

First-principles study on the electronic and magnetic properties of C- and N-doped ZnS nanowires

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Abstract. We comparatively study the electronic and magnetic properties of unpassivated (NP) and H-passivated (HP) ZnS nanowire (NWs) doped with one C (or N) atom in terms of the first-principle calculation. The result shows that C (or N) atom preferring to the surface position for both of the NP and HP NWs. All of the C-doped ZnS NWs show semiconductor character. The magnetic moments are mainly contributed by the C-2p orbital. The magnetic moments of the C, Zn, and S atoms in the super cell have the same direction, indicating FM coupling between them. While for N-doped ZnS NWs, it is interesting that an N atom substituting an S atom in the middle position of NP ZnS NWs change the host from semiconductor to metal. These results show that the doping atom, doping position, and surface condition can significantly change the properties of semiconducting ZnS NWs.

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Key words: nanowires, magnetic properties, density functional theory

1 Introduction

Diluted magnetic semiconductor (DMS) has attracted much attention because it brings the possibility of devices which combine information processing and storage functionalities in one material [1, 2]. During past years, a number of transition metal (TM) doped semiconductors with room temperature ferromagnetism are reported [3–5]. Whereas no convincing evidence can verify that the observed ferromagnetism in TM-doped DMSs is intrinsic [6]. To avoid these confusions, some groups have reported the intrinsic nonmagnetic elements, such as Li [7], Mg [8, 9], and Cu [10, 11] as dopants, can order ferromagnetism in some semiconductors hosts. It is more interesting that the nonmetal elements C and N can induce ferromagnetism in GaN [12], ZnO [13–16], and CdS [17]. These materials do not contain ions with partially filled *d* or *f* band, which provides us both a new opportunity for searching

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high-temperature spintronic material and a challenge to understand the origin of the magnetism in these materials [18].

ZnS is an important II-VI compound semiconductor with potential applications in electronics and optoelectronics because of its wide direct band gap [19,20]. Recently, both Fan *et al.* [21] and Long *et al.* [22] found that doping a few percent of C atoms into ZnS could result in ZnS to be promising FM semiconductor. With the recent emergence of nanoscience and nanotechnology, considerable efforts have been placed on the synthesis of ZnS NWs due to its excellent optical and optoelectronic properties remarkably different from the bulk [23–27]. The performance of nanodevices is dependent on the capability of controlling the electronic and magnetic properties of the selected nanostructures, which could be realized via appropriate dopants and doping methods [28–30]. Previous researches have performed on the magnetism in TM-doped ZnS NW [31,32]. However, to our knowledge, there was no the reported magnetic results on nonmetal elements doped ZnS NWs. In this work, we present a systematical theoretical investigation on the electronic and magnetic property of NP and HP WZ ZnS NWs doped with one C or N atom. Calculations indicate that the C (or N) atom prefer to the surface position of NWs. The interactions between the C, Zn, S, and H atoms in the super cell are FM coupling. Interestingly, substituting an S atom by an N atom in the middle position of the NWs significantly change the host from semiconductor to metal.

2 Theoretical method and computational details

The calculations are performed using spin-polarized density functional theory. All electrons treatment and double numerical basis set including *d*-polarization functions (DND) are chosen. The Direct Inversion in an Iterative Subspace (DIIS) approach is used to speed up Self-consistent field (SCF) convergence. We also apply thermal smearing to the orbital occupation to speed it up. For the accurate calculations, we have chosen an octupole scheme for the multipolar expansion of the charge density and Coulomb potential. The exchange-correlation interaction is treated by generalized gradient approximation (GGA) with the functional parameterized by Perdew-Burke-Ernzerhof correction (PBE) [33]. SCF calculations are done with a convergence criterion of 10^{-6} hartree on the total energy. All structures are fully optimized without any symmetry constraint with a convergence criterion of 0.002 hartree/Å for the force and 0.005 Å for the displacement. Mulliken population analysis [34] is performed to determine the charge transfer and magnetic moment on each atomic site.

3 Results and discussion

The structural optimizations are first performed for WZ ZnS solid. The optimized lattice parameters are $a = 3.89$ Å and $c = 6.37$ Å, which are in agreement with the experimental values: $a = 3.82$ Å, $c = 6.26$ Å [35]. The electronic property of the bulk WZ ZnS solid is also calculated direct band gap semiconductors. In our theoretical calculation, the band gap

for bulk ZnS is 2.23 eV, which are in accordance to the previously theoretical prediction by Yeh [36].

