Materials Science in Semiconductor Processing 35 (2015) 139–143

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Non-ferromagnetic behavior in Ag–N codoped ZnO: First-principle calculations

Wanjun Li [a,b], Liang Fang [a,*], Hong Zhang [b], Guoping Qin [a,b], Haibo Ruan [c], Chunyang Kong [b,*]

[a] State Key Laboratory of Mechanical Transmission, College of Physics, Chongqing University, Chongqing 401331, China
[b] Key Laboratory of Optoelectronic Functional Materials of Chongqing, College of Physics and Electronic Engineering, Chongqing Normal University, Chongqing, Chongqing 401331, China
[c] Research Center for Materials Interdisciplinary Sciences, Chongqing University of Arts and Sciences, Chongqing 402160, China

ARTICLE INFO

Available online 20 March 2015

Keywords:
Ag–N codoped ZnO
First-principle calculations
Ferromagnetism
The atomic relaxation

ABSTRACT

We employ density-functional theory within the generalized-gradient approximation to study the structural and electronic properties of Ag–N codoped ZnO. The calculations show a strong tendency towards formation of the nearest-neighbor Ag_{Zn}–N_O pairs shown to be in the spin polarized state with a total magnetic moment of 2.02 μ_B. Compared with the isolated Ag or N doped ZnO, it is found that Ag–N codoping can obviously enhance the local magnetic moment of Ag and N atoms due to strong p–d hybridization. However, Ag–N codoping system shows non-ferromagnetic behavior, which is other than Cu–N codoping system, where robust ferromagnetism is confirmed by both experimental and theoretical research. It is demonstrated that the atomic relaxation is responsible for diminishing the magnetic moments of Ag–N codoped ZnO. We therefore suggest that Ag–N codoped ZnO is unsuitable for spintronics applications.

1. Introduction

In the past decade, diluted magnetic semiconductors (DMSs) have attracted tremendous attention due to their potential applications in the development of emerging spintronics based devices [1–3]. Among them, ZnO doped with transition metal (TM) elements such as Mn, Co, Fe, Ni, V, Cr, has been intensively studied since room temperature ferromagnetism was theoretically predicted [4–8] and experimentally observed [9–15]. However, the origin and mechanism of the observed ferromagnetism is still under debate. This is because these TM dopants themselves are intrinsically magnetic, and thus their precipitates in ZnO may also contribute to the observed ferromagnetism [16,17]. Recently, therefore, the research on ZnO DMS has been primarily focused on the study for clarifying the origin and mechanism of the ferromagnetism in ZnO DMS [18]. It has been proposed that ferromagnetism is even possible in ZnO-based DMS when they are doped with a nonmagnetic ion (namely d^0 – ferromagnetism), which can avoid the problem related to magnetic precipitates. Ferromagnetism in nonmagnetic ion doped ZnO can help to further clarify the origin and mechanism of the ferromagnetic ordering in ZnO-based DMS [18].

Recently, nonmagnetic ion (Cu) doped ZnO have motivated researches to extensive study since the Cu-related secondary phases are non-ferromagnetic and the size mismatch between Cu and Zn is very small [19]. Although the origin of ferromagnetism in such system is controversial, theoretical and experimental investigations have confirmed that Cu-doped ZnO (ZnO:Cu) does exhibit

* Corresponding authors.
E-mail addresses: lfang@cqu.edu.cn (L. Fang), kchy@163.com (C. Kong).

