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The explanation of InN bandgap discrepancy based on experiments and first-principle calculations

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ABSTRACT

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1. Introduction

Indium nitride has been attracting researchers for the fact that it has relatively a narrow bandgap and a high electronic mobility among III-V compounds. However, experimentally the discrepancy of temperature requirement [1,2] and the scarcity of well-matching substrates impede the improvement of material quality. Theoretically, the well-known error of conventional local density approximation (LDA) leads to a negative gap for InN which brings troubles to the investigation of primary prosperities. For example, resorting to optical measurements, some groups asserted a wide bandgap $(\sim 1.9 \text{ eV})$ [3–5] while others proposed that InN has a narrower bandgap (~ 0.8 eV) [6–10]. On the basis that InN films which have wide bandgap are usually polycrystal and have a high density of unintentionally doped free electrons ($\sim 10^{20}$ cm⁻³), narrower bandgap supporters believed that Burstein-Moss shift [11] enlarges the optical bandgap. Afterwards, it was found that there is a strong electron accumulation layer on InN surface [12] and that strains also contribute to the variation of the bandgap [13,14], all of which further confuse the problem. Van de Walle [15–17] has done a systematic research to the formation energy of intrinsic defects and impurity defects in InN. It is confirmed that the formation energy of all the intrinsic defects except N vacancy is too high to generate in a considerable amount under room temperature in *n*-type InN. Comparatively, impurity defects (O_N, Si_{In}) have lower formation energies, so they supposed that impurities and N vacancy are

Indium nitride (InN) films with different free electron concentration and optical bandgap were grown either directly on sapphire substrate or on pre-covered gallium nitride (GaN) buffer through metalorganic chemical vapor deposition (MOCVD) method. Based on first-principle calculations, we confirm that the widening of InN optical bandgap reported before is caused by high density of free electrons. To find the contributor of the free electrons, the characteristic energetic levels of O_N , V_N and Si_{In} are investigated. We find that they are all high enough to uplift the optical bandgap from about 0.78 eV to 1.9 eV, which almost can't be enlarged further when it reaches 2.09 eV.

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the main contributors of free elections in InN. However, the conduction band structure and the position of defect levels, essential to interpret the blueshift of absorption edge, haven't been dealt with as far as my knowledge, which is the emphasis in our work.

In this Letter, we have grown high-quality InN films under different conditions using MOCVD, and afterwards X-ray diffraction (XRD) and absorption spectroscopy analysis are applied to characterize them. Simulation results combined with experimental data from this work and some previous works support the narrower gap in InN and attribute the origin of blueshift to Burstein–Moss shift. Based on the results given by Van de Walle, we choose three defects in InN with relatively low formation energy (O_N , V_N and Si_{In}) and calculate their energetic positions from which it can be seen that they are all high enough to push the absorption edge as high as about 1.1 eV.

2. Calculation details

The band structure is calculated using the density functional theory with local density approximation as implemented in VASP code [18]. In self-consistent calculation, the little region around Γ point, where LDA gives negative band gap, is excluded when integrating in reciprocal space. In this case, the occupying-sequence remains correct, so the convergent result will not influenced by the negative band gap. Frozen-core projected augmented wave methods [19] is utilized to describe the ion–electron interactions. The In4*d* electrons are explicitly treated as valence electrons. The cutoff energy of the plane wave is set to 400 eV. In doped system, a point defect is placed into a 96-atom cuboid superlattice suggested by Van de Walle [17]. Monkhorst–Pack special *k*-point grid

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 $(2 \times 2 \times 2)$ is used to integrate in Brillouin zone. Ion relaxation continues until Hellmann–Feynman forces acting on each atom are smaller than 0.01 eV/Å. The optimized wurtzite InN lattice constant are a = 3.527 Å, c/a = 1.61, u = 0.375 in good agreement with experimental values (a = 3.5446 Å, c/a = 1.609) [20].

In the calculation of absorption edge as the function of free electron density, we treat absorption edge as the energetic distance between valence band maximum (VBM) and Fermi level assuming the bandgap of perfect InN to be 0.78 eV. The free electron concentration is given out by dividing integrated DOS of conduction band under the given Fermi level by the volume of the superlattice. To get the energetic position of defects and impurities, we calculate the partial density of states (PDOS) of atoms nearest to them. In the case of O_N , the PDOS of the four nearest indium atoms (5s orbit) is plotted. We also give out the PDOS of the same four indium atoms (5s orbit) in pure InN for comparison. In the first plot, there is a significant peak comparing to the second one which indicates the defect level position of O_N . The method for V_N and Si_{In} is the same.

