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Pressure dependence of the band gap energy for the dilute nitride GaN_xAs_{1-x}

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A model is developed to describe the pressure dependence of the band gap energy for the dilute nitride GaN_xAs_{1-x}. It is found that the sublinear pressure dependence of E_- is due to the coupling interaction between E_+ and E_-. We have also found that GaN_xAs_{1-x} needs much larger pressure than GaAs to realize the transition from direct to indirect band gap. It is due to two factors. One is the coupling interaction between the E_+ and E_-. The other is that the energy difference between the X conduction band minimum (CBM) and the Γ CBM in GaN_xAs_{1-x} is larger than that in GaAs. In addition, we explain the phenomenon that the energy difference between the X CBM and the Γ CBM in GaN_xAs_{1-x} is larger than that in GaAs. It is due to the impurity-host interaction.

Keywords: *GaNAs; band gap energy; pressure dependence; dilute nitride*

1. Introduction

GaN_xAs_{1-x} has attracted much attention due to its interesting electronic properties and potential applications in microelectronic and optoelectronic devices. Unlike the conventional III – V semiconductor alloys, the band gap energy of the dilute nitride GaN_xAs_{1-x} decreases rapidly relative to that of bulk GaAs despite the fact that the band gap energy of GaN is much larger than that of GaAs [1–5]. The rapid reduction of the band gap energy can be described by the band-anticrossing (BAC) model [3, 4]. It should be noted that the BAC model is not only proposed to describe the composition dependence of the band gap energy for the dilute nitride GaN_xAs_{1-x}, but is also proposed to describe its pressure dependence. Although the BAC model describes the band gap energy of the dilute nitride GaN_xAs_{1-x} alloy depending on composition as well as pressure, there are still several problems which should be further investigated. The first one is that the BAC model is too simple to interpret the optical properties of the dilute nitride alloys because many effects are not included in the model. The second one is that more and more evidences prove that E_+ (the optical transition between the valence band and the second conduction subband) for the dilute nitride alloys evolves from the splitting of the L conduction band minimum (CBM) rather than the N level [6–8], which makes some scholars doubting whether it is reasonable to use the BAC model to explain the formation of E_+ and E_- (It is the Γ conduction band of the dilute nitride alloy. It also corresponds to the band gap energy of the dilute nitride alloys). In addition, there are three coupling interactions in GaN_xAs_{1-x}. One is the impurity-host interaction, another is the impurity-impurity interaction, the other is the host-host interaction. Deng et al. [5] considered that the BAC model should be expanded to include the impurity-host interaction, host-host interaction and the impurity-impurity interaction to give a complete description of the band structure of the dilute nitride alloys. In order to solve the above problems, we have developed a model.

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The model can describe the pressure dependence of the band gap energy for the dilute nitride GaN_xAs_{1-x} very well.

2. Physical model and discussion

Before presenting the model, let us analyze the band evolution of the dilute nitride GaN_xAs_{1-x}. When the N content is very small, incorporation of N in GaAs can introduce an isolate N level. With increasing the N content, on the one hand, two or more N atoms may be bonded to one Ga atom, leading to the formation of N–N pairs (containing two N atoms in the vicinity) and N clusters (three or more N atoms are included). These configurations correspond to different N-related impurity states and have different self-energy values, lower than the isolated N level [9]. On the other hand, these N-related impurity states mix with the states of the host material and form the mixed states. We can call them alloy states. When the N content is up to 0.2 %, the band E_+ is formed [3]. Under this condition, the mixing between the N-related impurity states and the host states is not sufficient. As the energy levels of the localized impurity states depending on pressure are much weaker than that of the extended host states, we can distinguish the energy levels of the localized and extended states by their different pressure behaviors. When the N content is large enough, the mixing between the N-related impurity states and the host states is sufficient. The alloy states are very stable. Under this condition, the applied pressure can no longer separate the N-related impurity states from the alloy states as distinct levels. The energy levels which different states correspond to cannot be distinguished by pressure [10].

Fig. 1 shows the pressure dependence of E_+ and E_- for $GaN_{0.015}As_{0.985}$ [11]. It can be seen that both E_+ and E_- move to higher energy as the pressure increases. However, an obvious difference between them can be found. The experimental data show that band E_+ increases superlinearly with increasing pressure while the pressure dependence of E_- is sublinear with a tendency of saturation at high pressure. It is also found that when the pressure is low, the increase of E_+ is lower than that of E_-. When the pressure is large enough, the situation is contrary. The increase of E_- is lower than that of E_+.

