Physics Letters A 373 (2009) 3091–3096

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Ferromagnetism in carbon-doped ZnO films from first-principle study

Xiaofang Wang, Xiaoshuang Chen *, Ruibin Dong, Yan Huang, Wei Lu **

National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai 200083, China

ARTICLE INFO

Article history:
Received 10 March 2009
Received in revised form 22 June 2009
Accepted 27 June 2009
Available online 1 July 2009
Communicated by R. Wu

PACS:
75.70.Cn
75.50.Pp
75.30.-m
72.80.Ey

Keywords:
First principles
Ferromagnetism
Supercell
Half-metallicity

ABSTRACT

First-principle calculations based on density functional theory have been performed on the nonmagnetic $2p$ light element C-doped ZnO thin films. The total energies and magnetism of the system are calculated with a ten-layer slab along $(10\bar{1}0)$ direction. The results show that the C-doped ZnO thin films are ferromagnetic. A single C is preferable to occupy the subsurface site. As the concentration of C atoms increases, the ferromagnetic coupling among the dopants is more favorable, and they tend to form a cluster around the Zn atom at the film surface. The ferromagnetism is predicted to be mainly from a p–d exchange-like p–p coupling interaction and a p–d exchange hybridization. The p–p coupling interaction is the dominative mechanism.

1. Introduction

The diluted magnetic semiconductors (DMS) have recently been one of the most prevailing focuses in the field of material science, due to their potential applications in spintronic devices [1,2]. To date, many efforts have been carried out for the search of high Curie temperature (T_C) ferromagnetism (FM) in oxide semiconductors, such as magnetic ion Ti, V, Cr, Mn, Fe, Co, and Ni-doped ZnO, TiO_2, SnO_2, In_2O_3, and HfO_2 materials [3–11], which are candidates for room temperature (RT) DMSs with highly industrial applications in spintronics. Among them, ZnO-based DMS, as a transparent conducting oxide, has good electrical and optical properties in combination with a large band gap of 3.3 eV, abundance in nature, absence of toxicity with varied applications as electrodes, window materials in displays, solar cells and various optoelectronic devices [12]. However, the sample growth is very sensitive to the preparation methods and conditions, making the experimental results quite contradictory to each other. One of the fundamental and key questions is whether the fabricated material is indeed a solid solution of $Zn_{1-x}TM_xO$ (TM = V, Cr, Mn, Fe, Co, etc.) or it remains as ZnO with embedded TM clusters, precipitates, or second phases, responsible for the observed magnetic properties. Mostly, the high T_C FM in ZnO-based DMSs is generally considered to be an intrinsic phenomenon [13], while some research works have indicated that the FM originates from secondary phases or metal clusters [14,15]. Meanwhile other groups have attributed it to the oxygen related defects [16]. Recently, the FM has been observed in pristine SnO_2 thin films [17]. Observation of FM in these undoped systems has opened a wider debate as to the origin of FM in these semiconductors. Theoretically, the FM of most DMS is considered to involve carriers (electrons or holes) in mediating interaction between dopants. For example, the Ruderman–Kittel–Kasuya–Yosida (RKKY) model is based on sp–d exchange between the sp itinerant carriers and the local d states of the transition-metal-doping elements. Other than that, superexchange, double exchange and bound magnetic polarons (BMPs) are invoked to explain the FM ordering. Moreover, Coey et al. extend the BMPs into the F-center-mediated BMPs to explain high T_C FM in oxides [18]. However, there is not unambiguous conclusion on whether the FM is intrinsic or not, and what mechanism is responsible for the FM?

The most recent attractive results that RT FM with T_C higher than 400 K is observed in C-doped ZnO have drawn our attention [19,20]. Pan et al. have theoretically reported ferromagnetic coupling among the C dopants and a magnetic moment of $2.02\mu_B$ per C. The result was confirmed experimentally by pulsed-laser deposition. In fact, the theoretical studies have predicted that anion substitutions in IIA-oxide can lead to FM, but the mechanism will be different compared to that of the cationic substitutions [21].

* Corresponding author. Tel.: +86 21 65420850 24309; fax: +86 21 65830734.
** Corresponding author. Tel.: +86 21 65420850 24315; fax: +86 21 65830734.
E-mail addresses: xschen@mail.sitp.ac.cn (X. Chen), luwei@mail.sitp.ac.cn (W. Lu).

0375-9601/$ – see front matter
doi:10.1016/j.physleta.2009.06.049

Yu et al. have reported the FM in N embedded ZnO:N films [12]. Bannikov et al. have reported the spin polarization induced by replacement of O atoms by $2p$ impurities (B, C and N) in nonmagnetic cubic $SrMO_3$ (M = Ti, Zr and Sn) perovskite [22]. Wu et al. have found that C substitution for either single B or N atom in the BN nanotubes can induce spontaneous magnetization [23]. Other than that, Peng et al. showed that the hole-induced magnetization in oxides and nitrides are an intrinsic host property when enough homogeneous holes are injected into the system, which provides a challenge to understand the origin of the magnetism in these materials with no doping of access magnetic ions [24]. In a word, it is a physically rich topic to study the C-doped ZnO.

