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Tuning magnetic properties of In₂O₃ by control of intrinsic defects

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Abstract – The electronic structure and magnetic properties of In_2O_3 with four kinds of intrinsic point defects (O vacancy, In interstitial, O interstitial, and In vacancy) have been theoretically studied using the density functional theory. The defect energy states of the O vacancy and In interstitial are close to the bottom of conduction band and act as shallow donors, while the defect energy states of the In vacancy and O interstitial are just above the top of the valence band and act as shallow acceptors. Without addition of any magnetic ions, all the hole states are completely spin polarized, while the electron states display no spin polarization. This implies that semiconducting In_2O_3 can display magnetic ordering, purely due to the intrinsic defects. However, the formation energies for neutral *p*-type defects are too high to be thermodynamically stable at reasonable temperatures. Nevertheless, it is shown that negative charging can greatly decrease the formation energies of *p*-type defects, simultaneously removing the local magnetic moments. We conlcude that $V_{In}^{\prime\prime\prime}$ and $O_I^{\prime\prime}$ will be the dominant compensating defects as In_2O_3 is doped with TM ions, such as Sn, Mo, V and Cr. This result is consistent with the general view that the *p*-type defect is a key feature to mediate ferromagnetic coupling between transition metal ions of dilute concentration in metal oxides.

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The unique combination of ferromagnetism and semiconducting properties has been extensively pursued for its promising usage in spintronics devices. Compared to the traditional half-metallic ferromagnets, such as CrO₂, Fe₃O₄, or manganite perovskites (La, Sr)MnO₃, the diluted magnetic semiconductor (DMS), where the transition metal replaces a cation on the semiconductor lattice, displays a great advantage due to the reduction of junction resistance and easy integration into today's semiconductor electronics. From both experimental and theoretical investigation, it has been commonly agreed that intrinsic defects play an important role for the ferromagnetism in DMS [1–4]. Especially from first-principles computational point of view, it has been clearly shown that *p*-type point defects, such as co-doping of N and the cation vacancy, efficiently mediate the ferromagnetic coupling between transition metal (TM) ions of dilute concentration [5–8].

Moreover, in addition to the magnetism introduced by introducing TM elements, unusual ferromagnetism with high Curie temperature and big net magnetic moments have been observed in many semiconductors without any addition of TM ions [9–11]. Notable cases are CaB₆ [12], HfO_2 [9,13,14], CaO [15,16], SiC [17] and in In_2O_3 [18]. It is noted that all the reported ferromagnetism in semiconductors without the addition of any TM, occurs in the thin-film form or nanoparticles. Lattice defects, usually oxygen vacancies, at the surfaces of thin films or in nanoparticles are suggested by experiments to be the origin of ferromagnetism [9–11]. However, according to the theoretical calculations, for all related systems, not the anion vacancy, but the *p*-type defects, especially the cation vacancy, show a stable ferromagnetic coupling. By using model Hamiltonians and *ab initio* calculations, it has been shown that the magnetic moments achieved in CaO originate from spin-parallel electrons in the degenerate molecular orbital associated to the cation vacancy [15]. However, later on, calculations on the formation energies of intrinsic defects in CaO show that the percolation of *p*-type defects to obtain the long-range ferromagnetic ordering cannot be achieved with the calculated equilibrium concentration of defects, even considering the most favorable equilibrium growth conditions [16]. In this paper, four kinds of intrinsic point defects (O vacancy, V_O ; In interstitial, In_I ; O interstitial, O_I ; and In vacancy, V_{In})



Fig. 1: Schematic illustration of atomic arrangements for the lattice of oxygen octahedron centered on the In site. (a) The In atom is located at the 8b position. (b) The In atom is located at the 24d position. The oxygen atoms are denoted by filled solid circles, the In atoms are denoted by the shaded circles. The open circles refer to the empty positions in IO, which can contain O_I or In_I .

in the wide band gap semiconductor $In_2O_3(IO)$ have been theoretically studied. The electronic structure and the delocalization of carrier density have been investigated and compared. The magnetic character of the hole states, induced by V_{In} and O_I , have been studied. Finally, the formation energies of all four point defects were calculated, taking into account the sample growth conditions and also possible charge states.

