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Magnetic and structural properties of Cr-based diluted magnetic semiconductors and alloys

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ABSTRACT

We applied supercell approach by using local spin density functional theory for Cr-doped GaN, CrN/ScN superlattices and the linear muffin-tin orbital method to predict the structural and magnetic properties of these novel diluted magnetic semiconductors (DMS), superlattices and their $Cr_xSc_{1-x}N$ alloys. The global energy minimum of CrN is obtained for rocksalt (RS) structure if the compound is expanded by 8% and the phase becomes stable in the ferromagnetic (FM) state. The global energy minimum for the stable state occurs at in-plane lattice constant of 3.9 Å. In addition, the structural and optical properties of single crystal CrN/ScN superlattices and $Cr_{1-x}Sc_xN$ alloys are studied in detail. We report an isostructural phase transition from wurtzite (w-CrN) to hexagonal (h-ScN) at a hydrostatic pressure of 21 GPa which is associated with anomalous optical and piezoelectric properties.

1. Introduction

The search for magnetic materials with optimized optical, electronic, structural and magnetic properties has attracted much attention. Exploiting the charge and spin degrees of freedom of electron in a single device are the main objective of the field of spintronics. The coupling between the charge carriers in a semiconductor and the electron spins of a ferromagnetic metal doped into the semiconductor can be utilized for many magneto/spin-electronic devices. There should be some efficient mechanism to inject spin-polarized charge carriers from a ferromagnetic metal into a well prepared surface of a non-magnetic semiconductor. The compound GaN has been extensively studied because of its promising applications in short wavelength opto-electronic devices [1]. Although wurtzite-structured ferromagnetic $Mn_xGa_{1-x}N$ samples have been grown using various techniques, there is a wide range of Curie temperatures T_c reported in Mn:GaN diluted magnetic semiconductor (DMS). The recent discovery of the room temperature ferromagnetism of single crystals Cr-doped GaN and the successful growth of bulk single crystals using a sodium flux growth method has increased the interest in DMSs [2]. The ferromagnetic to paramagnetic transition temperature of (Ga, Cr) N is observed at 280 K. This can be obtained from superconducting quantum interference devices (SQUID) magnetization measurement as well as from the temperature dependence of electrical resistivity that shows a change in slope at 280 K. A Curie temperature above 400 K has been observed for (Ga, Cr) N thin films grown on sapphire substrate by the electron cyclotron resonance assisted molecular beam epitaxy (ECR-MBE) technique [3].

The current industrial and technological interests in the field of spintronics has stimulated the search for new magnetic semiconductor materials such as the transition metal (TM) and rare earth (RE) doped III–V materials and superlattices. The transition metal nitrides, especially CrN and MnN have been studied extensively in the last two decades due to their extraordinary magnetic and optical properties [4–12]. Superlattices form when nanostructured multilayer coatings are deposited. In these materials repeating layered structures of two different materials with nanometer-scale dimensions are deposited onto a surface. Such materials are of great interest due to the flexibility in adjusting their parameters and properties to be fit with certain applications. This opens the possibilities to design new materials with desired properties. The demand for mirrors based on multilayer optics has gained a great momentum in the past decade. The amorphous multi-layers of pure metallic Sc and Cr with <1 nm layer thickness have been the key candidates for high reflectance soft X-ray mirrors in the wavelength range 24–44 Å. However, the use of these multi-layers for free electron laser applications as a hard coating on cutting tools is hindered by the fact that the Cr/Sc multi-layers are thermally unstable over 300 °C. The ScN is well known to have the largest energy gain among all transitions metal nitrides and thus it should be a good candidate for high hardness coatings. The hardness of a single

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crystal ScN films is 21 GPa [13] which is the same as that of TiN (21 GPa) [14]. CrN has been widely used in hard coating applications with hardness as large as 28 GPa [15,16]. Recently, CrN has been shown to be a semiconductor with vanishing density of states at Fermi level. The growth of epitaxial single crystal ScN thin films on MgO (0 0 1) and thin films of CrN using ultra high vacuum reactive magnetron sputtering and molecular beam epitaxy (MBE) have been reported [13,15,17–20]. Moreover, single crystal CrN/ScN superlattice X-ray mirrors have been fabricated. The high thermal and mechanical stability of ScN and CrN binaries allow them to serve as good alternatives to Cr/Sc multi-layers where the optical elements are subject to excess radiation, thermal, and/or mechanical loads [21]. In the light of these interesting findings, it would be very important from fundamental and industrial points of view to study the structural and optical properties of $Cr_{1-x}Sc_xN$ alloys as a function of Cr concentration and hydrostatic pressure.