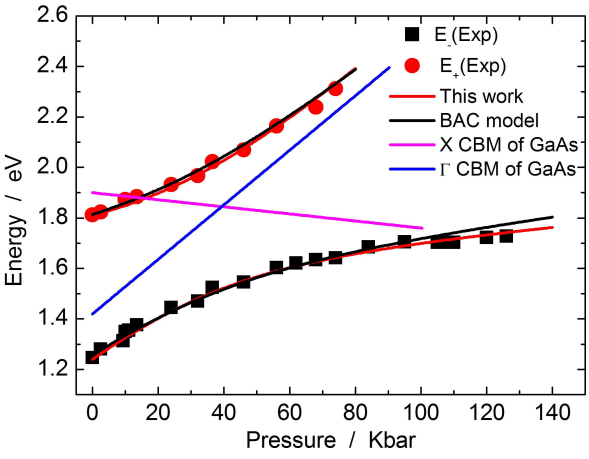

Fig. 1. Pressure dependence of E_+ and E_- for the dilute nitride GaN_xAs_{1-x}. The experimental data are from the literature [11].

If we want to explain the pressure dependence of E_+ and E_-, we must understand the coupling interactions in GaN_xAs_{1-x}. It is well known that there are three coupling interactions (the impurity-host interaction, the impurity-impurity interaction and the host-host interaction) in GaN_xAs_{1-x}. As the band evolution of the dilute nitride alloys is determined by the three coupling interactions, the best way to describe the pressure dependence of the band gap energy of the dilute nitride GaN_xAs_{1-x} is to take into account the three coupling interactions.

For $GaN_{0.015}As_{0.985}$, we consider that the deviation of the linearity for E_+ and E_- is due to the coupling interaction between E_+ and E_-. The reason is as follows. (1) For $GaN_{0.015}As_{0.985}$, the alloy states E_+ and E_- should be very stable. The energy levels which the localized and extended states correspond to cannot be filtered from both of them by applying pressure. When the pressure is introduced to change the interaction between the bands, both E_+ and E_- will interact with other bands as an individual band. (2) If the deviation of the linearity for E_+ and E_- is considered to be due to the coupling interaction between E_+ and E_-, three coupling interactions in GaN_xAs_{1-x} are taken into account

because the alloy states which E_+ and E_- correspond to include the N state and the perturbed host state.

Based on this analysis, we consider that the pressure can influence the band E_+ and E_- from two aspects. On the one hand, the pressure can lead to E_+ and E_- increasing similar to the bands in the conventional semiconductors. On the other hand, the hybridization effect between the states (which E_+ and E_-corropond to) becomes obvious when the pressure increases. The effect can push E_+ up and E_- down, leading to E_+ increasing superlinearly and E_- increasing sublinearly. As the hybridization effect is due to the pressure, the coupling interaction between E_+ and E_- should be dependent on pressure. When the pressure becomes large, the coupling interaction between them should increase.

Based on the above analysis, several assumptions are made: (1) Without considering the coupling interaction between E_+ and E_-, the bands E_+ and E_- increase linearly with increasing pressure. (2) The deviation of the linearity for E_+ and E_- is due to the coupling interaction between them. (3) The coupling interaction between E_+ and E_-depending on pressure can be in analogy to the coupling interaction between the N level and the Γ CBM of the host material depending on N content in the BAC model.

Based on the assumption (1), $E_{+,(P)}$ and $E_{-,(P)}$ without considering the coupling interaction between E_+ and E_- can be given as follows:

$$E_{+,(P)} = E_+(0) + \alpha Ps \tag{1}$$

$$E_{-,(P)} = E_-(0) + \beta P \tag{2}$$

where $E_+(0)$ is the energy of E_+ at 0 GPa and $E_-(0)$ is the energy of E_- at 0 GPa. α and β are pressure coefficients for $E_+$and E_- without considering the coupling interaction between E_+ and E_-, respectively.

Based on the assumption (2), the matrix can be given in the following expression:

$$\begin{vmatrix} E_{+,(P)} - E & V \\ V & E_{-,(P)} - E \end{vmatrix} = 0 \tag{3}$$

where V is the matrix element coupling E_+ and E_-. In the BAC model, the coupling interaction between the N level and the Γ CBM of the host material depending on N content can be given in the following equation:

$$V = C_{MN}\sqrt{x} \tag{4}$$

where C_{MN} is the coupling constant and x is the N content. Based on the assumption (3), the coupling interaction between E_+ and E_- can be given in the following form:

$$V = C_{E_+-E_-}\sqrt{\frac{P}{P_0}} \tag{5}$$

where $C_{E_+-E_-}$ is a parameter which describes the coupling strength between E_+ and E_-. It can be determined by fitting the experimental data. P_0 is an empirical parameter. In this work, $P_0 = 50$ GPa is used.

Based on equation 1, equation 2, equation 3, and equation 5, two solutions can be written as:

$$E(P)_{\pm} = \frac{1}{2}\left[E_{+(0)} + \alpha P + E_{-(0)} + \beta P \pm \sqrt{(E_{+(0)} + \alpha P - E_{-(0)} - \beta P)^2 + 4(C_{E_+-E_-})^2\frac{P}{P_0}}\right] \tag{6}$$

We use the model to fit the experimental data of E_+ and E_- for $GaN_{0.015}As_{0.985}$. In this work, $E_{-(0)}$ and $E_{+(0)}$ are obtained according to the experimental data. Here $E_{-(0)} = 1.24$ eV and $E_{+(0)} = 1.81$ eV are used [11]. The best agreement with the experimental data, as denoted by solid lines in Fig. 1, is obtained by setting $\alpha = 1.0 \times 10^{-2}$ eV/GPa, $\beta = 1.2 \times 10^{-1}$ eV/GPa and $C_{E_+-E_-} = 2.7$ eV in the model. We also used the BAC model to fit the experimental data. The result for the BAC model is also shown in Fig. 1. Compared with the BAC model, it can be seen that the model developed in this work can describe the experimental data better. The pressure coefficient for E_- shows that if the hybridization effect is not taken into account, the Γ conduction band of GaN_xAs_{1-x} is extended. The small pressure coefficient for E_+ may be due to the influence of the N level as the location of E_+ is very close to the isolate N level.

