Solid State Communications 151 (2011) 139–143

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Structural, electronic and magnetic properties of the 3d transition metal-doped GaN nanotubes

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ARTICLE INFO

Article history:
Received 6 July 2010
Received in revised form
2 November 2010
Accepted 3 November 2010
by A.K. Sood
Available online 10 November 2010

Keywords:
A. GaN nanotubes
A. Transition-metal atoms
C. Impurities in semiconductors
E. Density functional theory

ABSTRACT

We have performed first-principles calculations on the structural, electronic and magnetic properties of seven different 3d transition-metal (TM) impurity (V, Cr, Mn, Fe, Co, Ni and Cu) doped armchair (5,0) and zigzag (8,0) gallium nitride nanotubes (GaNNTs). The results show that there is distortion around 3d TM impurities with respect to the pristine GaNNTs for 3d TM-doped (5,5) and (8,0) GaNNTs. The change of total magnetic moment follows Hund's rule for 3d TM-doped (5,5) and (8,0) GaNNTs, respectively. The total density of states (DOS) indicates that Cr-, Mn-, Fe- and Ni-doped (5,5) GaNNTs as well as Cr-, Mn-, Ni- and Cu-doped (8,0) GaNNTs are all half-metals with 100% spin polarization. The study suggests that such TM-doped nanotubes may be useful in spintronics and nanomagnets.

1. Introduction

Carbon nanotubes (CNTs) have attracted a lot of interest due to their novel properties and potential applications in many fields [1–5]. Depending on their chirality, CNTs may be semiconducting or metallic and they can thus be used as transistors and interconnectors in electronic circuits [6]. However, the structural and electronic properties of CNTs can be modified by doping. For example, the 3d transition metal (TM) doped CNTs can lead to semi-metallic systems that are of interest for spintronics devices as well as nanomagnets [7].

The diluted magnetic semiconductors (DMSs), which have both ferromagnetic and semiconducting properties, are a unique type of promising materials for the fast emerging field of spintronics. The 3d TM-doped III–V (GaAs, GaN, etc.) and II–VI (ZnTe, ZnO, etc.) compound semiconductors have attracted considerable attention as promising DMSs for spintronic applications [8–11]. Though many DMS materials have been reported [12–15], it is still very important to find new DMS materials, especially for nanoscale DMS materials because magnetic nanostructures are a scientifically interesting and technologically important area of research with many current and future applications in permanent magnetism, magnetic recording, and spintronics [16]. The applications of the DMSs demand a host material which can accommodate a lot of substitute impurity and resist interstitial impurity. Compared with the III–V and II–VI compound semiconductors, the single-walled nanotubes just have two surfaces, in which the interstitial impurities can be removed more easily. Thus, it is reasonable to expect that III–V nanotubes doped with 3d TM will exhibit unique characteristics on electron spin polarization, which can be useful in the development of future nanoscale spintronic semiconductor devices.

Gallium nitride (GaN) is of great importance due to its optoelectronic properties, and high thermal and mechanical stability. The tubular structure of GaN was firstly observed as the defect in epitaxially grown GaN materials [17]. With epitaxial casting techniques, single-crystal GaN nanotubes (GaNNTs) were successfully synthesized in 2003 [18]. Theoretical studies have shown that the GaNNTs have about 2 eV band gap independent of their chirality [19,20]. GaNNTs would be wonderful candidates for the host materials of DMSs [21–23].

In this paper, the structural, electronic and magnetic properties of seven different 3d TM (V, Cr, Mn, Fe, Co, Ni and Cu) doped armchair (5, 5) and zigzag (8, 0) GaNNTs have been investigated using the projector-augmented-wave (PAW) potential approach

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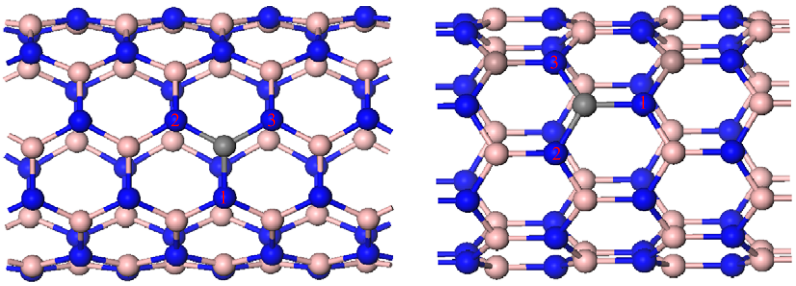
doi:10.1016/j.ssc.2010.11.002



(a) TM-doped (5,5) GaNNT. (b) TM-doped (8,0) GaNNT.

Fig. 1. Structure models of the TM-doped (5, 5) GaNNT (a) and (8, 0) GaNNT (b), where the yellow, blue and gray balls denote Ga, N and TM atoms. The blue balls marked with red numbers denote the nearest-neighbor atoms of the TM. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to the density-functional theory (DFT) within the generalized-gradient approximation (GGA) implemented in the Vienna ab initio simulation package (VASP). The rest of the paper is organized as follows. Section 2 gives the details of our DFT calculation method. In Section 3, we firstly present the models of the doped configurations, then the results for the electronic and magnetic properties mainly including total density of states (DOS), projected density of states (PDOS), magnetic moments and the amounts of charge transfer. Finally, the conclusions of the work are given in Section 4.