3. Experiments

InN samples were grown by MOCVD method either directly on *c*-plane (0001) sapphire substrates (sample I) or on sapphires which were pre-deposited with GaN buffers (sample II). Trimethylindium (TMIn), trimethyl-gallium (TMGa) and ammonia (NH₃) were used as precursors. High-purity nitrogen was used as carrier gas. Before growth, sapphire wafers were heated under a hydrogen flow at 1050 °C for 20 min, followed by 3-min-nitridization under a flow of NH3 and H2 mixture. For sample I, InN films were deposited subsequently for 40 min under 580 °C and atmospheric pressure with the flow rate of TMIn and NH₃-H₂ mixture to be 200 SCCM (standard cubic centimeter per minute) and 3 SLM (standard liter per minute) respectively. For sample II, a 120 nm GaN buffer layer was deposited before the growth of InN. The parameters in the preparation of samples I and II are the same except for GaN buffer layer. High quality of crystallization of the samples was confirmed by XRD measurements. Each sample was also examined by Hall and absorption spectroscopy.

4. Results and analysis

4.1. Samples characterization

XRD patterns (Fig. 1) tell that samples are well-oriented in (0001) direction. The free electron concentration and electronic mobility are 1.49×10^{20} cm⁻³ and 128 cm²/Vs for sample I while the values for sample II are 1.9×10^{19} cm⁻³ and 595 cm²/Vs determined by Hall measurement. Although Hall measurements overestimate the free electron concentration due to the contribution of the electron accumulation layer $(10^{13} \text{ cm}^{-2} \text{ as indicated by})$ Mahboob [12] and Chang [21]), taking into account the thickness $(\sim 400 \text{ nm})$ and the free electron concentration of our sample, it is reliable to regard the values given by Hall measurements as the values for the bulk because the amounts of free electrons on the surface layer are less than the total amounts by at least one order of magnitude. We fit the absorption spectroscopy to $(h\nu\alpha)^2 \sim h\nu$ plot where α is absorption coefficient, hv is photon energy. As shown in Fig. 2, extrapolations of the linear part to abscissa give a wider optical bandgap (1.27 eV) for sample I and a narrower one (0.85 eV) for sample II. The positions of the XRD peaks for sample I and sample II are almost the same, indicating similar crystallization. We neglect the influence of strains to bandgap due to the fact that it is minor (\sim tens of meV) [14] in the energetic range of our interest (\sim eV).



Fig. 1. X-ray diffraction (XRD) patterns of as-grown InN sample I and sample II. GaN buffer layer in sample II is detected.



Fig. 2. Absorption spectrum of the two samples in this work where hv is photon energy and α is absorption coefficient. Dot lines guide eyes to the intercepts on abscissa which indicate the absorption bandgap.

4.2. Explanation of bandgap discrepancy through ab-initio band structure calculations

To explain the discrepancy between larger bandgap of InN in previous literatures and recently-proposed narrower bandgap using Burstein-Moss shift, we have calculated the absorption edge as the function of free electron concentration as shown in Fig. 3. The band structure is also drawn in Fig. 4. In good agreement with results in previous literatures [22], there is a negative bandgap (-0.0013 eV), nearly equal to zero, in the small region around Γ point where should be excluded in k-sampling. VBM is a p-like state which couples strongly with In4d states because they share the same symmetry. As shown in Fig. 4, the energetic distance from In4d to VBM amounts to 13.4 eV, much smaller than the experimental value (14.9 eV [23]). So the overestimated p-d coupling pushes VBM upwards and decreases the calculated bandgap. In Fig. 3, it can be seen that data of InN films in this work and from other previous works distribute approximately along the calculated line, indicating that Burstein-Moss shift is the essential cause of bandgap blueshift. From structure of conduction band (Fig. 4), the curve is sharp below 1.31 eV-meaning a small DOS while smooth above 1.31 eV-meaning a large DOS. So, when Fermi level reaches upto 1.31 eV, the absorption edge is 2.09 eV (1.31 eV + 0.78 eV) in our model and becomes less sensitive to further increase of free electrons, in consistency with the fact that there are scarce



Fig. 3. (Color online.) Absorption bandgap of InN as a function of free electron concentration with an assumption of 0.78 eV for the bandgap of perfect InN. Solid line travels the DFT-LDA calculated result and red circles indicate the values of samples in this work. Some previous data is shown in the figure as a reference.