2. Methodology

We perform first-principle investigation of (Ga,Cr)N system using supercell technique. By using spin-polarized density functional theory the magnetic structure of the system can be calculated. The von Barth and Hedin spin polarized exchange and correlation potential [22] is used in the local spin density functional approximation. A full potential linear muffin-tin-orbital (LMTO) method [23] was used. Experimental X-ray diffraction pattern clearly shows a wurtzite structure for (Ga,Cr)N single crystals with $a=3.192$ Å and $c=5.191$ Å. The axial ratio c/a of CrN adopts a value of 1.626 which is slightly larger than that of pure GaN. This can be explained by the fact that Cr atomic radius (1.40 Å) is larger than that of Ga (1.26 Å). The bond length of Ga–N is 1.947 Å. In the wurtzite structure, the lattice vectors are (in units of a) ($\sqrt{3}/2$, $-1/2$, 0), (0, 1, 0) and (0, 0, c/a). The unit cell contains two cations located at (0, 0, 0) and (2/3, 1/3, 1/2), and two anions positioned at (0, 0, 3/8) and (2/3, 1/3, 7/8). A 32 atom supercell composed of eight wurtzite primitive cells of GaN, i.e., the lattice vectors have been doubled along all three directions, thereby accommodating 16 Ga and 16 N atoms. The nearest two neighbors of Ga atoms are replaced by Cr atoms so that the supercell formula unit becomes $Cr_2Ga_{14}N_{16}$. By doing so, we can ensure that the Cr spins couple ferromagnetically or antiferromagnetically. We implemented self-consistent tight binding linear muffin tin orbitals (TB-LMTO) method [24], the atomic sphere approximation (ASA) and by knowing the ASA potential, to calculate the ground state charge density. We have used the gradient-corrected spin-polarized exchange-correlation functional as per the original Perdew–Wang formulation [25].

Spin-polarized bands have been calculated with a minimal basis set consisting of s, p, and d orbitals ($l=2$) for Ga, Cr, and N atoms. The fully occupied 3d states of Ga are considered as relaxed band states in the self-consistent iterations. Excluding the valence states of Ga, Cr, and N, the core electrons were kept frozen in their isolated atomic form. The atomic sphere radii of Ga, Cr and N atoms used are 1.227, 1.227 and 1.015 Å, respectively. Two different types of empty spheres at the high symmetry positions consistent with the $P6_3mc$ space group were used. Thus the wurtzite unit cell is divided into a total of eight overlapping atomic spheres (four real atoms and four empty spheres). We have used (6, 6, 4) Monkhorst-Pack **K** mesh which corresponds to 144 k points in the irreducible cubic Brillouin zone (BZ) and the BZ integration has been done using the improved tetrahedron method [26].

3. Results

3.1. Magnetic and structural properties of Cr-doped GaN from first principles

We proceed by examining the stability of CrN in cubic zinc-blende (ZB), wurtzite (WZ) and Rocksalt (RS) structures for both ferromagnetic (FM) and antiferromagnetic (AFM) states. Fig. 1 depicts the total energy of CrN for both FM and AFM states. The Rocksalt structure with a global energy minimum lower than that of metastable ZB structure, which has a minimum at larger lattice constant, is the stable structure for CrN. At about 8% lattice expansion, the ferromagnetic state (FM) becomes stable. The NaCl structure global minimum occurs at a lattice constant of a value of 3.9 Å as indicated by Fig. 1. Table 1 summarizes our theoretical results for the bulk compounds *Rocksalt*-CrN (the stable phase when the lattice constant is expanded by 8% as shown by figure) and w-GaN. The table indicates that Cr-doped GaN system exhibits a magnetic moment of $2.70\mu_B$ per Cr atom. The nearest neighbor atoms adopt magnetic moments of $+0.025\mu_B$ per Ga atom and $-0.025\mu_B$ on nearest neighbor N sites. Thus, Cr-doped GaN exhibits ferromagnetism. These results are in excellent agreement with LMTO calculations [23]. Also, our calculations indicate that lowering the Cr concentration enhances the Cr–Cr separation in the Cr-doped bulk GaN and thus leads to ferromagnetic coupling between the two Cr atoms. We then proceed to calculate the structural properties of $Cr_{1-x}Ga_xN$ alloys as a function of Ga concentration using recently published first-principles valence force field approach (for more details see Ref. [27] and references therein) that we applied to study the structural and piezoelectric properties of disordered $Sc_xGa_{1-x}N$ alloys.

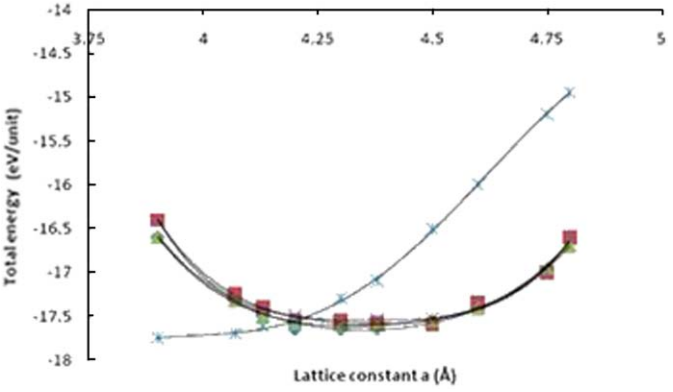

Fig. 1. Total energy vs. lattice constant a for CrN. Square symbols represent wurtzite WZ AFM state. The triangle symbols are for zinc-blende ZB AFM. The star symbols represent the NaCl FM state.

Table 1
Calculated lattice constant, a, axial ratio c/a, the Cr–Cr distance d_{Cr-Cr}, the distances between Ga and anions $d_{Ga\text{-}anion}$, and equilibrium volumes V_0,Bulk modulus B_0 and magnetic moments μ for the ferromagnetic state of *Rocksalt*-CrN and w-GaN.

Compound	a (Å)	c/a	d_{Cr-Cr} (Å)	$D_{Ga\text{-}anion}$ (Å)	V_0 (Å^3)	B_0 (GPa)	μ (μ_B)
Rocksalt-CrN	4.320	1.630	3.21		113.0	405	2.70
w-GaN	3.162	1.631		1.947	44.65	210	0.025