Pressure dependence of the band gap energy for dilute nitride and antimony $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$

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Dilute nitride and antimony GaNAsSb alloy can be considered as an alloy formed by adding N and Sb atoms into the host material GaAs. Under this condition, its band gap energy depending on pressure can be divided into two regions. In the low pressure range, the band gap energy is due to two factors. One is the coupling interaction between the N level and the Γ conduction band minimum (CBM) of GaAs. The other one is the coupling interaction between the Sb level and the Γ valence band maximum (VBM) of GaAs. In the high pressure range, the band gap energy depends also on two factors. One is the coupling interaction between the N level and the X CBM of GaAs. The other one is the coupling interaction between the Sb level and the Γ VBM of GaAs. In addition, it has been found that the energy difference between the Γ CBM and the X CBM in GaNAsSb is larger than that in GaAs. It is due to two factors. One is the coupling interaction between the N level and the Γ CBM of GaAs. The other is the coupling interaction between the N level and the X CBM of GaAs.

Keywords: GaNSbAs; N level; band gap energy; Sb level; dilute nitride

1. Introduction

Dilute nitride and antimony $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$, has attracted a great deal of attention due to its unusual properties and promising applications in optoelectronic devices operating at the wavelength of $1.55\ \mu\text{m}$ [1]. Compared with $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{As}_{1-y}$, the advantage of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ is that its band gap energy is lower than that of $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{As}_{1-y}$ with equivalent In content for a the given N composition. Similarly to $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{As}_{1-y}$, the band gap energy of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ exhibits a very large band gap bowing [2, 3]. Usually, the band gap energy of dilute nitride alloys, depending on composition, can be described by the band anticrossing (BAC) model [4–7]. For $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$, it is found that its composition dependence of the band gap energy cannot be described well only by using the simple BAC model. In order to solve this problem, Lin et al. used a double BAC model to calculate the band structure of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$. The double BAC model can be considered as a combination of a conduction BAC (CBAC) model

and a valence BAC (VBAC) model [2, 8]. It has been found that the results are in good agreement with the experimental data. Wang et al. reported the pressure dependence of the band gap energy for $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ [9, 10]. It is surprising to find that when the pressure is high enough, the direct band gap of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ can be changed into the indirect band gap. Although Wang et al. have analyzed the physical mechanism of the phenomenon [9], there are still several problems to be solved. One problem is how the coupling interaction between the N level and the Γ CBM of GaAs (hereafter, we call it the N- Γ CBM coupling interaction) influences the pressure dependence of the band gap energy of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$. The second one is whether the N- Γ CBM coupling interaction is the only factor influencing the pressure dependence of the band gap energy. The third one is why dilute nitride and antimony $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ needs larger pressure to realize the transformation from the direct band gap to the indirect band gap than GaAs. In this paper, these problems will be discussed.

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2. Theoretical consideration

Dilute nitride and antimony $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ alloy can be considered as an alloy formed by adding a small quantity of N and Sb atoms into GaAs. Under this condition, GaAs is the host material. If we want to understand the pressure dependence of the band gap energy of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$, the band evolution of the Γ CBM and the Γ VBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ depending on pressure should be known, and the effect of N and Sb contents on the pressure dependence of the Γ CBM and the Γ VBM of GaAs should be clarified.

Fig. 1. Dependence of the bandgap energy of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ on pressure. The experimental data are from the literature [9].

Fig. 1 shows the experimentally observed pressure dependence of the band gap energy of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ measured by photoluminescence (PL) [9, 10]. It can be seen that the band gap energy increases sublinearly with increasing pressure in the low pressure region. One reason for the sublinear increase of the band gap energy with pressure is the N- Γ CBM coupling interaction. It is well known that both the N level and the Γ CBM of GaAs can shift to the higher energy with increasing pressure. However, the Γ CBM of GaAs increases much faster than the localized N level [11, 12], so the energy difference between them becomes smaller. The decrease of the energy difference can enhance the N- Γ CBM coupling interaction. The enhanced N- Γ CBM coupling interaction can inhibit the increase of the Γ CBM of

$\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$, causing that the pressure dependence of the Γ CBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ is weaker than that of GaAs.

Fig. 2. Dependence of the bandgap energy of $\text{GaN}_{0.005}\text{As}_{0.973}\text{Sb}_{0.022}$ and $\text{GaN}_{0.015}\text{As}_{0.985}$ on pressure. The experimental data are from the literature [9, 11].

