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Structure Properties of InN Quantum Dots in GaN Semiconductor

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Abstract: Using the first-principles calculation with 64 and 128 atom supercells the geometric and electronic structures of InN quantum dots (QDs) embedded in wurtzite GaN were simulated. After optimizing the stress and total energies, electronic structures of the stable systems were further calculated. The electronic densities of states show distinguishing quantum-confine-effects along different axes. Moreover, the curves of energy band edge appear in InN QDs. Compared with the typical band-edge shape of quantum well under the polarization that leads to the separation of electrons and holes in space, we found that the separation problem could be eliminated due to the curves of energy band edge in QDs, which is favourable for enhancement of the transition probability of the electrons and holes.

Key words: quantum dots; quantum confine effects; density of states
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1 Introduction

Semiconductor quantum dot (QD) structures have attracted much attention due to their significant application potential in the manufacture of opto-electronic devices. Recently, epitaxial growth of quantum dots has been widely developed. With the improvement of growth technology, high quality quantum dots with better size and density have been produced. Simultaneously, research activity in III-nitride quantum dots material has always been intense. Most of the recent researches have been focused on InGaN quantum dots. Actually, for InGaN alloys, it was frequent to observe InN due to the phase separation. In addition to the large lattice mismatch between InN and GaN, the growth of InN quantum dots becomes more difficult[1]. Therefore, the simulation of the physical properties from theoretic study seems useful to guide the experiment, especially the microcosmic structure properties of InN quantum dots embedded in GaN semiconductors.

In this work, we perform the theoretical simulation using the first-principles calculation, including the establishment of quantum dot models, optimization of the crystal structures, computation of the electronic density of states (DOS), analysis of the energy band structures.

2 Geometric Structures

The geometric structures of InN quantum dots were simulated by employing first-principles calculation together with the density functional theory. To investigate the atomic and electronic structure properties of real crystal from the original and basic physical law, the Vienna *Ab-initio* Simulation Package (VASP) basing on the quantum-mechanical molecular dynamics was used. The pseudopotentials were used for a considerable reduction of the number of plane-waves per atom when computing the

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Kohn-Sham equation[2~4]. Cooperating with a plane wave basis set, the calculation efficiency of extendible and periodical systems has significantly improved. Executing VASP with a high-powered computer (Lenovo 1800), we simulated the structure properties of InN quantum dots embedded in GaN semiconductor.

2.1 Structure Model

InN has small band-gap energy of 0.7 eV[5], which enables to construct quantum dot in GaN semiconductor. InN has two structures, wurtzite and zinc blende. In normal conditions, wurtzite structure is more stable. For this reason we construct the wurtzite structure model for InN quantum dot.

As we know, the most important property of the quantum dot is three-dimensional (3D) confinement. Thus, when designing the quantum dot structures, InN quantum dots should be surrounded by GaN. A simple model is constructed by 2 × 2 × 2 unit cells which composes of 32 atoms. Expanding the supercell along b-axis, we got a 64 atoms model in which InN quantum dots congregate in lower left corner, denoted as 64-q in Fig.1 (a). In addition, we enlarge the size of InN quantum dot by expanding the supercell up to 128 atoms (denoted as 128-q) in order to fit better with the experiment. For comparison we also construct two structures, in which InN are distributed uniformly in GaN, denoted as 64-u and 128-u.

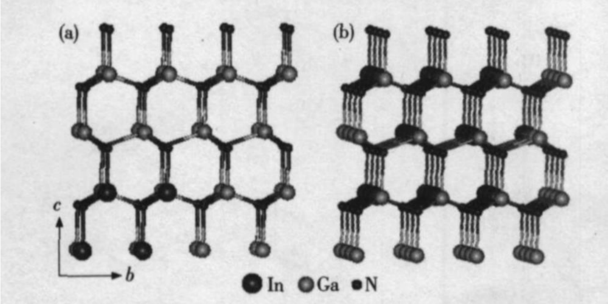

Fig.1 Supercells of InN/GaN quantum dots with 64 (a) and 128 atoms (b), where b and c are basis vectors of crystal cell

2.2 Structure Optimization

In order to obtain steady structures consisting with actual crystal, structures of the models should be optimized. This means the atom position should be adjusted to reduce the strain to the lowest level and to obtain the structures with the smallest total energies. In practice, the relaxation of the stress makes the premise of the formation of quantum dots. The popular technique of self-assembled growth bases on the control of stress of epitaxial layer[6] to format quantum dots with a relatively homogeneous size distribution. Some researches of the strain evolution during InN quantum dots growth on GaN[7,8] revealed that, about more than 80% of the total mismatch stress is released in 2D growth. The formation of 3D InN islands under the residual stress demonstrates that the relaxation plays an important role for the lattice structure of QD.

