Dual Manipulation of Ferromagnetism in Co-Doped ZnO Thin Films by Surfactant and n-Type Carriers

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We present a conceptually-new approach “dual manipulation effect” using the surfactant passivation and the electron carrier doping for mediating intrinsic ferromagnetism in Co-doped ZnO dilute magnetic semiconductor (DMS) thin films. The first-principles calculations show that the surface passivation by hydrogen serves as a magnetism switch for the Co-O-Co magnetic coupling at the surface of the thin film, and thus can control the spin polarization of the doped Co atoms. Meanwhile, the electron carrier doping can further function as an effective layerlike ferromagnetism mediator for the underneath layer. The dual manipulation effect sheds light on the essential magnetism origin of n-type Co:ZnO DMS thin films, and may be used as an alternative strategy for enhancing the ferromagnetism in other n-type DMS oxides thin films.

Key words: Surface passivation, Carriers doping, Ferromagnetism, Zinc oxide thin film

I. INTRODUCTION

Dilute magnetic semiconductors (DMSs), where transition metal (TM) atoms are introduced into the cation sites of the semiconductor host, have stimulated extensive interests because of the potential usages of both charge and spin for spintronic devices [1–3]. Recently, DMS oxides have attracted much attention as essential materials for practical semiconductor spintronic applications such as spin filters or spin polarizers [4]. In particular, theoretical calculations based on the mean field approximation predicted a room-temperature (RT) ferromagnetism in ZnO base, triggering extensive studies of TM:ZnO alloys with a special focus on Co:ZnO as the most promising candidate for an RT ferromagnetic (FM) semiconductor [5, 6]. Actually, a number of studies have reported RT FM behaviors in Co-doped ZnO DMSs by employing different fabrication techniques [7–9]. Meanwhile, there were also disparate claims about lack of ferromagnetism [10, 11]. Thus, whether RT ferromagnetism is an intrinsic property remains still unclear in nature.

Based on the first-principles calculations, Walsh et al. and Raebiger et al. proposed that the possibility of an intrinsic origin can be realized by the assistant of the electron doping in bulk oxides [12, 13]. However, experimentally a variation of magnetization with increase of the electronic dopant contents in the structurally perfect Co-, Mn-, and Cu-doped ZnO thin films was observed [14–17]. Hence, the role of carriers doping on the ferromagnetism in ZnO DMS films is still unclear. Moreover, it has been suggested that the surfactant effect plays an important role in the occurrence of many fascinating phenomena, such as stabilization of dopants and enhancement of surface conductivity, in III-V and IV-group DMSs [18, 19]. However, the underlying physical mechanism induced by surfactant modulation in TM:ZnO thin film systems is not discovered. Therefore, understanding the behavior of surfactant and carrier mediation for intrinsic ferromagnetism is not only important for further increasing the functionality efficiencies in ZnO-based DMSs, but also for the exploration of other DMS materials such as TiO$_2$, Si, GaAs, and GaN.

In this work, we investigate how the surfactant and carrier simultaneously manipulate the local magnetic order at the polar $<0001>$ orientated surface and inner of wurtzite ZnO thin films by first-principles. We find that the surface passivation by H can control the spin polarization of doping Co atoms, while the electron carriers doping can further function as an effective layerlike ferromagnetism mediator for the underneath layers. Therefore, the FM Co-O-Co coupling can be switched on and off via surfactant passivation, and the ferromagnetism could be enhanced further by electron carriers doping. Our findings manifest a unique dual manipulation effect of realization of intrinsic ferromagnetism in the wide-gap transparent n-type conductive oxides.
II. COMPUTATIONAL METHODS

Our first-principles calculations were performed using a plane wave basis set with the projector augmented plane-wave (PAW) method [20] as implemented in the Vienna ab initio simulation package [21]. The overall framework is spin-polarized density-functional theory (DFT) [22]. The exchange-correlation interaction is described within the generalized gradient approximation (GGA) in the form of PW91 [16]. Although GGA underestimates the band gap of ZnO, the description of Co-doped ZnO is qualitatively similar to that of methods which better account for electronic correlations [23]. The energy cutoff is set to 350 eV, and the atomic positions are allowed to relax until the energy and force are less than $10^{-4}$ eV and $10^{-2}$ eV/Å, respectively.