The first-principles calculations in this paper were performed using the projector-augmented wave [19] (PAW) method as implemented in Vienna Ab initio Simulation Package (VASP) package [20,21]. The generalized gradient approximation (GGA) [22] was used for treating the exchange-correlation potential. The atomic geometries were fully optimized until the Hellmann-Feynman forces on each ion were less than 0.01 eV/Å. A plane-wave energy cutoff of 620 eV, $1 \times 1 \times 1$ k-points grids and the Gaussian smearing method with a $0.05 \,\mathrm{eV}$ smearing width were used for the relaxation calculations, while the $820\,\mathrm{eV}$ energy cutoff, $2 \times 2 \times 2$ k-points grids and tetrahedron method were applied for the final total energy calculations with optimized crystal structures. Using those numerical parameters, the total energies for an 80 atoms unit cell were converged to $0.02 \,\mathrm{eV}$. This convergence criterion is enough since we are not calculating exchange integrals, which are of the order of meV.

IO has an ordered cubic vacancy structure [23], which is similar to the fluorite structure but one fourth of the anion sites are vacant. There are 32 cations and 48 anions in one cubic unit cell. One fourth of the cations occupy the 8b (denoted as In1) positions and other cations occupy the 24d positions (denoted as In2). All the anions are in one symmetry position of 48e. As shown in fig. 1, each cation resides at the center of a distorted cube with two



Fig. 2: (Color online) Spin-resolved total density of states (DOS) for IO with various native defects. The valence band minimum is set to 0. The vertical solid lines denote the Fermi energies for each defect conditions.

empty corners. These empty sites have the symmetry of 16c. In fact, it has been shown that empty sites play an important role in the defect chemistry of Sn- or Modoped IO [24–27]. The O_I is suggested to sit at this position. In this paper, we have theoretically studied four types of point defects into the lattice of IO. The magnetic properties and electronic structure of V_{In} , sitting at the position In1 or In2 show a similar behavior, thus, we only present the results for V_{In} at the 8b site in this work. O_I or In_I are located on the empty 16c site. All the ionic positions have been fully optimized.

Figure 2 shows the calculated density of states for the ground state of IO, containing various neutral defects. First, according to the relative position of the Fermi energy, it can be easily seen that V_O and In_I act as shallow donors, while O_I and V_{In} act as shallow acceptors. This observation is consistent with the previous experimental and theoretical results [28,29]. Secondly, the ground states of two *p*-type defects are spin-polarized, while the ground states of two *n*-type defects are non-spin-polarized. The total magnetic moment induced by each *p*-type point defect is equal to the number of holes, *i.e.* 3 and $2\mu_B$ for V_{In} and O_I , respectively.

Next, the carrier density of IO with various neutral defects, O_I , V_{In} , V_O , and In_I , are presented in fig. 3. Here the hole density is obtained by integrating the unoccupied states between E_F and $E_F + 0.5 \text{ eV}$, and the electron density is obtained by integrating the occupied states between $E_F - 2 \text{ eV}$ and E_F . The isosurfaces of 0.02 eÅ^{-3} are shown for all the carrier densities. From the figure we can see that the shape of the isosurface for the holes has an obvious *p*-orbital character, while the isosurface for the electrons has a spherical *s*-orbital character.

Figure 4 shows the spatial distribution of spins in one cubic unit cell of IO with *p*-type point defects, O_I and V_{In} . First, almost all of the magnetic moments are located at oxygen sites. For the O_I , 43% of the



Fig. 3: (Color online). The carrier spatial distributions for intrinsic neutral defects O vacancy, In interstitial, O interstitial and In vacancy. The red and grey spheres represent the O and In ions, respectively. The yellow spheres represent the isosurface of $0.02 e \text{\AA}^{-3}$.