If the pressure dependence of the band gap energy at Γ was only due to the N- Γ CBM coupling interaction, two phenomena should be observed. (1) The pressure dependence of the band gap energy for $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ should be as strong as that of the $\text{GaN}_x\text{As}_{1-x}$ on the condition that the N contents in $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ and $\text{GaN}_x\text{As}_{1-x}$ are the same. The reason is that the N- Γ CBM coupling interaction in $\text{GaN}_x\text{As}_{1-x}$ should be as large as that in $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ when $\text{GaN}_x\text{As}_{1-x}$ and $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ have the same N content. (2) If the $\text{GaN}_x\text{As}_{1-x}$ has a larger N content than $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$, the pressure dependence of $\text{GaN}_x\text{As}_{1-x}$ should be weaker than that of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$. The reason is that the larger the N content is, the stronger is the N- Γ CBM coupling interaction. Fig. 2 shows the pressure dependence of the band gap energy of $\text{GaN}_{0.015}\text{As}_{0.985}$ and $\text{GaN}_{0.005}\text{As}_{0.973}\text{Sb}_{0.022}$ [11]. It has been found that although the N content in $\text{GaN}_{0.015}\text{As}_{0.985}$ is larger than that in $\text{GaN}_{0.005}\text{As}_{0.973}\text{Sb}_{0.022}$, the pressure dependence of the band gap energy of $\text{GaN}_{0.005}\text{As}_{0.973}\text{Sb}_{0.022}$ is weaker than that of $\text{GaN}_{0.015}\text{As}_{0.985}$. The phenomenon shows that if the N content in $\text{GaN}_x\text{As}_{1-x}$ is as large as that in $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$, the pressure dependence of the

band gap energy of $\text{GaN}_x\text{As}_{1-x}$ should be stronger than that of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$, which suggests that there should be another factor which can influence the pressure dependence of the band gap energy of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$.

It has been reported that a Sb level lying below the Γ VBM of GaAs should be introduced after the incorporation of Sb atoms into GaAs. The coupling interaction between the Sb level and the Γ VBM of GaAs (hereafter, we call it the Sb- Γ VBM coupling interaction) can push the Γ VBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ up, leading to the reduction of the band gap energy [2]. Here, we consider that the Sb- Γ VBM coupling interaction may be another factor which influences the pressure dependence of the band gap energy. The reason is as follows. We know that the Γ VBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ evolves from the Γ VBM of GaAs. The Γ VBM of GaAs decreases with increasing pressure [13]. When the pressure is applied, the pressure dependence of the Sb level should be weaker than that of the Γ VBM of GaAs as the Sb level is a localized level. Under this condition, the energy difference between the Γ VBM of GaAs and the Sb level decreases. The decrease of the energy difference can enhance the Sb- Γ VBM coupling interaction. The enhanced Sb- Γ VBM coupling interaction can inhibit the declining of the Γ VBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$, causing that the pressure dependence of the band gap energy of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ is weaker than that of $\text{GaN}_x\text{As}_{1-x}$ with the same N content.

The decrease of the band gap energy with pressure in the high pressure range in Fig. 1 is relative to the movement of the X CBM and the Γ VBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$. The pressure dependence of the band gap energy in this pressure range is due to two factors. One is the Sb- Γ VBM coupling interaction. We have deduced the factor based on the above analysis. The other is the coupling interaction between the N level and the X CBM of GaAs (hereafter, we call it the N-X CBM coupling interaction). It should be noted that the N-X CBM coupling interaction cannot be too large. The reason is as follows. The X states are essentially antibonding p-like, while the N localized states are s-like with the same A1 symmetry as the states of Γ CBM of GaS, so the X-N coupling should be small. From

Fig. 1, we can see that the pressure dependence of the band gap energy of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ at X is only a little larger than that of GaAs at X, which shows that the N-X CBM coupling interaction indeed has a small influence on the pressure dependence of the X CBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$.

In order to describe the pressure dependence of the band gap energy of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$, the model developed in literature [14] has been used. The model in literature [14] can be written as follows:

$$E_g(P) = E_{g(0)} - \frac{\alpha P^2}{P + \beta} - \frac{\sigma_0^2}{\lambda P} (P \geq P_0) \quad (1)$$

$$E_g(P) = E_{g(0)} - \frac{\alpha P_0^2}{P_0 + \beta} - \frac{\sigma_0^2}{\lambda P_0} - \eta \{P_0 - P\} (P < P_0) \quad (2)$$

in which $E_{g(0)}$ denotes the energy of the indirect band gap of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ at X when the pressure is 0 kbar. It also corresponds to the energy of the X CBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ relative to the Γ VBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ at 0 kbar. P is the pressure, P_0 can be considered as the turning point of pressure. When the pressure is not smaller than P_0 , equation 1 can be used to describe the pressure dependence of the band gap energy. In other case, equation 2 can be used to describe the pressure dependence of the band gap energy. α and η are the pressure coefficient in the high pressure range and the pressure coefficient in the low pressure range, respectively, σ_0 corresponds to the energy difference between the Γ CBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ and the X CBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ (hereafter, we call it the X- Γ CBM energy difference) at standard atmospheric pressure. Its value reflects the fluctuation of the conduction band in $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$. β and λ are the empirical parameters. In this work, $\beta = 1000$ kbar and $\lambda = 2.07 \times 10^{-2}$ eV/kbar are used. $E_{g(0)} = 1.78$ eV, $\alpha = 1.12 \times 10^{-2}$ eV/kbar, $\sigma_0 = 0.48$ eV $\eta = 50$ kbar and $P_0 = 50$ kbar are obtained by fitting the experimental values in Fig. 1. The fitting result is shown in Fig. 1. It is obvious that the fitting result can describe the experimental data very well. We can use $E_{g(0)}$ obtained in the theoretical considerations and the direct band

gap energy at 0 kbar to obtain the X- Γ CBM energy difference. It is found that the X- Γ CBM energy difference is about 0.47 eV. It agrees well with the result obtained by fitting the experimental data, which shows that the fitting result is very reasonable.