We choose proper calculating parameters to relax the system. First of all, optimize the equilibrium lattice constant by keeping the wurtzite structure. For structures 64-q and 128-q in Fig.1, the equilibrium lattice constants we obtained are 0.329 96 and 0.338 40 nm, respectively. Compared with the results calculated from Vegard's law using the experimental lattice constants of InN (0.354 5 nm) and GaN (0.318 9 nm) as criterion, the relative errors are 2.04% and 1.51%, respectively. On the basis of the equilibrium lattice constants, we optimize the supercell structures by automatically adjusting the atom positions and volumes until approaching the lowest total energies. The total energies of two quantum dot structures before and after relaxation are listed in Table 1. Comparing with the uniform distribution structures correspondingly, we conclude that the total energies of the QD structures are lower and higher after and before relaxation, respectively. This indicates that there has a strong local stress between InN QDs and surrounding GaN matrix. The local stress has been released after relaxation. In addition, the change ratio of the total energy is larger for the 128-q structure, which suggests that the bigger

Table 1 Structures and total energies

eV

Structures	Total energies	
	Pre-relaxation	Post-relaxation
64-q	−380.920 6	−383.499 6
64-u	−380.962 4	−382.146 7
128-q	−735.706 2	−741.354 8
128-u	−736.045 2	−739.701 3

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QD is more stable.

3 Quantum Confine Effect

The electronic density of states (DOS) represents the electronic states per unit energy in per reciprocal space. Via VASP software we calculate the total DOS and the partial DOS of each atom. Commonly, the DOS is plotted as a function of energy to reflect the distribution of electronic states in different energy regions. However, this diagram is unable to reflect DOS distribution in real space. In order to clearly reveal the quantum confine effect of charge carriers, the DOS distribution in the real space is proposed at the first time in which the value of DOS is shown in different grey levels with the energy as ordinate axis and the position of each atom or molecule as abscissa axis, as shown in Fig. 2. Based on this method, we gain an insight into the quantum confine effects along each direction.

Fig. 2 shows the DOS distribution in the real space along *b*- and *c*-axis. Both diagrams demonstrate the shape and depth of the electron and hole wells. The electron well is deeper than the hole's, which means the band offset of the bottom of the conduction band is larger than that of the top of the valance band. Comparing the band offsets along *b*- and *c*-axis, we found a remarkable band curve along *b*-axis. This is related to the band gap variation at different positions for the same molecule. This phenomenon is more notable in *c*-axis.

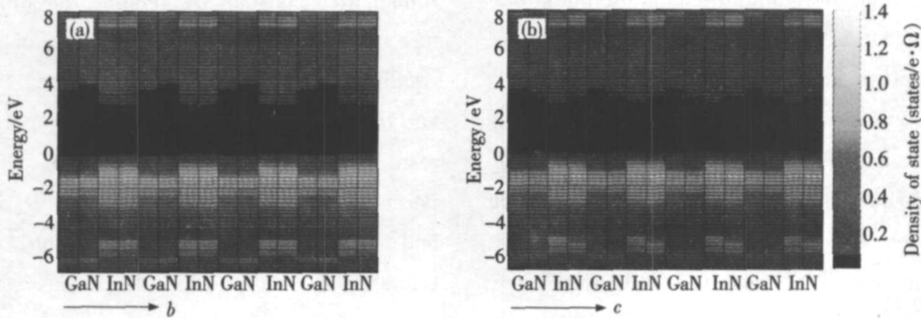

Fig. 2 The densities of states along *b*-axis (a) and *c*-axis (b). The abscissa axis represents the molecular position of GaN or InN. The ordinate axis represents the energy. And the different grey levels correspond to the density of states.