The local density approximation (LDA) gives usually incorrect occupation of the 3d TM impurity induced energy levels. However, GGA is a quite good correction to LDA and gives reasonable results. The GGA has been extensively used in the literature to study the TM-doped GaAs and ZnTe DMS materials [24,25]. Recently, the effective on-site Coulomb interaction correction for TM impurities in semiconductors via LDA+U has been discussed in the literature [26]. However, our main focus in this paper is to understand the delocalization of magnetic moments of the 3d TM impurities in GaNNTs. The LDA+U may improve the results quantitatively but the overall qualitative picture of delocalization of magnetic impurities will not change. Therefore, in this paper we use the Perdew–Burke–Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA) [27] to investigate the structural, electronic and magnetic properties around different substitutional 3d TM impurities doped at cation sites in the GaNNTs.

2. Calculation methods

The calculations are performed within the framework of DFT using the PAW potential and a plane-wave basis set, as implemented in the VASP [28–32]. The electron exchange and correlation is treated by using the PBE formulation of the GGA [27]. The models are constructed in a periodically tetragonal supercell with lattice constants of $a = b = 20$ Å. To minimize interaction between two adjacent TM atoms, the lattice constant c along the tube axis is taken to be four and two times the periodic length for the armchair (5, 5) and zigzag (8, 0) GaNNTs, respectively. The Brillouin zone integration is performed by using the Gamma centered Monkhorst–Pack scheme [33] with $1 \times 1 \times 11$ k-points. To avoid the numerical instability due to level crossing and quasi-degeneracy near the Fermi level, we use the first order Methfessel–Paxton method with a width of 0.2 eV. In order to find the ground geometries of the doped systems, the conjugate-gradient (CG) minimization scheme is utilized. The optimization will continue, until the convergence tolerance of total energies of the last two sequential steps is less than 10^{-4} eV/atom as well as the maximum force on each atom being less than 0.02 eV/Å.

3. Results and discussion

A GaNNT can be constructed by rolling a honeycomb-like graphitic GaN sheet into a cylinder, like the way of constructing silicon carbide nanotubes (SiCNTs) [34]. We first optimize the structures of pristine armchair (5, 5) and zigzag (8, 0) GaNNTs. The calculated Ga–N bond lengths of (5, 5) and (8, 0) GaNNTs are about 1.88 and 1.89 Å and the average diameters are about 8.99 and 8.32 Å, respectively, in accordance with previously reported values [19,35]. These results suggest that the method used in the present calculations is suitable for describing the properties of GaNNTs. Fig. 1(a) and (b) display the structure models of the 3d TM (TM = V, Cr, Mn, Fe, Co, Ni and Cu) doped (5, 5) and (8, 0) GaNNTs, respectively, in which the blue, yellow and gray balls denote N, Ga and TM atoms. The TM atom substitutes for a cation site (Ga site) in a pristine (5, 5) or (8, 0) GaNNT, and contributes three electrons to the anion (N) dangling bonds. This results in the doped ions having $3d^2$, $3d^3$, $3d^4$, $3d^5$, $3d^6$, $3d^7$ and $3d^8$ configurations for V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+} and Cu^{3+}, respectively.

We perform calculations on GaNNT-based DMSs using four and two unit cells as a supercell for 3d TM-doped (5, 5) and (8, 0) GaNNTs, respectively. $Ga_{39}(TM)N_{40}$ and $Ga_{31}(TM)N_{32}$ correspond to 1.25% and 1.56% of 3d TM impurities in (5, 5) and (8, 0) GaNNTs, respectively. In order to investigate the structural stability of the 3d TM-doped GaNNTs, as a comparison study the energy differences per supercell between the 3d TM-doped GaNNTs and pristine GaNNTs ($\Delta E = E_{GaNNT+TM} - E_{GaNNT}$) are estimated firstly and the results are listed in Table 1. The negative energy differences obtained for V-, Cr-, Mn-, Fe- and Co-doped (5, 5) and (8, 0) GaNNTs imply that these TM-doped GaNNTs are more stable than the corresponding pristine GaNNTs. The small positive energy differences for Ni- and Cu-doped (5, 5) and (8, 0) GaNNTs mean that these two TM-doped GaNNTs can still exist stably. The optimized local atomic bond lengths around the substitutional 3d TM impurity, including the bond lengths between the TM atom and its nearest-neighbor N atoms (d_{TM-N}) as well as the ranges of bond lengths between its nearest-neighbor N atoms and next nearest-neighbor Ga atoms (d_{N-Ga}) are also listed in Table 1. It can be clearly seen that, firstly, all the TM–N bond lengths in 3d TM-doped (5, 5) and (8, 0) GaNNTs are shorter than the N–Ga bond lengths in pristine (5, 5) and (8, 0) GaNNTs, respectively. Secondly, the N–Ga bond lengths around 3d TM impurities in 3d TM-doped (5, 5) and (8, 0) GaNNTs are different from the N–Ga bond lengths in pristine (5, 5) and (8, 0) GaNNTs, respectively. Obviously, there is distortion around 3d TM impurities for both 3d TM-doped (5, 5) and (8, 0) GaNNTs. This is because the introduced TM impurity changes the interaction between N and Ga atoms and the resulting geometric structure changes significantly. It is interesting to note that the N–Ga bond lengths around the TM impurity site in 3d TM-doped (5, 5) and (8, 0) GaNNTs decrease