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Spin Electronic States of Wurtzite GaN Nanostructures

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Spin electronic states of wurtzite GaN nanostructres were studied by using ab initio molecular orbital calculations. Two models of pyramidal GaN clusters were constructed with the cluster axes parallel to the crystallographic c axis in the wurtzite. The atom at the apex of the cluster is nitrogen or gallium. We computed the lowest energy spin electronic states, spin densities, static electric fields, highest occupied molecular orbitals, and lowest unoccupied molecular orbitals for both clusters. The spin multiplicities of the clusters were found to be 13 and 3, depending on whether the atom at the apex was nitrogen or gallium, respectively. The GaN clusters were spontaneously spin-polarized in the lowest-energy states. Highly spin-polarized states were induced by the unpaired electrons on the surfaces of the nanostructures.

Key words: spin polarization, nanostructure, GaN, ab initio molecular orbital calculation, spin multiplicity, magnetization

1. Introduction

Tonomura observed magnetic fields in cobalt microclusters¹⁾ while, at a much smaller scale, many magnetic properties have been predicted in molecules²⁾. How small could the magnetic materials be when they show ferromagnetic properties? There is a difference in the definitions of magnetization between condensed matter and molecules.

In case of ferromagnetic materials, the magnetic properties are due to spin-polarization of the delectrons. The magnetic moment is the criterion of the strength of magnetization.

Molecular magnets, however, often have no delectrons. Both the spin directions and the atomic coordinates can be optimized simultaneously in relatively small molecules by newly developed generalized Car-Parrinello procedure³⁰ while their magnetic properties were often validated when they have stable high spin states since their magnetic moments are considered to be small.

Recently, magnetic properties have been theoretically predicted in many non-magnetic materials^{4,5,6,7,8)}. The typical size of these materials is smaller than Tonomura's microclusters and larger than magnetic molecules. In our previous studies, it was shown that zincblende GaN tip structures were spontaneously spin-polarized with the rate ranging from 11-34 $\%^{8}$.

Eventually, wurtzite GaN pyramidal microstructure was created[®]. In this short article, we will first show the peculiar spin electronic states of pyramidal nanostructures of wurtzite GaN and their spontaneous spin polarization at the level of unrestricted-Hartree-Fock (UHF) method.

2. Calculations of Spin Electronic States

2.1 Modeling Wurtzite GaN Nanostructure

We constructed two cluster models for GaN in the wurtzite structure (see Fig. 1). The axes of the cluster models are along the crystallographic c axis. There are two possible cluster models for the wurtzite pyramidal structure depending on the sort of the The atomic distances in the atom on the apex. clusters follow the bulk atomic distances¹⁰. The dangling bonds are terminated by hydrogen atoms. Both cluster models are comprised of six layers. In Fig. 1, only the cluster with a nitrogen atom on the apex is shown. The models are carefully constructed so that the whole atoms are within a sphere with a constant radius that is measured from the apex atom. The geometry optimization is not included since the atomic distances in these small clusters vary only within 1 % from the bulk structure under an optimization procedure.



Fig. 1. Cluster model: large, medium, and small (white) spheres signify gallium, nitrogen, and hydrogen atoms, respectively.

The stoichiometry, axis, and type of atom at the apex for each model are summarized in Table 1.

Table 1Structure of the GaN probe models.

Name	Stoichiometry	Atom at the apex
Cluster A	Ga ₁₆ N ₁₄ H ₁₅	N
Cluster B	Ga ₁₄ N ₁₆ H ₁₅	Ga

2.2 Calculational method

We used unrestricted Hartree-Fock (UHF) calculations with STO-3G basis set to determine spin electronic states for the GaN clusters. UHF and STO-3G are explained in detail in the typical quantum chemistry textbooks¹¹. Only the valence electrons are considered in calculations and the core electrons and nuclei are treated as effective core potentials.

Cluster models A and B have a 3-fold axis around the c axis. We could take advantage of the symmetry of the clusters in computation. During the electronic calculaitons, however, the symmetry was ignored since the symmetric electronic structures do not necessarily reveal the lowest energy.