Fig. 4. DFT-LDA calculated band structure of pure wurtzite InN including several In4*d* bands. The dash line points out the position of VBM which, for simplicity, is set at 0 eV. The energetic distance between In4*d* level and VBM is 13.4 eV as indicated in the figure.

works reporting an optical bandgap higher than 2.09 eV except the situations where InNO alloy forms. There might be a correction to the value 1.31 eV due to the influence of negative bandgap. We ignore it in this Letter because the region around Γ point where LDA gives negative bandgap is very small, which is shown in Fig. 4. Wu et al. [24] dealt with the InN bandgap issue using Kane's two band $\mathbf{k} \cdot \mathbf{p}$ model [25], but their model includes too many hypotheses and simplifications which weaken its reliability. Difference between their model and experimental data enlarges as free electron concentration increases.

4.3. Find the contributors of free electrons

As discussed above, perfect InN has a narrower bandgap ($\sim 0.8 \text{ eV}$) and the wider absorption edge ($\sim 1.9 \text{ eV}$) found in previous works results from high density of free electrons in these samples whose crystallization quality was confined by the growing methods at that time. The work followed will be engaged to find the origin of the unintentionally doped free electrons. In wider bandgap samples, the absorption edge is as high as 1.9 eV which is the approximate position of Fermi level. If we suppose that InN has a bandgap of 0.78 eV, the Fermi level is about 1.12 eV



Fig. 5. (Color online.) Partial density of states for O_N , V_N and Si_{In} . For O_N , blue line is 5s orbit of four indium atoms nearest to oxygen. For V_N , blue line is 5s orbit of four indium atoms nearest to nitrogen vacancy. For Si_{In} , blue line is 3s orbit of four nitrogen atoms nearest to silicon. The black lines are presented for comparison. In O_N and V_N , black lines are 5s orbit of four indium atoms nearest to one nitrogen in pure InN. In Si_{In}, black line is 3s orbit of four nitrogen atoms nearest to one indium in pure InN.



Fig. 6. Defect levels of O_N, V_N and Si_{ln} which are possible electron contributors in as-grown InN films with VBM at 0 eV. We assume that fundamental bandgap of InN is 0.78 eV as proposed in recent works and the absorption bandgap of highly-degenerated InN samples is 1.9 eV grown mainly before 2003. The units (eV) are omitted in this figure.

(1.9 eV - 0.78 eV) higher than conduction band maximum (CBM). Because only defects whose energetic levels locate above Fermi level are able to ionize, we then calculate the energetic positions of O_N, V_N and Si_{In}. In Fig. 5, we give the PDOS (s orbit) of atoms nearest to the defects (blue lines) as well as that in pure InN (black lines). We can see that there are distinct peaks in blue curves which mark the positions of defect levels. To illustrate clearly, we abstract them and put into Fig. 6 from which we find the defect levels of them are all higher than 1.9 eV. That is to say, all of the three defects can ionize when the Fermi level is as high as 1.9 eV and contribute to Burstein Moss shift. It is well known that LDA method usually underestimates the positions of defect levels in conduction band. That is to say the actual positions are higher than the calculated ones. Still, our conclusions will not be changed. Duan et al. [26] have investigated N vacancy and they found that the defect levels are well above the CBM, in agreement with our results. This might be due to the fact that InN have the lowest CBM among III-V compounds [27].

5. Conclusions

In summary, inspired by the concept of Burstein-Moss shift, we simulate the relation between absorption edge and free electron concentration based on DFT-LDA methods, which is in good agreement with experimental data. This verifies that the band gap of InN is around 0.78 eV, not the widely accepted value of 1.9 eV. High density of free electrons is the cause of blue shift of InN absorption edge which is usually used to determine band gap approximately. We also give a schematic in which energetic positions of the four *n*-type defects with low formation energies are shown. We can see that they are all high enough to ionize when Fermi level is lifted upto 1.9 eV and in turn help to widen absorption edge. Hence, they are the potential contributors of free electron density in InN because of their low formation energy and low ionization energy. However, DOS of conduction band starts to increase sharply from the energy of 2.09 eV above VBM, determining that absorption edge can rarely reach higher than 2.09 eV.

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