The pristine ZnS nanowire (P-ZnS) is cut from the bulk ZnS along the [0001] direction with six low free-energy (0 $\bar{1}$ 10) facets. The super cell consists of 24 Zn and 24 S atoms, in which one S atom is replaced by a C (or N) atom. This corresponds to a doping concentration of 2%. It is well known that the effect of the surface on the physical properties is very important on the nanoscale. To study the effect of the surface dangling on the NWs, first-principles calculations on the electronic and magnetic properties of the HP NWs are performed simultaneously. We considered four different configurations for substitutional doped ZnS NWs. One group is that a C (or N) atom substitute a S atom in the middle of the NWs with and without surface dangling, the other is that a C (or N) atom substitute a S atom in the surface of the NWs, denoted as M(NP), M(HP), S(NP), and S(HP), respectively.

The structural optimization is then performed for P-ZnS. In our calculation, P-ZnS is a direct band gap semiconductor with band gap (2.90 eV), in agreement with the previous work [37]. Finally, four kinds of C-doped ZnS NWs are optimized. The optimized structures are plotted in Fig. 1(a). After relaxation, the local structure around the C dopant is slightly suppressed with the Zn atoms move closer to the C atom. Especially for the S(NP), the C atom push the Zn atom away and connect with the S atom after structural optimization.

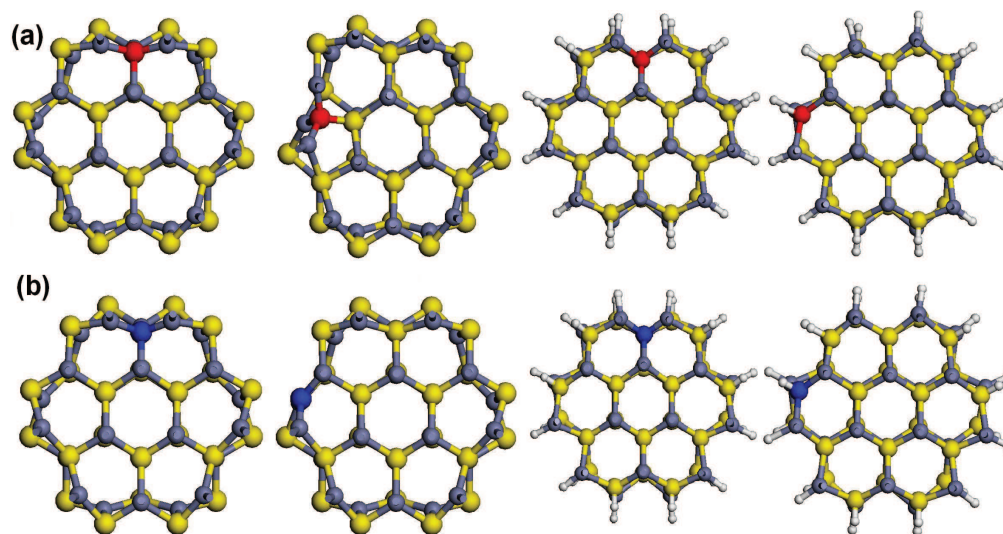


Figure 1: The top-view of C-doped (a) and N-doped, (b) ZnS NWs. The yellow, gray, red, blue, and white balls represent S, Zn, C, N, and H atoms, respectively.

As an indication of the stability of the C dopant, the binding energy is estimated from $E_{b1} = E_{\text{tot}} - E_p + E_s - E_C$ and $E_{b2} = E_{\text{tot}} - E_p + E_s - E_C - 24 \times E_H$ for NP and HP NWS, respectively. Where E_{tot} is the total energy of C-doped ZnS NWs and E_p is the corresponding energy of

P-ZnS. E_S , E_C and E_H are the energies of an isolated S, C, and H atom. It is clear that the more negative the E_b is, the higher the stability of a NWs will be. The results are presented in Table 1. We can also see that C atom prefer to the surface position for both of the NWs. While previous researches on Mn-doped InP NWs have revealed that the middle position was preferred for NP and the surface position was preferred for HP NWs [38, 39]. Hence, the preferred substitutional position is dependent not only on surface condition but also on the given materials.