UHF method and STO-3G basis set have limitations. UHF cannot create exact eigenfunctions. Thus, our computational results will be rather a hypothetical than a rigorous quantum chemical discussion. Larger computation, however, will be necessary for more precise calculations. Only the combination of UHF and STO-3G allows us to calculate the present cluster models with reliable rigor. The feasibility of UHF and STO-3G are discussed elsewhere⁸⁰.

We used Gaussian94 and Spartan version 5 for Hartree-Fock calculations.

2.3 Calculations of Spin Polarization

We conducted total energy calculations for each cluster with specification of the z-components of the spin. The z-component in the UHF method implies difference of the numbers of the majority and minority spins. All our calculations were done only at the ground states.

The details of calculations of spin polarization can be found in our previous work⁸⁾.

We performed the calculations for the possible spin multiplicities ranging from one (singlet spin state) to 19 or 21 (see Figs. 2). The total energies of the clusters are measured from the total energies at singlet in Figs. 2. In case of Cluster A with a nitrogen atom on the apex, the spin multiplicity with the value 13 gives the lowest total energy. On the contrary, the cluster with a gallium atom on the apex indicates relatively low spin multiplicity with the value three (triplet).



Fig. 2 Total energy and spin multiplicity of wurtzite GaN. Total energies of GaN clusters (a) with a nitrogen atom at the apex (Cluster A in Table 1), and (b) with a gallium atom at the apex (Cluster B in Table 1). Energies in the singlet spin states are $E_1 = -847928.48994240 \text{ eV}$ and $E_2 = -747439.35498720 \text{ eV}$.

2.4 Spin Electronic States

The electron densities, static electric fields, spin densities, highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) at the lowest energies are computed and the results are shown in Fig. 3.



Fig. 3 (a), (b) Static electric fields on equi-electron density surfaces of GaN clusters with N and Ga at the apices, respectively. The gradation from bright to dark indicates the electric fields: the dakr regions are electron-rich and the bright regions are electron-poor. (c), (d) Spin densities of GaN clusters with N and Ga at the apices, respectively. The dark and bright regions are rich in the majority and the minority spins, respectively. (e), (f) Top views of HOMOs and LUMOs of GaN clusters with N and Ga on the apices, respectively. HOMOs are shown in the mesh. LUMOs are transparent. (g), (h) Side views of (e) and (f).

The top views of the static electric fields are shown on the surface of equi-electron density in Figs. 3 (a) and (b). The color gradation changes from dark to bright along the static electric fields. The dark regions are electron rich and the bright regions are electron poor.

In Fig. 3 (a), Cluster A with a nitrogen atom on the apex is presented. The areas about the nitrogen atoms are dark, that is electron rich, which indicates the high electronegativity of nitrogen. Such an electronic property was observed in our previous calculations⁸. The gallium atoms on the second layer (three large atoms around the apex nitrogen in the top view) are electron richer than the gallium atoms on the fourth layer (the green regions on both sides of the dark nitrogen atoms). The coordination numbers of the gallium atoms on the second layer and on the fourth layer are two and three, respectively. The former gallium atoms have more dangling bonds with unpaired electrons than the latter ones have.

The static electric fields on the equi-electron density plot of Cluster B are shown in Fig. 3 (b). The nitrogen atoms on the second layer are electron rich, similarly as in Cluster A.

(c) and (d) show the spin densities of Clusters A and B, respectively. The dark and bright regions are rich in the majority and the minority spins, respectively.

In case of Cluster A, spin polarization is clearly seen in the spin density calculations (Fig. 3 (c)). The nitrogen atoms on the third layer posses the majority spin while the gallium atoms on the fourth layer are covered by the minority spins. The atoms on the first and the second layers are quite neutral in the spin density plot. As can be seen in (e) and (g), the HOMOs are localized on the third and the fourth layers while the LUMOs are on the first and the second layers, which do not contribute to the spin polarization. It is observed that only the electrons in the HOMOs are spin-polarized in Cluster A.

