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Enhancing magnetic vacancies in semiconductors by strain

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Although cation-vacancies can induce localized magnetic moments in semiconductors, the collective magnetism is impeded by low vacancy concentration. To improve the vacancy concentration, we study the effect of external hydrostatic strain on the vacancy formation energy. Our first-principles calculations discover that vacancy formation energy is significantly reduced in ionic semiconductors with the monotonic volume contraction, while only slightly decreased in covalent semiconductors. Especially for ZnO, the equilibrium concentration of cation-vacancies has been improved by 10^9 times. We predicted that strain can be used to produce “ d^0 magnetism” in ionic semiconductors much easier in experiments. © 2012 American Institute of Physics. [doi:10.1063/1.3685488]

In the field of spintronics, magnetic semiconductors that combine nonvolatile magnetic storage and conventional semiconductor electronics can offer the possibility of spin polarized currents and electrical control of magnetic effects.^{1,2} Traditionally, elements containing d or f electrons are believed to be responsible for local magnetic moments, leading to intensive research on diluted magnetic semiconductors (DMSs), in which magnetic moments are introduced by doping magnetic atoms.^{3–5} Recently, there has been increasing evidence that semiconductors can form localized magnetic moments and exhibit collective magnetism without containing d or f electrons.^{6–10} It has been shown that defects with sp -type orbital character have an open-shell electronic configuration and carry the localized magnetic moments.^{11–15} Compared with DMS, d^0 magnetism has exciting advantage of high spin state, high magnetic temperature, and is free of metal cluster,⁹ providing the great potential in semiconductors-based spintronics.

On the other hand, although theoretical studies have predicted that strong magnetism can be formed in many semiconductors, only few materials exhibiting room-temperature magnetism have been observed in experiments, such as highly oriented pyrolytic graphite (HOPG),¹⁶ ZnO,^{17–19} HfO₂,⁶ 4H-, and 6H-SiC.^{20,21} Generally, cation-vacancies can induce the localized magnetic moments, but its concentration is limited by the high formation energy. Under thermal conditions, the equilibrium concentration of vacancies is much lower than the magnetic percolation threshold,²² which is the critical concentration resulting in collective magnetism of local moments. This can also explain why it is difficult to produce magnetic semiconductors without d or f elements.

Thus, the most important issue in this field is how to reduce the vacancy formation energy to make the preparation of magnetic semiconductors easier.

Typically, the total energy of host can be expressed as $E = a(V - V_{\text{equ}})^2$ near the equilibrium position, where a is the elastic constant and V_{equ} is the equilibrium volume of the host.²³ It is expected that the dangling bonds and free space created by cation-vacancies would weaken the bonds of the host, resulting in reduced elastic constant a' . As schematically shown in Fig. 1, ΔE would be reduced by volume contraction. Since the vacancy formation energy is proportional to ΔE , the vacancy concentration should be increased by the volume contraction. However, it is not clear whether this model works for semiconductors, especially with different chemical bonds.

In this work, we explore the possibility of enhancing cation-vacancy concentration by strain engineering through performing comprehensive first-principles calculations. We take BN and ZnO with wurtzite structures in our studies to represent different semiconductors, i.e., ionic and covalent semiconductors. To study the vacancies, we adopted a

FIG. 1. (Color online) Schematic plot of total energy vs volume for host and host+vacancy. ΔE means the energy difference between host and host+vacancy.

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FIG. 2. (Color online) Differential electron density plots for (a) BN and (b) ZnO, respectively. The dark balls denote B (Zn) atoms, while light ones are N (O) atoms.

supercell with $3 \times 3 \times 2$ unit cells, which is enough to avoid the interaction between them.²⁴ The detailed electronic structure calculations are performed by means of the density functional theory (DFT) as implemented in the *Vienna ab initio simulation package*²⁵ using the projector augmented wave method for the electron-ion interaction^{26,27} and the plane wave cut-off energy of 400 eV.

First of all, we investigate the intrinsic properties of wurtzite BN and ZnO. As revealed by first-principles calculations, the larger energy gap appears in BN structure and the smaller one comes from ZnO. To confirm the types of chemical bonds in these semiconductors, we plot in Fig. 2 the differential electron density, which is defined as the electron density difference between self-consistent charge density and the superposition of atomic charges. It clearly shows that wurtzite BN is connected through the covalent bonding between boron and nitrogen atoms, while ZnO forms ionic bonds.