Table 1: The binding energy (E_b , in eV), total magnetic moment (μ_{tot} , in μ_B), local charge (Q_C , in a.u.), and local magnetic moment (μ_C , in μ_B) of C atom in ZnS NWs. The nearest-neighboring magnetic moment of Zn, S and H atoms (μ_{Zn} , μ_S and μ_H , in μ_B) are also shown.

C-doped	E_b	μ_{tot}	Q_C	μ_C	μ_{Zn}	μ_S	μ_H
M(NP)	-139.92	2.00	-0.65	1.29	0.18	0.48	–
S(NP)	-141.11	0	-0.64	0	0	0	–
M(HP)	-187.11	2.00	-0.70	1.23	0.21	0.18	0.35
S(HP)	-188.47	2.00	-0.70	1.11	0.26	0.13	0.47

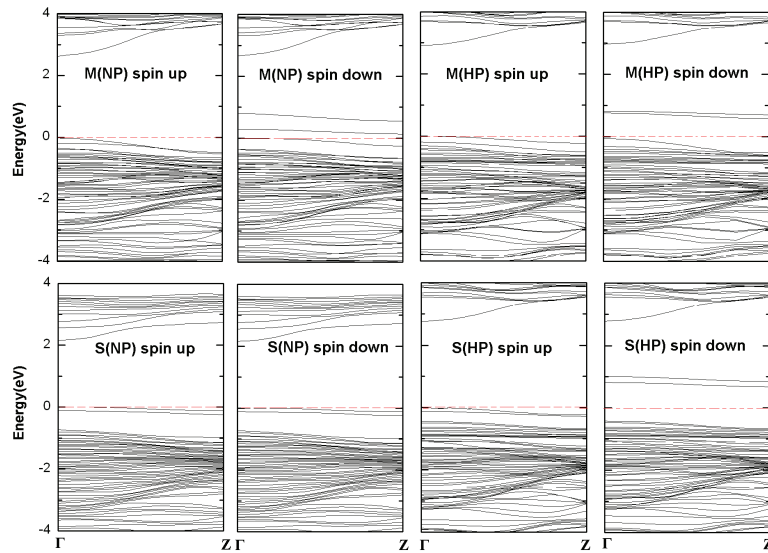


Figure 2: Electronic band structures for C-doped ZnS NWs.

Fig. 2 shows the calculated band structures for both of the C-doped NWs along the $\Gamma-Z$ direction. We can see that the band structures of spin-up and spin-down states are identical for S(NP), indicating that there is no spin polarization for S(NP). The bottom of conduction band and the top of valence band are both located in Γ point of the Brillouin zone, indicating a direct band gap semiconductor for S(NP). While for M(NP), M(HP), and S(HP), the top

of valence band is located in Γ point of the Brillouin zone, but the bottom of conduction band is not, indicating an indirect band gap semiconductor. Furthermore, there exist certain localized states in the vicinity of Fermi level for M(NP), M(HP), and S(HP), which results in the significantly narrower band gaps than the pristine values. The band gaps are only 0.14, 0.71 and 0.85 eV for the M(NP), M(HP), and S(HP), respectively. The results indicate that the doping position and surface condition can significantly change the electronic properties of semiconducting ZnS NWs.