Fig. 1 also shows the pressure dependence of the X CBM and the Γ CBM of GaAs. It can be seen that the pressure corresponding to the intersection point is about 39 kbar. However, the pressure at which the crossover between the X CBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ and the Γ CBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ occurs, is about 82.5 kbar, which suggests that the X- Γ CBM energy difference of GaAs becomes large after incorporation of N and Sb atoms. A similar behavior is also observed in $\text{GaN}_x\text{As}_{1-x}$, which shows that the incorporation of N atoms can lead to a larger X- Γ CBM energy difference in $\text{GaN}_x\text{As}_{1-x}$ and $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$. It is interesting whether the incorporation of the Sb atoms also has a similar effect as the N atoms on the X- Γ CBM energy difference of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$. We suggest that the incorporation of Sb atoms has no influence on the X- Γ CBM energy difference of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$. The reason is that although the incorporation of Sb atoms can introduce the Sb level into GaAs, the energy difference between the Sb level and the Γ CBM of GaAs is very large, so the coupling interaction between them is very small. As the coupling interaction between the Sb level and the Γ CBM of GaAs is very small, its influence on the Γ CBM of GaAs can be ignored. It has been reported that the energy difference between the Sb level and the X CBM of GaAs is larger than that between the Sb level and the Γ CBM of GaAs, so the coupling interaction between the Sb level and the X CBM of GaAs should be smaller than that between the Sb level and the Γ CBM of GaAs. As the influence of the coupling interaction between the Sb level and the Γ CBM of GaAs on the Γ CBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ can be ignored, the influence of the coupling interaction between the Sb level and the X CBM of GaAs on the X CBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ can be also ignored. The investigation reported by Lin et al. [2] supports this opinion. Their investigation shows that the conduction band and the valence band are

independently manipulated by incorporating N and Sb, respectively, which suggests that the Sb level has no influence on the Γ CBM and the X CBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$.

Fig. 2 shows that even if the pressure is larger than 120 kbar, we still do not see the turning point between the X CBM and the Γ CBM of $\text{GaN}_x\text{As}_{1-x}$. Compared with GaAs, it is found that the X- Γ CBM energy differences in $\text{GaN}_x\text{As}_{1-x}$ and $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ are larger than that in GaAs. The fitting results also support this opinion. In GaAs, the X- Γ CBM energy difference is about 0.46 eV [15]. In the above model, the parameter σ_0 represents the X- Γ CBM energy difference of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ at standard atmospheric pressure. Its value is 0.48 eV, which shows that the X- Γ CBM energy difference in $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ is larger than that in GaAs. The phenomenon can be explained as follows. At standard atmospheric pressure, a rapid decline of the Γ CBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ with increasing N content is due to the strong N- Γ CBM coupling interaction. It is well known that the X CBM of dilute nitride $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ evolves from the X CBM of GaAs, which is very similar to the X CBM of the dilute nitride $\text{GaN}_x\text{As}_{1-x}$ and $\text{GaN}_x\text{P}_{1-x}$ [14, 16–18]. As the energy of the X CBM of GaAs is higher than that of the N level, the N-X CBM coupling interaction could inhibit the downward movement of the X CBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$. Based on the above analysis, it can be seen that the X CBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ decreases much more slowly than the Γ CBM of $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$, causing that the X- Γ CBM energy difference in $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ is larger than that in GaAs.

3. Conclusion

In conclusion, the pressure dependence of the band gap energy for dilute nitride and antimony $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ has been analyzed. It is found that the band gap energy depending on pressure can be divided into two regions. In the low pressure region, the band gap energy is due to two factors. One is the N- Γ CBM coupling interaction. The other one is the Sb- Γ VBM coupling interaction. In the high pressure region, the band gap

energy is also due to two factors. One is the N-X CBM coupling interaction. The other one is the Sb- Γ VBM coupling interaction. In addition, we have found that the increase of the X- Γ CBM energy difference for $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$ is due to two factors. One is the N- Γ CBM coupling interaction. The other one is the N-X CBM coupling interaction. The Sb level has no influence on the X- Γ CBM energy difference in the dilute nitride and antimony $\text{GaN}_x\text{Sb}_y\text{As}_{1-x-y}$.

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