The Γ CBM and the X CBM of GaAs depending on pressure are also shown in Fig. 1. It can be seen that the Γ CBM of GaAs moves up to higher energy rapidly with increasing pressure while the X CBM of GaAs moves down to lower energy. The energy difference between the Γ CBM of GaAs and the X CBM of GaAs becomes small with increasing pressure. When the pressure is large enough, the energy difference between them becomes zero. Under this condition, if the pressure goes on increasing, the X CBM of GaAs will be lower than the Γ CBM of GaAs and the band gap of GaAs will change from the direct band to the indirect band gap. It is reported that the pressure which the crossover between the X CBM of GaAs and the Γ CBM of GaAs corresponds to is 3.9 GPa to 4.2 GPa [12–15]. For GaN_xAs_{1-x}, it is found that when the pressure does not exceed 12 GPa, GaN_xAs_{1-x} still has a direct band gap, which shows that GaN_xAs_{1-x} needs much larger pressure than GaAs to realize the transition from the direct band gap to the indirect band gap. It is due to two factors. One is the coupling interaction between the E_+ and E_-. The other is that the energy difference between the X CBM and the Γ CBM in GaNAs is larger than that in GaAs.

Let us examine the first factor in great detail. Usually, the pressure dependence of the X CBM is much weaker than that of the Γ CBM so the difference of the pressure dependence between the X CBM of GaNAs and the X CBM of GaAs should be small. However, it is found that the pressure dependence of the Γ CBM for GaNAs is much weaker than that for GaAs. The reason is as follows. In GaAs, E_+ does not exist so there is no E_+ to influence the movement of the Γ CBM of GaAs. In GaN_xAs_{1-x}, the Γ CBM of GaN_xAs_{1-x} increases more slowly with increasing pressure than that of GaAs due to the coupling interaction between E_+ and E_-.

It is an interesting question why the energy difference between the X CBM and the Γ CBM in GaN_xAs_{1-x} is larger than that in GaAs. It is due to the impurity-host interaction. We know that the incorporation of N dopant in GaAs introduces a localized N level. When the N content is large, the coupling interaction between the localized N level and the Γ CBM of GaAs is very large. Because of the strong coupling interaction between them, the Γ CBM of GaN_xAs_{1-x} will be pushed down as the energy of the Γ CBM of GaAs is lower than that of the N level. For the X CBM of GaN_xAs_{1-x}, we know that it evolves from the X CBM of GaAs. In studying GaN_xP_{1-x} alloy, it is found that the coupling interaction exists between the N level and the X CBM of GaP [16–18]. As GaN_xAs_{1-x} alloy is similar to GaN_xP_{1-x} alloy, the coupling interaction should also exist between the X CBM of GaAs and the N level. As the X CBM of GaAs lies above the N level, the coupling interaction between them should inhibit the decline of the X CBM of GaN_xAs_{1-x}, leading to the X CBM of GaN_xAs_{1-x} decreasing more slowly than the Γ CBM of GaN_xAs_{1-x}. This is the reason for that the energy difference between the X CBM and the Γ CBM in GaN_xAs_{1-x} is larger than that in GaAs.

It should be pointed out that the pressure dependence of the band gap for GaN_xAs_{1-x} is very different from that for GaN_xP_{1-x} [16]. For the dilute nitride GaN_xP_{1-x}, as the energy difference between the X CBM of GaNP and the Γ CBM of GaN_xP_{1-x} is very small, it does not need large pressure to realize the transition from direct to indirect band gap. The small energy difference between the X CBM and the Γ CBM in GaNP is mainly due to that the Γ CBM of GaN_xP_{1-x} evolves from the N level while the location of the N level in GaP is close to the X CBM of GaP.

3. Conclusions

In conclusion, we analyze the band evolution of the dilute nitride GaN_xAs_{1-x}. It is found that the sublinear pressure dependence of the band gap energy is due to the coupling interaction between E_+ and E_-. A model is developed to describe the pressure dependence of the band gap energy. The model may be used to describe the pressure dependence of the band gap energy for other dilute nitride alloys. We also find that it needs much larger pressure for GaN_xAs_{1-x} than for GaAs to realize the transition from the direct band gap to the indirect band gap. It is due to two factors. One is the coupling

interaction between the E_+ and E_-. The other is that the energy difference between the X CBM and the Γ CBM in GaNAs is larger than that in GaAs.

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