Polarization is a basic property of wurtzite III-nitrides, including the spontaneous and piezoelectric polarizations, which orients along *c*-axis. The large lattice mismatch between InN/GaN quantum dots heterogeneous structure would give rise to a biggish piezoelectric polarization. The magnitude of the built-in electric fields induced by the piezoelectricity and spontaneous polarization is estimated to be in the order of MV/cm[9~11]. Therefore, the electronic structure properties along *c*-axis are significantly different. The large band curve along *c*-axis in Fig. 2 (b) gives a typical example of the polarization effect. Around QD, the curves of the bottom of the conduction band and the top of the valance band are depicted in Fig. 3(a). Comparing with the normal quantum well (QW) structure, the shape of the conduction band edge of the QD is similar along *c*-axis, which is attributed to the polarization. However, the valence band edges of the QD and the QW exhibit the reverse shape. As we know, electrons

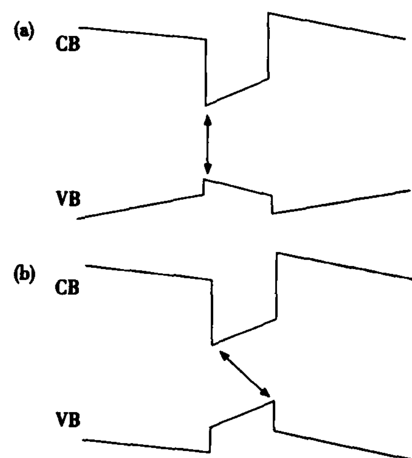

Fig. 3 The energy band edge structures along *c*-axis. (a) quantum dot; (b) quantum well. CB: conduction band; VB: valance band.

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and holes generally congregate in the lower location of the electron and hole wells, as shown in left and right of the wells of Fig. 3(b), respectively. In the light of this, the electron and hole are separated in the QW structure. On the contrary, electrons and holes congregate in the same spatial position in the QD structure, thus the charges are congregated. This performance is favourable for enhancement of the transition probability of electrons and holes, and brings an exciting evidence for the application of InN QDs also.

4 Energy Band Structure

Generally speaking, the numerical calculation of the valence band is quite nicety and believable when applying the local density approximation (LDA). However, the conduction band is often lower than the experimental value. But it won't affect the analysis of the electronic properties. Here we mainly observe the different energy band structures engendered by 64-q and 64-u, as shown in Fig. 4. Both of them are similar except for the energy splitting in the QD structure. Especially, the lowest two bands of the bottom of conduction band are totally apart and form an individual energy band. This can be attributed to the split of the degenerate energy level due to the descending of the crystal symmetry in the InN QD. Detailed observation shows that the splitting mainly causes the ascending of the second band of the bottom of the conduction band and slight descending of the top of the valence band, resulting in the change of the energy band gap. Considering the above results, we conclude that local modification

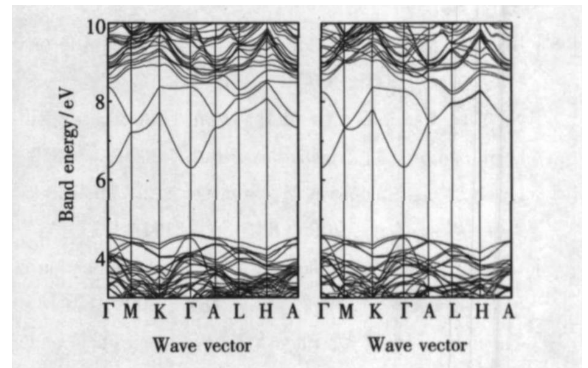

Fig. 4　Energy band structures of InN/GaN quantum dot (a) and $In_{0.125}Ga_{0.875}N$ bulk (b).

of the energy band edge induced by QD is closely related to the whole energy band structure. However, it was hard to analyze the quantum confine effects directly from the energy band structure. This reflects in another way that the validity of the new proposed method of DOS in the real space for analyzing the quantum confine effects of QD.

5 Conclusion

The first-principles theory was used to simulate the geometric and electronic structures of InN QDs embedded in GaN semiconductor. By optimizing the structure, the stable QD structures have been constructed. A new method that clearly demonstrates the quantum-confine-effects in quantum structure has been proposed at the first time to reflect the DOS distribution in the real space. Electrons and holes concentrate in the same spatial space of the QDs structure reveals that the QD structure is favorable for enhancement of the transition proba-bility of the electrons and holes.

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GaN半导体中 InN量子点的结构性质

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摘要: 采用第一性原理模拟计算纤锌矿结构 GaN半导体中 InN量子点的结构性质。建立 64和 128个原子的超原胞量子点模型,进行结构优化以获得稳定的吻合实际的系统,并模拟分析电子结构。从态密度空间分布图看到不同轴向的量子势阱形状各异、深度不一,说明量子点的限域效应存在着各向异性的特点。*c*轴极化方向引起量子点结构带边的弯曲形状与传统的量子阱结构不同,使得电子空穴没有发生空间分离,有利于电子空穴的跃迁几率的提高。

关 键 词: 量子点; 量子限域效应; 电子态密度

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