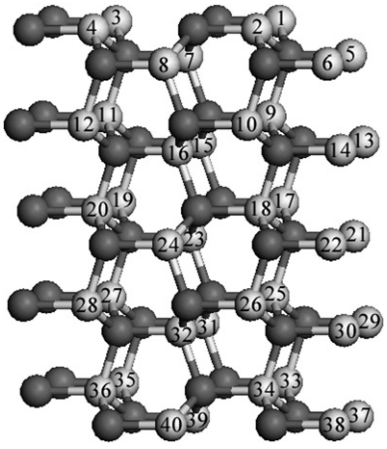

Fig. 1. The side view of the ten-layer slab for wurtzite ZnO $(10\bar{1}0)$ surface, which consists of 40 Zn and 40 O atoms. The darker and lighter spheres represent Zn and O atoms, respectively.

In this Letter, we present a theoretical study of the electronic and magnetic properties of C-doped ZnO thin films, using the slab supercell model. We focus on the possibility of the magnetization for ZnO films induced by nonmagnetic *sp* impurities.

2. Method of calculation

The details about the geometry of the used supercell are given in Fig. 1. The ZnO surface is modeled by a 2×2 ten-layer slab, containing 40 Zn and 40 O atoms in the supercell [25]. Each slab is separated from the other by a vacuum region of 12 Å along $(10\bar{1}0)$ direction, so that the surfaces do not couple with each other. To preserve symmetry, the top and bottom layers of the slab are taken to be identical. All the layers are allowed to relax without any symmetry constraint. Calculations of the total ener-

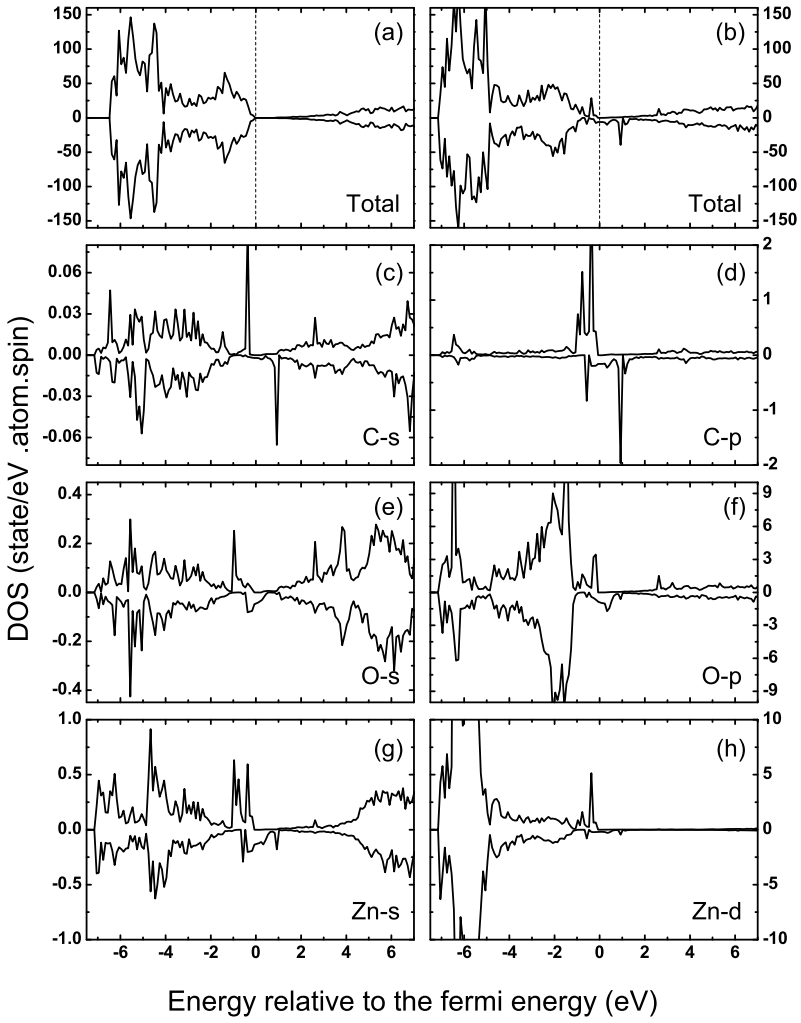

Fig. 2. Total spin polarized DOS for (a) undoped $Zn_{40}O_{40}$ slab; (b) C-doped $Zn_{40}C_2O_{38}$ slab, where C atom sites at the $(10\bar{1}0)$ film subsurface; (c), (d) Partial spin polarized DOS for the C $2s$ and $2p$, respectively; (e), (f) Partial spin polarized DOS for the O $2s$ and $2p$, respectively, where the O atoms are the next nearest neighbors to the C dopant; (g), (h) Partial spin polarized DOS for the Zn $4s$ and $3d$, respectively, where the Zn atoms are the nearest neighbors to the C dopant. Positive DOS represent the majority spin, while negative DOS represent the minority spin. The Fermi level has been shifted to 0 eV.