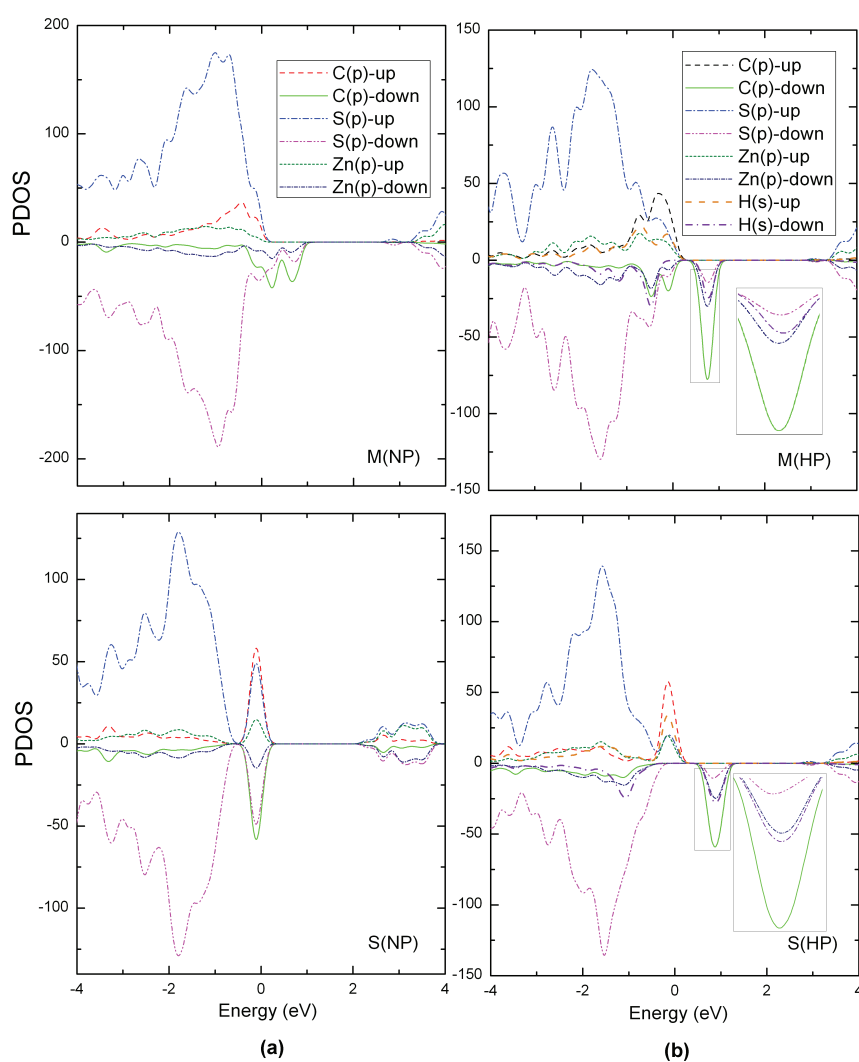


Figure 3: The PDOS for the C-doped ZnS NWs. The inset is an enlargement of the peak around the Fermi level.

For an insight into the magnetism in C-doped ZnS NWs, the partial density of states (PDOS) of the C atom and its nearest neighboring Zn, S, and H atoms are calculated and plotted in Fig. 3(a) and (b) for NP and HP ZnS NWs, respectively. These figures show that the doped C atom can significantly change the PDOS near the Fermi level and lead to spin polarization of the valence band. Strong coupling between p orbital of C, S, and Zn atoms near the Fermi level can be seen. For M(NP), M(HP), and S(HP), the spin-up bands are fully occupied, while spin-down bands are empty. The localized states in the vicinity of Fermi level are mainly contributed by the C- $2p$ valence electrons. It would introduce the occupied states in the band gap of the P-ZnS, which gives rise to the narrow gap of doped NWs. While for S(NP), the spin-up and spin-down bands are both fully occupied. Furthermore, the PDOS of spin-up and spin-down states are symmetrical for S(NP), confirming its no spin polarization character.

In order to confirm the PDOS results, Mulliken population analysis is performed to determine the charge transfer and magnetic moment on each atomic site. The magnetic properties of all doped structures are computed and the results are presented in Table 1. For M(NP), M(HP), and S(HP), the total magnetic moments are $2.00 \mu_B$, which is mainly contributed by the C atom. While each of nearest neighboring Zn, S, and H atoms also contribute a small part due to hybridization. The magnetic moments of the C, Zn, S, and H atoms in the super cell have the same direction, indicating FM coupling between them. While for S(NP), the mag-