Spin polarization is not so obvious in Cluster B since the net spin polarization is low. In Fig. 3 (d), the spin density is plotted for the cluster. The spin multiplicity is triplet. It is shown, however, that the nitrogen atoms on the second layer are slightly spinpolarized with the majority spin. The HOMOs and the LUMOs are located mainly on the fifth and the sixth layers (see Figs. 3 (f) and (g)). The HOMOs in Cluster B do not contribute to the spin polarization. It is simply due to that only two electrons are polarized in Cluster B in our calculations.

The computational results in Figs. 3 for both cluster models implies that the electronic structure is symmetric when the system has the lowest energy spin multiplicity, which was hypothetically suggested in our previous work for zincblende GaN nanostructures⁸.

2.5 Spin-Polarized Electrons

Cluster A with a nitrogen atom on the apex in Fig. 3 (c) clearly shows the spin polarization and (e) and (g) reveal the electrons in the HOMOs are spin-polarized. We will show the top view of the Cluster A with the spin-polarized orbitals more explicitly in Fig. 4 (a).



(b)

Fig. 4 (a) Top view of Cluster A with a nitrogen atom at the apex. The orbitals are occupied by spinpolarized electrons. (b) Top view of Cluster B with a gallium atom at the apex. The distribution of spinpolarized electrons is not clear.

Only the orbitals with spin-polarized electrons are shown in Fig. 4. Fig. 4 (a) reveals that the orbitals on the surface of the cluster have spin-polarized electrons. The atoms on the cluster surface have unpaired electrons in their dangling bonds. The clear contrast is observed: the atoms which are located in the inner part of the cluster are not spinpolarized where they have no unpaired electrons. Non-spin-polarized orbitals appear as an empty space.

Such a spin electronic state was not observed in

Cluster B with a gallium atom on the apex of the pyramidal structure since the spin polarization is low (See Fig. 4 (b)). The distribution of the spin-polarized electrons is not so clear as in Fig. 4 (a).

3. Conclusions

Spin electronic structures of wurtzite GaN nanostructures were obtained through UHF molecular orbital calculations. The pyramidal structures of wurtzite GaN are found to be spinpolarized. Especially, the cluster with a nitrogen atom on the apex has large spin polarization. The spin-polarized electrons are localized in the HOMOs that are sited on the surface of the nanostructure. The atoms on the outer part of the cluster have unpaired electrons and contribute to spin polarization. On the contrary, the spin polarization of the cluster with a gallium atom on the apex was at a low level.

In the heavily spin-polarized structures, magnetization may be induced. Our pyramidal GaN clusters may be one of the candidates that posses magnetic moment among nanoscale non-magnetic materials. Inclusion of the magnetic moments in the calculations is our future task.

References

- 1) A. Tonomura, M. Matsuda, J. Endo, T. Arai and K. Mishima: Phys. Rev. Lett., 44,1430 (1980).
- 2) K. Fink, C. Wang and Y. Staemmler: Int. J. Quant. Chem. 65, 633 (1997).
- 3) T. Oda, A. Pasquarello, S. J. Pennycook, S. T. Pantelides: *Phys. Rev. Lett.*, 80, 3622 (1998).
- 4) A. Mielke and H. Tasaki: Commun. Math. Phys. 158, 341 (1993).
- 5) S. Watanabe, M. Ichimura, T. Onogi and Y. A. Ono: Jpn. J. Appl. Phys. 36, L929 (1997).
- 6) S. Blügel: Phys. Rev. Lett. 68, 851 (1992).
- 7) M. Sawamura, T. Maruyama, K. Mukasa: J. Mag. Soc. Jpn. vol. 23, pp. 721, 1999.
- 8) M. Sawamura, T. Maruyama, K. Mukasa: J. Mag. Soc. Jpn. vol. 23, pp.1165, 1999.
- 9) T. Akasaka, Y. Kobayashi, S. Ando and N. Kobayashi: Appl. Phys. Lett. 71, 2196 (1997).
- 10) S. J. Pearton: *GaN and Related Materials*, p. 268 (Gordon and Breach Science Publishers, Amsterdam, 1997).
- 11) A. Szabo and N. Ostlund: *Modern Quantum Chemistry*, p. 184 and p. 189 (Macmillan, New York, 1982).