Since the wurtzite structure is not centrosymmetric, thin layers grown along the crystallographic c-axis may present either the [0001] or [0001] growth direction. Along this direction, pure hexagonal O and Zn layers alternate so that the resulting (0001) surfaces can be either Zn- or O-terminated. It was revealed that the (0001) O-ended surfaces are experimentally active and theoretically stable in energy [24, 25]. Hence, in this work we focus on the O-terminated (0001) slab films simulated by periodically repeating the ZnO bilayers along the c-axis of the unit cell. Each slab film model consists of ten ZnO planes and is separated by a vacuum region of 12 Å. We use a (3x3) two-dimensional (2D) unit cell containing nine atoms per plane to mimic the thin films.

III. RESULTS

First, we determine the occupation nature of the dopant in ZnO thin films. For this purpose, two doping Co ions are placed at different cation sites within different planes including the in-plane and out-plane which are respectively parallel and perpendicular to the {0001} surface, as shown in FIG. 1. Importantly, our energetic results show that from surface to inner layer of the film, the Co ions prefer to be substituted within the film, the Co ions prefer to be substituted within the first, second, and third bilayers, respectively.

Next, we consider the clean O-terminated (0001) films without and with n-type carriers doping. In the case of clean surface without carriers doping, the calculated results show that the magnetic exchanges between the Co ions are all of AFM characters as listed in Table I, which is similar to the magnetic properties in the bulk [27]. As is known that the carriers mediated ferromagnetism by electron doping was ever proposed to reconcile the observed ferromagnetic signals in bulk materials [12, 28]. While for the thin films with n-type carriers doping, our magnetic results show that the ground states from surface to the inner layers are all AFM states even under a quite large doping level of 6 electrons per cell. The underlying physical reason will be discussed later. Importantly, this indicates that carriers doping alone cannot serve as an effective ferromagnetism mediator in the ZnO DMS film [29].

Hydrogen is inevitably present on the film surface to saturate the dangling bonds during specific sample growth. Experiments have indicated that unintentional incorporation of H in the sample synthesis significantly contributes to the energetic and magnetic properties of the films, suggesting that H may play an impor-

<table>
<thead>
<tr>
<th>Level</th>
<th>Configuration</th>
<th>∆E/meV</th>
<th>Ground state</th>
<th>$M/\mu_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>C1</td>
<td>−60</td>
<td>AFM</td>
<td>±2.75</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>−42</td>
<td>AFM</td>
<td>±2.61</td>
</tr>
<tr>
<td></td>
<td>C3</td>
<td>−53</td>
<td>AFM</td>
<td>±2.54</td>
</tr>
<tr>
<td></td>
<td>C1−H</td>
<td>146</td>
<td>FM</td>
<td>2.24</td>
</tr>
<tr>
<td></td>
<td>C2−H</td>
<td>−8</td>
<td>AFM</td>
<td>±2.39</td>
</tr>
<tr>
<td></td>
<td>C3−H</td>
<td>−37</td>
<td>AFM</td>
<td>±2.44</td>
</tr>
<tr>
<td>2 e/cell</td>
<td>C2−H</td>
<td>18</td>
<td>FM</td>
<td>2.36</td>
</tr>
<tr>
<td></td>
<td>C3−H</td>
<td>−48</td>
<td>AFM</td>
<td>±2.41</td>
</tr>
<tr>
<td>5 e/cell</td>
<td>C3−H</td>
<td>21</td>
<td>FM</td>
<td>2.35</td>
</tr>
</tbody>
</table>