To examine the formation ability of cation-vacancies, we define formation energy as $E_f = E_D - E_T + \mu_{\text{cation}}$, where E_D is the energy of semiconductors with vacancies, E_T is the total energy of perfect semiconductors, and μ_{cation} is the chemical potential of cations. In our studies, we only consider the equilibrium growth condition, which means μ_{cation} is taken as the binding energy of the bulk. Our spin-polarized DFT calculations show that localized magnetic moments are produced by the cation-vacancies, which are $1.1 \mu_B$ and $1 \mu_B$ per cation-vacancy for BN and ZnO, respectively. On the other hand, to create a cation-vacancy in semiconductors, the calculated E_f is 8.51 eV and 5.75 eV for BN and ZnO, respectively. Under thermal dynamics with 1500 K, according to $N = N_c \cdot \exp(-E_f/K_B T)$, the concentration of cation-vacancies is only 10^{-28} Nc (for BN) and 10^{-20} Nc (for ZnO), where N and Nc means the cation-vacancy and cation concentration of these semiconductors. It is clear that the produced cation-vacancies are far below the magnetic percolation threshold. The low concentration definitely impedes the magnetic interaction between localized magnetic moments. As a result, there is no collective magnetism but paramagnetism that can be observed in experiments. Therefore, to get semiconductors with collective magnetic order, it is highly desired to increase the concentration of cation-vacancies.

To explore the possibility of improving the cation-vacancies, an external hydrostatic strain is applied through compressing all three cell dimensions of the supercell equally. Figure 3 shows the calculated total energy as a func-

tional of hydrostatic strain. Interestingly, these semiconductors show totally different response to strain. For BN and BN+V_B, the calculated energy curves vs volumes are almost identical, indicating that they have similar elastic constant. It means that created cation-vacancy only slightly modifies the structure of supercell. On the other hand, for the ionic semiconductors, ZnO, the energy of defected hosts show different curves with the pristine structures as a function of volume, indicating that cation-vacancies induce significant changes in the crystal structures in these ionic semiconductors.

From the calculated total energy of defected and perfect semiconductors, we can see that the formation energy of cation-vacancies shows totally different behaviors under strain. For BN, the calculated formation energy is hardly reduced, indicating the concentration of cation-vacancies cannot be increased under strain. However, for ZnO, it is clear that the formation energy is greatly reduced. According to the calculated formation energy, the equilibrium concentration of cation-vacancies is about 10^{-11} Nc for ZnO with a temperature of 1500 K. Therefore, the loaded strain has improved the cation-vacancies concentration by 10^9 times for ZnO. Since the previous studies have reported that cation-vacancies can be easier produced at nanoscale,²⁸ we suggest that magnetic semiconductors may be obtained by directly applying pressure to ionic nano systems, which is the direct experimental method to verify our prediction.

Although we have discovered that the loaded strain can largely improve the cation-vacancy concentration in ZnO,

FIG. 3. (Color online) The plots of total energy as a function of lattice strain for (a) BN and (b) ZnO, respectively. The energy of structures without strain is taken as reference. (c) and (d) are the plots of formation energy as a functional of lattice strain for BN and ZnO, respectively.

FIG. 4. (Color online) Atomic displacement (indicated by solid arrows) of BN and ZnO by creating cation-vacancies. The dark balls mean B (Zn) atoms, while light ones are N (O) atoms.

the intrinsic mechanism is still not clear. To explore the structural deformations, we plot the atomic displacement induced by creating cation-vacancy in Fig. 4. For BN, only the nearest neighbor (NN) bonds around vacancy are strongly contracted, while the next NN bonds are only slightly modified. As we know, the covalent bonding in BN is a kind of localized interaction. Therefore, the stress induced by cation-vacancy can be released locally, leading to the large distortion around cation-vacancy. However, for ionic ZnO, the ionic bonds can interact each other through long range coulomb interaction. Thus, the vacancy induced not only the displacements of nearest neighboring anions but also the distortion of the further neighbors, as shown in the Fig. 4(b).

From the above analysis, we can see that the local stress caused by vacancies can be released by bond contraction. If the contraction is confined in the NN bonds, the elastic constant of the defected host is not largely modified. i.e., the defected host has almost the same energy-volume relation, just as the case in BN. However, if the stress is released beyond the NN bonds, the elastic constant will be modified. As a result, the formation energy of cation-vacancies is reduced, as explored in ZnO. Therefore, our results show that chemical bonds play a crucial role in determining the formation ability of cation-vacancy in semiconductors.

To confirm that the bonding character determines the effect of the loaded strain, we also investigated the formation ability in ZnSe, which has more covalent character. Our DFT calculations show that the formation energy can be reduced by 0.13 eV and 0.39 eV with a strain of 2% and 4%, respectively. Compared with the 0.52 eV and 1.64 eV in ZnO, the effect of the loaded strain is clearly reduced by the covalent character in semiconductors.

In summary, we have performed spin-polarized DFT calculations to study the formation ability of cation-vacancies under the loaded strain. Our results show that vacancy formation energy is significantly reduced in ZnO with

the monotonic volume contraction, while only slightly decreased in BN. The different effect of loaded strain is well explained by the type of the chemical bonds of semiconductors. Based on our observations, we suggest that strain can be used to engineer the defect-induced magnetism in semiconductors.

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