation factor $y = 0.074$, and order parameter $S = 0.50$. Therefore, the conclusions given by Tycko[8] and Degen,[9] including that $Ga_{0.515}In_{0.485}P$ and $Al_{0.297}Ga_{0.703}As$ epilayers show the disorder structure, are incorrect.

In this paper, we have derived the expressions for the ordering degree and the modulation factor of A and B atoms in $A_xB_{1-x}C$ epilayers of ternary III–V semiconductor alloys. By using these expressions, we can identify correctly the alternating atom-enhanced planes, compositional modulation, atomic ordering degree on the group-III sublattices and the fine structure of NMR spectra of $A_xB_{1-x}C$ epilayers.

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[†] In the Ref.[8], the area A_2 should be revised as
$A_2 = 1.5[(x+y)(1-x-y)^2(x-y) + (x+y)(x-y)(1-x+y)^2 + (1-x+y)(x-y)^2(1-x-y) + (x+y)^2(1-x-y)(1-x+y)]$.
Assistant Editor A. Loudon has informed one (JCL) of us that R. Tycko *et al* will publish an erratum on ≪ Physical Review B ≫.