Note: The second and third bilayers are 2 and 5 electrons per cell.
tant role in the process of dopant incorporation [30]. Thus, we analyze now the O-terminated (0001) surface passivated by one monolayer (ML) H, as shown in FIG. 1(b)–(d). Interestingly and importantly, it is found that the calculated energy difference between the AFM and FM states $\Delta E = E_{AFM} - E_{FM}$ for the surface bilayer doping case surprisingly turns to a large positive value, i.e., 146 meV as presented in Table I, suggesting a significantly spontaneously FM ordering by surfactant passivation. Whereas for the underneath bulklike cases (as shown in FIG. 1 (c) and (d)), the AFM ground states remain unchanged with negative $\Delta E$ values as illustrated in Table I.

To explore how the H passivation affects the magnetic properties of the ZnO film surface, we calculated the layer projected density of states (LDOS) for these model structures. FIG. 2 shows the LDOSs of Co and O bonded to Co at the two uppermost layers in the surface bilayer structure (FIG. 1(b)) without and with H adsorption. It can be observed that for the clean surface O, i.e., O1 shown in the top panel of FIG. 2(a), its 2p states are significantly spin polarized and considerably hybridized with the Co 3d states. The spin polarized O 2p states are around the Fermi level, and thus result in a higher number of 2p holes in the O valence bands (VBs), which are in good agreement with those reported in previous literatures [24]. Based on these, we propose that it is the holes of O 2p induced by surface polarization that seriously compensate the intrinsic donor carriers in the n-type ZnO films and make the mechanism of carrier mediating ferromagnetism ineffective. Hence, the AFM interactions always dominate for the clean surface structures. When the H atoms are adsorbed on the O surface, an interesting phenomenon occurs. As seen from the top panel of FIG. 2(b), the H 1s states are high hybridized with the surface O 2p states at the deep energy range of about −10 eV under the Fermi level, making the VBs of the surface O considerably move down. Due to the significant s-p hybridizations, a part of VB electrons are transferred from H 1s states to O 2p states. This redistribution of electrons fundamentally eliminates the O 2p holes, brings extra electrons for the surface states, and consequently mediates the magnetic exchanges between the Co ions in the subsurface cation layer from AFM to FM interactions. The elimination of surface p holes by H passivation is also confirmed from the LDOSs of surface O for the clean and H-passivated structures with no Co doping as shown in the bottom panels of FIG. 2 (a) and (b). Furthermore, there is an obvious difference between the films with and without Co doping, namely, the LDOSs of surface O for the Co-free films are not significantly spin-polarized (bottom panels of FIG. 2 (a) and (b)), which is due to the absence of p-d hybridizations in this system.

For the underneath bulklike layers, our results show that their magnetic ground states are not changed by H-passivation. However, we note that the absolute values of the energy differences for the second and third bilayers become smaller, as presented in Table I. The underlying physical reason can be discovered from the LDOS analysis. FIG. 3(a) displays the LDOS for the second bilayer in the clean surface structure. It can be observed that similar to the surface bilayer, the upper O (marked as O1 in FIG. 3) bonded to Co is spin polarized and consequently the spin-split VB holes are introduced, which limit the function of carrier mediation. As the surface is passivated by H, the VBs of the upper bonding O are shifted down in energy as illustrated in FIG. 3(b). Compared with the surface bilayer, however, the 1s states of H cannot be effectively hybridized with the 2p states of the upper O in the second bilayer due to their larger mutual distance. Hence, the 1s electrons of H are basically localized around the surface and cannot penetrate into the deeper layer to mediate the FM interaction. This strong localization of surface electrons is probably induced by the transverse confinement in the surface of the 2D films, and has been detected by scanning tunneling microscopy in experiment [31]. This indicates that if the magnetic mechanism of carriers mediating acts, extra electrons need to be doped.