Fig. 4: (Color online). The spin spatial distribution in one cubic unit cell of p-type defect: (a) O interstitial, (b) In vacancy doped IO. The red (black) circles represent the position of oxygen ions, the green (grey) circles represent the positions of In ions. The arrows on each atomic position represent the spin on each ion site, which is integrated within the radius of oxygen or In ions. The ionic radius of oxygen is taken as 1.24 Å, and the ionic radius of In is taken as 0.94 Å.

magnetic moments reside on the O_I site, while for the V_{In} case, 66% of the magnetic moments are distributed on the six O nearest neighbors (NN) of the V_{In} site. The magnitude of the magnetic moments decrease with the distance from the point defect site. Both *p*-dopants cause electron deficiency in the three delocalized *p*-orbitals of the oxygens, leading to the formation of local moments. In the case of the *n*-type V_O , it

Table 1: Calculated formation energies ΔH (eV) for various neutral defects in different experimental sample growth conditions.

Growth condition	$\Delta H(\mathbf{V}_{In})$	$\Delta H(O_i)$	$\Delta H(\mathrm{In}_i)$	$\Delta H(\mathbf{V}_O)$
O rich, In rich	8.7	4.3	5.2	4.0
O rich, In poor	4.8	4.3	9.1	4.0
O poor, In rich	8.7	6.9	5.2	1.4

instead introduces additional electrons. These electrons will fill up the empty 5s-like state of In, which has a singlet ground state. In_I could in principle contribute with a moment of 1μ B, due to the singly occupied 5p-state. However, according to our calculations the magnetic moment due to In_I is 0μ B. This is not an intuitive result, and could be related to the overestimation of charge delocalization by GGA.

From the above electronic structure and magnetic properties discussions, it is shown that the intrinsic *p*-type defects can introduce magnetization to the semiconducting IO. Our results may explain recently observed ferromagnetism in pure In_2O_3 [18]. Our results are also supported by Xiao *et al.* [30], who find V_{In} to induce ferromagnetism at $\text{In}_2\text{O}_3(001)$ surfaces. We turn now to investigate the formation energy of the studied point defects, which is calculated through the expression [31,32]

$$\Delta H_f(D^q, E_F, \mu) = [E_T(D^q - E_T(H))] - \sum_{\alpha} n_{\alpha}(\mu_{\alpha}^{elem} + \Delta \mu_{\alpha}) + q(\Delta E_F + E_V), \quad (1)$$

where the first two terms, $E_T(D^q)$ and $E_T(H)$, are the total energies of the supercells with and without defect, respectively. In the third term, n_{α} is the number of atoms added $(n_{\alpha} > 0)$ or removed $(n_{\alpha} < 0)$ to create the defect while $\mu_{\alpha}^{elem} + \Delta \mu_{\alpha}$ is the atomic chemical potential ($\alpha = \text{In}$ or O). The elemental reference, μ_{α}^{elem} , is chosen to be the total energy per atom of In-tetragonal solid and of O_2 gas molecule. Under thermodynamic equilibrium the atomic chemical potential must satisfy the constrain of $2\Delta\mu_{In} + 3\Delta\mu_O = \Delta H_f (\text{In}_2\text{O}_3) \text{ (where } \Delta H_f (\text{In}_2\text{O}_3) \text{ is}$ the calculated formation energy of In_2O_3) so that they can be chosen between the limits of O-rich [In-poor, $\Delta \mu_O = 0$ and $\Delta \mu_{In} = \frac{1}{2} \Delta H_f$ (In₂O₃)] and O-poor [In-rich, $\Delta \mu_{In} =$ 0 and $\Delta \mu_O = \frac{1}{3} \Delta H_f$ (In₂O₃)] conditions. The last term in eq. (1) accounts for a change of the defect charge state, q, where $E_F = \Delta E_F + E_V$ is the Fermi energy referenced to the valence band maximum (VBM) of the defect free supercell, E_V . The Fermi energy varies between the VBM $(\Delta E_F = 0)$ and the bottom of the conduction band (CBB). Table 1 shows the calculated formation energies for four neutral defects. According to the calculated results for IO, the formation energy of the neutral *p*-type defects is quite high, and thus a non-equilibrium enhancement factor is



