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The evolution of the band gap energy of the P-rich $GaN_xP_{1-x}(0<x\leq0.05)$ on composition and temperature

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ABSTRACT

We analyze the evolution of the band gap energy of the P-rich GaNP on composition and temperature by modifying the BAC model. In the modified BAC model, the effects of the composition and the temperature on the parameters in the BAC model are considered. It is found that the coupling constant becomes small after considering the effect of the composition on the N level. It is also found that the temperature dependecnce of the band gap energy becomes large with increasing N content. This is due to two factors. One is that the localized degree of the N states becomes weak with increasing N content. The other one is that the coupling interaction between the N level and the Γ conduction band of GaP becomes large with increasing N content.

1. Introduction

III–V dilute nitride alloys have recently attracted wide interest due to their potential application in optoelectronic devices. The incorporation of a small amount of nitrogen into GaAs or GaP can lead to huge band gap bowing [1–5], which shows that dilute nitride alloys are very different from conventional III–V semiconductor alloys. Since Shan et al. successfully used the band-anticrossing (BAC) model to describe the compositional dependence for the band gap energy of InGaNAs [6], the BAC model has been widely used to describe the band gap energy of dilute nitride alloys. However, whether the compositional dependence of the band gap energy for the P-rich GaN_xP_{1-x} can be interpreted by the BAC model is still in controversy [7–12]. Even if the BAC model is suitable to describe the band gap energy of GaN_xP_{1-x}, it is too simple to interpret the optical properties of the P-rich GaN_xP_{1-x} because many effects are not included in the model. For example, very few of them considered the effects of the temperature and composition on the N level and the coupling constant [5,9,10]. In this paper, we analyze the evolution of the band gap energy of the P-rich GaN_xP_{1-x} $(0<x\leq0.05)$. Based on the analysis, we consider that the band gap energy of the P-rich GaNP can be described by the BAC model. We also consider the influences of the temperature and the composition on the parameters in the BAC model.

For the compositional dependence of the band gap energy of the dilute nitride alloys, the variation of the valance band maximum (VBM) is usually so small that its contribution to the band gap reduction can be ignored. The band gap reduction is mainly from the conduction band minimum (CBM). In order to describe the evolution of the CBM for the As-rich GaNAs, the impurity band model and the BAC model have been put forward. The impurity band model argued that the CBM evolved from the interacting N-related impurity states (isolated N centers, N pairs and Clusters) and it did not require the participation of host conduction band states [13]. For the BAC model, it was considered that the formation of the CBM was due to the repulsion between the N level and the Γ conduction band state of the host material [5]. Although the P-rich GaNP is very similar to the As-rich GaNAs, it should be noticed that the location of the N level in GaP is very different from that in GaAs so the evolution of the CBM for the P-rich GaNP should be different from that for the As-rich GaNAs. We consider that neither the impurity band model nor the BAC model can describe the CBM evolution of the P-rich GaNP fully. Its CBM evolution is due to two factors. One is the effect of the band gap narrowing by heavily doping. The other one is the coupling interaction between the N level and the Γ conduction band of GaP. When the N content is very small, the N level can be considered as an isolated level. The coupling interaction between the N level and the Γ conduction band of GaP can be ignored. With increasing N content, the distance between the N atoms becomes small and the part of the wave function which overlaps between the N atoms becomes large. The N-related impurity level can be enhanced and

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gradually form N impurity band. Under this condition, the band gap reduction is dominated by the broadening of the N impurity band. It is very similar to the commonly observed band gap narrowing in heavily doped semiconductors. If the N content goes on increasing, the coupling interaction between the N level and the Γ conduction band of GaP becomes large. The coupling interaction can push down the CBM of GaNP. When the N content is large enough, the coupling interaction between the N level and the Γ conduction band of GaP is very large. Under this condition, the band gap shift is dominated by the coupling interaction between the Γ conduction band of GaP and the N level. In this composition range, the variation of the band gap energy can be described by the BAC model. As the composition range dominated by the band gap narrowing due to heavy doping is very small, we can describe the band gap energy of the P-rich GaNP by the BAC model approximately.

The BAC model can be described in the following form [1]:

$$E_{\pm} = \frac{1}{2}\left[E_N + E_C \pm \sqrt{(E_N - E_C)^2 + 4(C_{MN})^2 y}\right] \quad (1)$$

where E_N and E_C are the energy of the localized N-related level relative to the top of the valance and the energy of the CBM for GaP, respectively. C_{MN} is a term which describes the coupling interaction between the N level and the Γ conduction band of GaP. The E_- energy corresponds to the Γ (CBM) of the dilute nitride. It also corresponds to the band gap energy of GaNP. The E_+ energy corresponds to the energy of the optical transition between the valence band and the second conduction subband. E_N and C_{MN} are empirical parameters which can be determined by experiment.