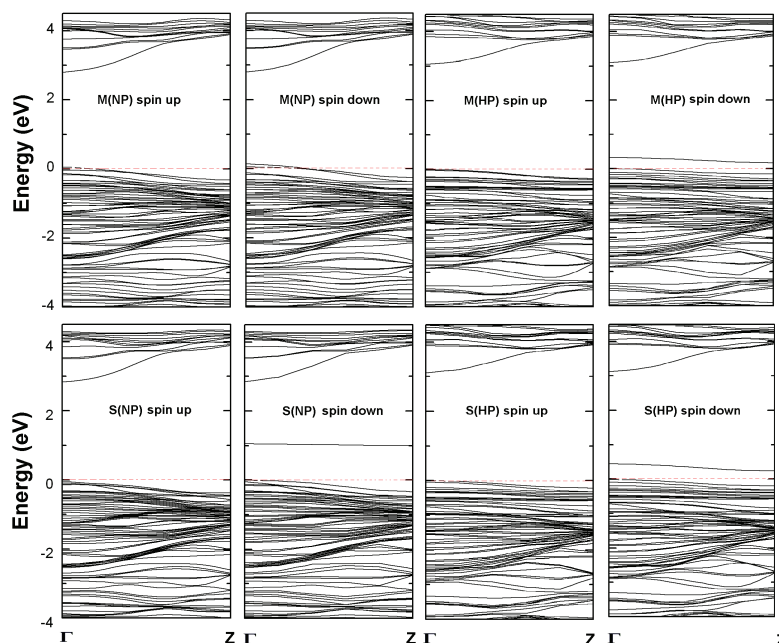


Figure 4: Electronic band structures for N-doped ZnS NWs.

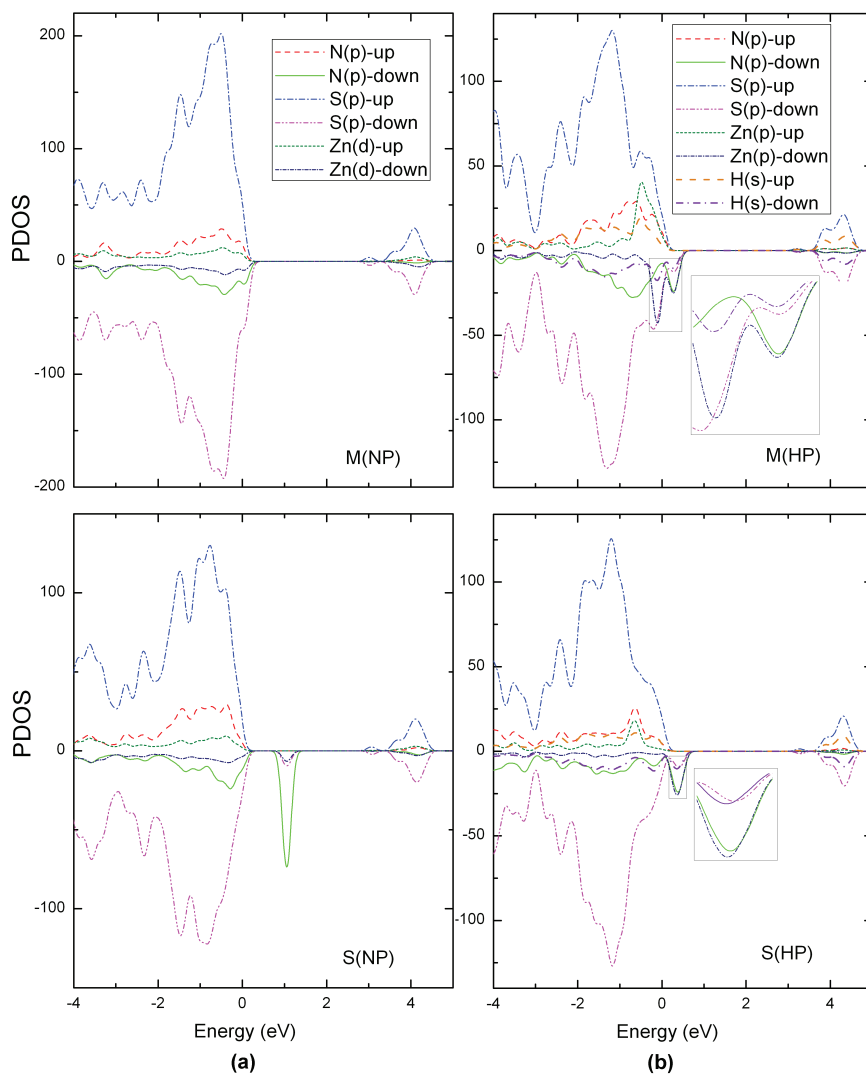


Figure 5: The PDOS for the N-doped ZnS NWs. The inset is an enlargement of the peak around the Fermi level.

netic moments of C atom and nearest neighboring Zn atoms and second nearest neighboring S atoms are all zero, confirming its non-polarized nature. By analysis, we find that the newly formed C-S bond length is only 1.89 Å. The local charge of the S atom is -0.34 e, while the local charges of other S atoms are less than -0.50 e. There exists electron transfer between S and C atom, which quenched the magnetic moment of C atom.