Fig. 5: (Color online). Formation energy of IO with intrinsic *p*-type defects, considering experimental growth conditions of O poor (In rich) and O rich (In poor). The band gap is normalized to be the experimental gap $E_g = 3.75 \text{ eV}$. The valence band maximum as determined by the In₂O₃/Si valence band offset by [34] is displayed as a dashed line.

needed in order to achieve a defect concentration high enough to observe magnetic ordering. Thus, we assess a more complete formalism for various defects in their most stable charge states as described in amongst others [16,33]. Figure 5 shows the calculated formation energies of the *p*-type defects in their most stable charge states as a function of Fermi energy E_F (see footnote ¹). As one can see, the formation energy of p-type defects can be greatly decreased by the the formation of their negative charge states, which means that the *p*-type defects are most likely formed if a high-energy electron reservoir is given. However, the hole states created by the *p*-type defects will be compensated and simultaneously, the magnetic moments will disappear. One way to favor formation of negatively charged *p*-type defects in thin coatings of In_2O_3 , is to pin the Fermi energy closer to the CBM by depositing In_2O_3 on a Si-substrate. The In_2O_3/Si valence band offset (VBO), reported as 1.62 eV [34], is included as a dashed line in fig. 5 (recently a revised value of $1.0 \,\mathrm{eV}$ has been suggested by other authors [35]). Alternatively, certain TM, such as Sn [24], Mo [26], V and Cr [4], acting as n-type electron donors, can induce the formation of negatively charged intrinsic defects by charge transfer from electron donors to unfilled acceptor states. The formation energy calculation in [26] shows that the addition of neutral O_I results in the doping energy gain of 3 eV for Mo in IO and their calculated DOS shows how charge is transferred from Mo_{In} to O_I acceptor states. The low formation energy of the negatively charged p-type defects which we find in this study is consistent with this point of view. However, we also present that $V_{In}^{\prime\prime\prime}$ (see footnote ¹) is more energetically favorable than $O_I^{\prime\prime}$ in a large range of E_F values, especially at oxygenrich conditions. Furthermore, we have recently studied similar charge transfer from doped Cr in IO to neutral *p*-type defects [36]. We find a significant increase in the total energy difference between antiferromagnetic and ferromagnetic coupling of two Cr ions at dilute concentration, from 0.001 eV to 0.25 eV for V_{In} and from $-0.03 \,\text{eV}$ to 0.120 eV for O_I , respectively. These results imply a that *p*-type defects, and especially V_{In} , will compensate for and mediate ferromagnetic coupling between TM ions at dilute concentration in IO.

In this paper, the electronic structure and magnetic properties of IO with four types of intrinsic defects (V_O , In_I , O_I and V_{In}) have been theoretically studied. From the calculated electronic structures we may conclude that the hole states induced by the *p*-type defects reside on the oxygen ion sites and that they display an anisotropic, spatially delocalized distribution. The electron carriers donated by n-type defects display an isotropic, s-like orbital character. The holes induced by *p*-type defects are spin-polarized, while the electron carriers show no spin polarization. The calculated formation energies for various intrinsic defects with neutral charge state indicate that a non-equilibrium enhancement factor is needed to achieve any substantial percolation of these defects. However, negative charging of the *p*-type defects significantly decreases their formation energy, but simultaneously removes the local magnetic moments. Finally, our results suggest that $\mathbf{V}_{In}^{\prime\prime\prime}$ and $\mathbf{O}_{I}^{\prime\prime}$ be the dominant compensating defects as In₂O₃ is doped with TM ions, such as Sn, Mo, V and Cr.

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¹We use the Kröger-Vink notation for charged defects, where ' corresponds to charge -1 and \bullet to charge +1.

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