http://dx.doi.org/10.1016/j.mssp.2015.02.083
1369-8001/

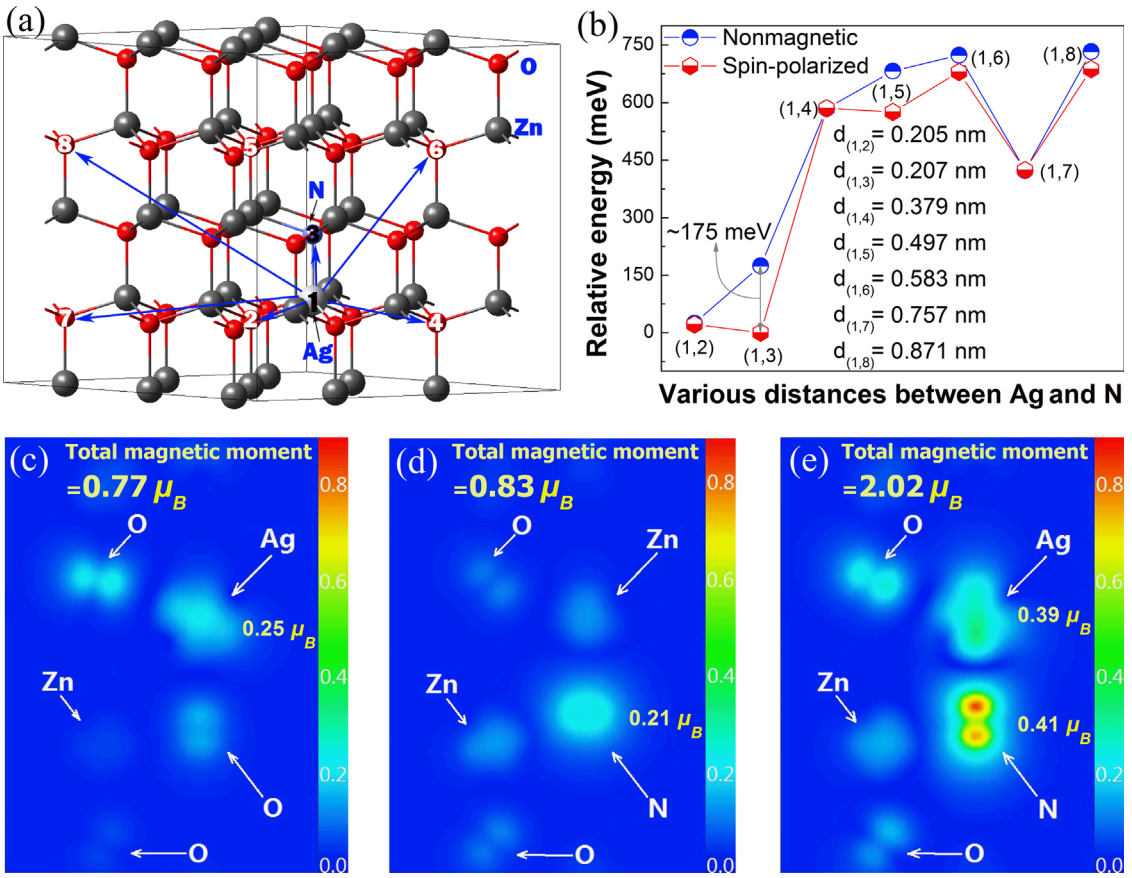

Fig. 1. (a) The $3 \times 3 \times 2$ supercell of the w-ZnO with the Ag_{Zn}–N_O complex. (b) Relative energy of ZnO containing N_O (1) and Ag_{Zn} (2–8) with various distances calculated both spin- and non-polarized. (c)–(e) Local spin density slices plotted on the (110) plane of the Ag-doped, N-doped, and Ag–N codoped ZnO system.

significant room temperature ferromagnetism [20–24]. Even, ZnO:Cu codoped with nitrogen can also influence ferromagnetism of ZnO:Cu system. Experiment reported in Refs. [25] and [26] found the observed magnetic moment in ZnO:Cu system decreased due to nitrogen codoping, whereas experiments reported by Herng et al. [27] have confirmed that ferromagnetism can be enhanced in Cu-doped ZnO by N_2O annealing, where XPS measurement revealed that N was incorporated into the sample. Meanwhile, Buchholz et al. [28] reported that ferromagnetic ZnO:Cu films prepared by PLD could only be obtained in *p*-type films by nitrogen incorporation. Further theory reported in Ref. [29] has demonstrated that the total magnetic moment of ZnO:Cu can be enhanced by codoping with N element, which is mainly due to the p–d hybridization of Cu–N and Cu–O, as well as p–p coupling interaction between N and O at the Fermi level. Like Cu, Ag and its oxides are also not magnetic. Therefore, Ag-doped ZnO may also help to understand the origin and mechanism of the ferromagnetic ordering in ZnO-based DMS. More recently, He et al. [30] reported that room temperature ferromagnetism had been observed in Ag-doped ZnO ceramic samples, and its magnetization increased with increasing Ag content. Furthermore, Shen et al. [31] also predicted based on first-principle calculations that ZnO doped by a nonmagnetic 2p light element (N) is ferromagnetic due to a p-d exchange-like p–p coupling interaction involving holes, which was experimentally confirmed by Jindal et al. [32]. It is interesting whether or not codoping N (or Ag) can influence the ferromagnetic ordering of ZnO:Ag (or ZnO:N) system. To our best knowledge, moreover, investigation on ferromagnetism in Ag–N codoped ZnO system has not reported in the literature up to now. In this work, we report a first principles study of the ferromagnetic behavior of Ag–N codoped ZnO. We found Ag–N codoping system shows non-ferromagnetic behavior. Therefore, we suggest that Ag–N codoped ZnO is unsuitable for spintronics applications.

2. Computational details

Our first-principles calculations are performed based on the plane-wave pseudopotential DFT method as implemented in the Vienna *ab initio* simulation package (VASP) [33], to investigate the electronic and magnetic properties of N, Ag, and Ag–N codoped ZnO. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) scheme was used for treating the exchange and correlation potential. Pseudopotentials with $3d^{10}4s^2$, $2s^22p^4$, $4d^{10}5s^1$ and $2s^22p^3$ valence electron configurations