For comparing, we further study the electronic and magnetic properties of N-doped NP ZnS NWs. The optimized structures are plotted in Fig. 1(b). After relaxation, the local struc-

ture around the N dopant is slightly suppressed with the Zn atoms move closer to the N atom, the relaxed Zn-N average bond length is 2.00 Å for M(NP) and 1.95 Å for S(NP). The binding energy is estimated by the same way as C-doped ZnS NWs. The results are presented in Table 2. We can see that N atom prefer to the surface position, the same as C atom.

Table 2: The binding energy (E_b , in eV), total magnetic moment (μ_{tot} , in μ_B), local charge (Q_N , in a.u.), and local magnetic moment (μ_N , in μ_B) of N atom in ZnS NWs. The nearest-neighboring magnetic moment of Zn, S and H atoms (μ_{Zn} , μ_S and μ_H , in μ_B) are also shown.

N-doped	E_b	μ_{tot}	Q_N	μ_N	μ_{Zn}	μ_S	μ_H
M(NP)	-140.08	0.70	-0.98	0.18	0.02	0.42	–
S(NP)	-140.22	1.00	-0.73	0.91	-0.03	0.09	–
M(HP)	-187.06	1.00	-0.98	0.33	0.09	0.16	0.36
S(HP)	-188.32	1.00	-0.97	0.36	0.08	0.11	0.41

Fig. 4 shows the calculated band structures for both of the N-doped NWs along the Γ –Z direction. The S(NP), S(HP), and M(HP) show semiconductor properties, the same as C-doped ZnS NWs. There exist certain localized states in the vicinity of Fermi level, which results in the significantly narrower band gaps than the pristine values. The band gap is only 1.00, 0.18, and 0.24 eV for the S(NP), M(HP), and S(HP), respectively. It is interesting that M(NP) shows metallic properties, indicating that substituting an S atom in the middle position of ZnS NWs significantly change the electronic property of the material.

The PDOS of the N atom and its nearest neighboring Zn, S, and H atoms are calculated and plotted in Fig. 5(a) and (b) for NP and HP ZnS NWs, respectively. These figures show that the doped N atom changes the PDOS near the Fermi level. Strong coupling between p orbital of N, S, and Zn and s orbital of H atoms near the Fermi level can be seen. The localized states in the vicinity of Fermi level are mainly contributed by the N-2 p valence electrons. It would introduce the occupied states in the band gap of the P-ZnS, which gives rise to the narrow gap of N-doped NWs.

The magnetic properties of N-doped ZnS NWs are also computed and the results are presented in Table 2. Except M(NP), the total magnetic moments are 1.00 μ_B for N-doped ZnS NWs, the same as N-doped ZnO [16]. For M(NP), M(HP), and S(HP), a number of magnetic moments are introduced into neighboring Zn, S, and H atom due to hybridization, the same as C-doped ZnS NWs. The magnetic moments of the N, Zn, S and H atoms in the super cell have the same direction, indicating FM coupling between them. While for S(NP), the total magnetic moments are mainly contributed by the N atom. The magnetic moments of the N (or S) and Zn atoms in the super cell have the opposite direction, indicating AFM coupling between them.

4 Conclusion

The structural, electronic, and magnetic properties of ZnS NWs doped with one C or N atom have been studied by using the first-principles method systematically. The obtained results

indicate that the C (or N) atom prefer to the surface position of ZnS NWs. All of C-doped ZnS NWs show semiconductor character. The magnetic moments are mainly contributed by the C-2p orbital, while each of nearest neighboring Zn, S and H atom also contribute a small part. The magnetic moments of the C, Zn, S and H atoms in the super cell have the same direction, indicating FM coupling between them. For N-doped ZnS NWs, it is interesting that an N atom substituting an S atom in the middle position of NP ZnS NWs significantly change the host from semiconductor to metal. Calculation indicates that the doping atom, doping position, and surface condition can significantly change the properties of semiconducting ZnS NWs.

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