In the BAC model, the N-related level E_N for the P-rich GaN_xP_{1-x} is usually considered as a constant. In fact, it is not the truth. We consider that it is dependent on composition, which is similar to that for GaNAs [3]. The reason can be explained from two aspects. On the one hand, it is hard to control the locations of the atoms in the growth process. With increasing N content, two or more N atoms may be bonded to the same Ga atom, leading to the formation of N–N pairs (where two N atoms are in close vicinity) and N clusters (containing three or more N atoms). These N pairs and clusters have different self-energy lower than the isolated N level $E_{N(0)}$ [14–16], which shows that the N level should decrease with increasing N content. On the other hand, there are a large number of unique complex configurations about the N-clusters. Each configuration should correspond to a nitrogen level E_N. In the band anticrossing (BAC) model, the nitrogen level E_N should be considered as a statistical mean as it can be given only one value, which also shows that E_N is dependent on composition. As the composition range is very small for dilute nitride alloys, E_N can be considered to decrease linearly with increasing N content in the small composition range.

In addition, it is reported that E_N is temperature dependent [9]. We assume that the N level has the similar temperature dependence as the host material GaP. The temperature dependence of the host matrix E_g for GaP can be determined using the Varshni formula [4]

$$E_g = E_{g(0\ \mathrm{K})} - \frac{\alpha T^2}{T+\beta}. \quad (2)$$

where $E_{g(0\ \mathrm{K})}$ is the band gap energy of GaP at 0 K. T is the temperature in Kelvin, α and β are Varshni's fitting parameters. Here, we choose $E_{g(0\ \mathrm{K})} = 2.86$ eV, $\beta = 372$ K [4].

Considering the above factors, E_N can be expressed in the following equation.

$$E_N(T,x) = E_{N(0\ \mathrm{K},0+)} - \frac{\lambda T^2}{T+\eta} - \gamma x, \quad (2)$$

in which, $E_{N(0\ \mathrm{K},0+)}$ is the isolated N level at 0 K when the N content is very small. λ and γ are temperature coefficient and composition coefficient, respectively [3].

The acceptable range of E_N for GaN_xP_{1-x} at 300 K is 2.15–2.25 eV [9]. It is reported that the isolated N level at 300 K is 2.25 eV in experiment [17]. E_N for other values matches to the N pairs or the N clusters [9]. As E_N is compositional dependent, it is necessary to obtain the start point of the N level and the composition coefficient in order to describe E_N. We know that the start point of the N level should be an isolated level so $E_N = 2.25$ eV is used at 300 K in this work. For InNAs, it is reported the composition coefficient γ for the N level is equal to 2.0 eV [18]. The acceptable range of E_N for GaN_xP_{1-x} in the compositional range ($0 < x \le 0.05$) at 300 K is 2.15~2.25 eV [9], which shows that the composition coefficient γ for the N level of GaN_xP_{1-x} with N content no more than 5% is about 2.0 eV. Here we assume that the N level for GaN_xP_{1-x} have the same composition dependence as that for InNAs.

We use the modified BAC model to fit the experimental data at room temperature. The experimental data are from literatures [9,10,19–22]. $E_{C(300\ \mathrm{K})} = 2.78$ eV is adopted in this work [5]. We obtain $C_{MN} = 2.91$ eV by fitting the experimental data. Fig. 1 shows the fitting results. It can be seen that the fitting results agree well with the experimental values. Compared with the results reported in Ref. [9] and Ref. [10], our results agree better with the experimental values. If the effect of the composition on the N level is not considered, $C_{MN} = 3.16$ eV is obtained [23], which shows that the coupling interaction between the N level and the Γ conduction band becomes small after considering the effect of the composition on the N level. In addition, we notice that $C_{MN} = 2.7$ eV is reported for GaNAs [10], which indicates that the coupling constant for GaNP is a litter larger than that for GaNAs. We also notice that the energy difference between the N level and the Γ conduction band of GaP is larger than that between the N level and the Γ conduction band of GaAs. It is very interesting that why the coupling constant for GaNP is still larger than that for GaNAs in the condition that the energy difference between the N level and the Γ conduction band of GaP is larger than that between the N level and the Γ conduction band of GaAs. The origin is still unclear. The large difference in the coupling constant between GaNP and GaNAs may be due to the energy difference between the N level and the Γ conduction band of the host material.

Fig. 2 shows the temperature dependence of the band gap energy for the P-rich GaN_xP_{1-x}. The experimental data are from literature [9].

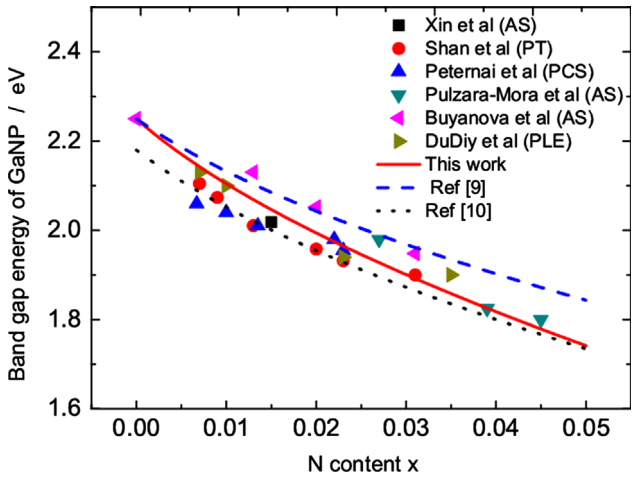

Fig. 1. Experimentally observed dependence of the energy gap energy on N content for GaN_xP_{1-x}. The experimental values are measured by several measurement techniques, such as absorption spectra (AS), photocurrent spectra (PCS), photo-modulated transmission (PT), and photoluminescence excitation (PLE).