To check this scenario, we now investigate the electron doping effects on the magnetic and electronic properties for the underneath layers after surface passivation. The electron doping is set at different doping levels from 1 to 6 electron(s) per supercell. FIG. 4(a) shows the resulting energy differences dependent on the doping levels for the second and third bilayers. Interestingly, it is observed that the magnetic orders are transformed from AFM state to FM state with the increase of the doping level for both bilayers. Particularly, it is found that the transition doping levels for the sec-

![FIG. 2](image-url)
FIG. 3 LDOSs of Co and O at the upward layer relative to the Co plane in the second bilayer of the structure of FIG. 1(c). (a) Clean surface, (b) without and (c) with further electron doping under H adsorption.

FIG. 4 (a) The diagram of energy differences dependent on the doping levels, and (b) a simple physical picture for the dual manipulation effect induced by the combination of H passivation and electron carriers doping on the magnetic transform progress. The gray thin slice represents the H adsorption layer on the O surface, and the pink and dark green layers illustrate the AFM and FM exchange interactions, respectively.

ond and third bilayers are 2 and 5 electrons per cell as listed in Table I, indicating the realization of FM ordering towards the inner cation layer needs more electrons compared to the outer cation layer. This implies that electron carriers doping can further function as an effective layerlike ferromagnetism mediator from surface to inner after surfactant passivation.

FIG. 3(c) presents the LDOS for the representative second bilayer within the transitional doping level of 2 electrons after H passivation. It can be observed that the O and Co ions trap extra electrons after electron doping compared to the LDOS in FIG. 3(b) for the electron undoping case, albeit the electron transfer is minor. Another important corroboration is that with increase of electron doping, the average magnetic moment per Co, \( M \), becomes smaller as tabulated in Table I. This substantially manifests that the carrier mediation via charge transfer plays a dominating role in realizing the FM ordering between the Co ions in the inner layers of ZnO DMS film.
IV. DISCUSSION

Based on all the above calculations, we propose a novel physical picture of “dual manipulation effect” to shed light on the origin of ferromagnetism in Co-doped ZnO thin films, which is schematically depicted in FIG. 4(b). The adsorption of H plays a decisive role in the realization of FM ordering. As it is switched on, the carriers mediated ferromagnetism begins to play its role. When it is switched off, the spontaneous ferromagnetism disappears even under quite significant electron doping levels. Hence, the surfactant passivation controls the spin polarization of doping Co atoms and serves as a magnetic switch named by us. The subsequent electron carriers doping can further function as an effective layerlike ferromagnetism mediator for the bulklike inner cation layers of the thin films as revealed earlier. Thus the FM Co-O-Co coupling can be switched on and off via surfactant passivation, and the ferromagnetism could be further mediated by the combination of the carriers doping.

Actually, the simple theoretical picture of dual manipulation effect and its underlying physical mechanism indeed provide insight into the seemingly strange behaviors observed in experiments. For example, in Ref.[32], although the residual electron carrier concentrations are higher than $10^{20}$ cm$^{-3}$, these structurally perfect Co:ZnO thin films with bare surfaces are absent of intrinsic FM interactions and present paramagnetic behaviors. On the contrary, in Refs.[33, 34], it is reported that obviously spontaneous magnetization is realized after surface states saturated by H, albeit the films are in the insulating state. In addition, it has been observed that the magnetizations of TM:ZnO films are enhanced with increase of the doping carriers, and close to 2.0 $\mu_B$ Co-doped and 4.5 $\mu_B$ Mn-doped at the electron concentration of $10^{21}$ cm$^{-3}$ [15]. As our calculations have shown that the surface of TM:ZnO thin films plays an important role in mediating the magnetic interactions, instructive clues to the origin of these unusual experimental observations may be found by reexamination of the surface states in these films. Finally, this dual manipulation ferromagnetism is intrinsic in nature, and thus we believe it has important implications for future experimental proceedings of n-type DMS thin films.

VI. ACKNOWLEDGEMENTS

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