Electronic and optical properties of vacancy-doped WS$_2$ monolayers

Jian-wei Wei; Zeng-wei Ma; Hui Zeng; Zhi-yong Wang; Qiang Wei; Ping Peng

AIP Advances 2, 042141 (2012)
https://doi.org/10.1063/1.4768261
Electronic and optical properties of vacancy-doped WS$_2$ monolayers

Jian-wei Wei, Zeng-wei Ma, Hui Zeng, Zhi-yong Wang, Qiang Wei, and Ping Peng

1 School of Optoelectronic Information, Chongqing University of Technology, Chongqing 400054, P.R. China
2 School of Physical Science and Technology, Yangtze University, Jingzhou 434023, P.R. China
3 School of Science and Technology of Materials, Hunan University, Changsha 410082, P.R. China

(Received 22 August 2012; accepted 2 November 2012; published online 12 November 2012)

Monolayers of tungsten disulfide doped with atomic vacancies have been investigated for the first time by density functional theory calculations. The results reveal that the atomic vacancy defects affect the electronic and optical properties of the tungsten disulfide monolayers. The strongly ionic character of the W-S bonds and the non-bonding electrons of the vacancy defects result in spin polarization near the defects. Moreover, the spin polarization of single W atomic vacancies has a larger range than for one or two S atomic vacancies. In particular, increased intensity of absorption and red shift of optical absorption are universally observed in the presence of these atomic defects, which are shown to be a fundamental factor in determining the spin transport and optical absorption of tungsten disulfide monolayers. Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4768261]

I. INTRODUCTION

Because of the discovery and characterization of graphene, two-dimensional nanomaterials have attracted considerable attention in recent years. Similar to graphene, other layered inorganic materials, such as layered transition metal dichalcogenides, have also captured people’s interest. Typically, monolayer tungsten disulfide (M-WS$_2$) has one molecular-layer thickness with a lateral size up to microns, and is composed of three atom layers associated with the W-S bonds. Moreover, weak van der Waals interactions exist between the neighboring WS$_2$ layers. Broad applications of WS$_2$ nanotubes have been developed. WS$_2$ nanostructures have been extensively used in many applications, such as solid lubricants, catalysts, and tips in scanning probe microscopy. The WS$_2$ films can be used as advanced absorber materials in TiO$_2$ solar cell because of their unique geometric and electronic structures. The electronic structures of both single crystals and single layer WS$_2$ have been investigated theoretically and experimentally. In particular, the smooth edges and uniform width of ultra-narrow WS$_2$ nanoribbons have been fabricated in the templates of single- and double-walled carbon nanotubes, and the electronic spin transport properties have been systematically studied based on the edge structures of the WS$_2$ nanoribbon. The study found that depending on the width, WS$_2$ nanoribbons behave either like metals or semiconductors.

In the violent synthesis process, atomic defects are very common and affect the properties of WS$_2$. Single-atomic defects have been identified by means of annular dark-field imaging and scanning transmission electronic microscopy, in which the authors revealed the key role of atomic defects in the plastic deformation process. However, the effects of atomic defects in the WS$_2$...
monolayer have not been examined based on the electronic and optical properties of the monolayer. In this paper, M-WS\textsubscript{2} doped with atomic vacancies has been investigated in detail for the first time using density functional theory (DFT). The calculations show that M-WS\textsubscript{2} exhibits obvious spin polarization and optical variation related to the atomic vacancies.

II. MODEL AND METHODOLOGY

Differing from the hexagonal unit cell\textsuperscript{15} our rectangular supercell of pristine WS\textsubscript{2} includes 108 atoms, with dimensions in the x, y, and z directions of 19.415, 16.849, and 16.000 Å, respectively. Three basic types of atomic vacancy configurations of M-WS\textsubscript{2} are considered according to previous experiment results.\textsuperscript{4} As seen in Fig. 1(a), the three models VS\textsubscript{1}, VS\textsubscript{2} and VW with vacancy defects were designed by removing one S atom at point A, two S atoms at point A, and one W atom at point B, respectively. To avoid strong edge effects,\textsuperscript{18} the supercell extends continuously in the WS\textsubscript{2} plane with periodic boundary conditions. A large vacuum (about 13 Å) separation is introduced between the M-WS\textsubscript{2} layers to eliminate the interaction of neighboring layers.

We have studied the geometric structure, the electronic and optical properties of M-WS\textsubscript{2} with the atomic vacancy defects using first-principles calculations. Prior to calculating the quantities of interest, all of the structures were fully relaxed using the SIESTA\textsuperscript{19, 20} code, until the resultant force acting on each atom was less than 0.01 eV/Å. The calculations of the electronic properties were carried out under the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional. The ion–electron interactions were treated with the standard norm-conserving Troullier–Martins pseudopotential. The double-\(\zeta\) plus polarization (DZP) basis sets were used to expand the wavefunctions and the plane-wave cutoff energy was chosen to be 200 Ry. A Monkhorst–Pack k-point mesh of 5 × 6 × 2 was used to calculate the Brillouin zone integration. The tolerance of the density matrix was set to 10\textsuperscript{-4}, and the cutoff radius of orbital-confining to 0.25 eV. The relaxation of all structures was carried out at 300 K.

The optical properties were calculated through the complex dielectric constant \(\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2\) using the CASTEP code.\textsuperscript{21} The imaginary part about the frequency can be written as\textsuperscript{22}

\[
\varepsilon_2(q \rightarrow Q, \hbar \omega) = \frac{2\pi e^2}{\Omega_{2D}} \sum_{k,v,c} |\langle \Psi_k^c | \mathbf{u} \cdot \mathbf{r} | \Psi_k^v \rangle|^2 \delta(E_k^c - E_k^v - E),
\]
where \( \mathbf{u} \) and \( \mathbf{r} \) refer to the polarization vector of the incident electric field and the position vector. \( \Omega, \varepsilon, \) and \( \varepsilon_0 \) represent the volume of the supercell, the charge of electron, and the dielectric constant of free space, respectively. \( \Psi_k^c \) and \( \Psi_k^v \) are the conduction and valence band wave functions at \( k \). \( \varepsilon_2 \) is a physical parameter characterizing the electronic transitions between the valence bands and the conduction bands. The real part \( \varepsilon_1 \) can be obtained by a Kramers-Kronig transform.\(^{23}\) Considering the influence of the non-local potential, the following correction is introduced for the matrix elements\(^{24}\)

\[
\langle \Psi_k^c | \mathbf{P} | \Psi_k^v \rangle = \frac{1}{i \omega m} \langle \Psi_k^c | \mathbf{P} | \Psi_k^v \rangle + \frac{1}{\hbar \omega} \langle \Psi_k^c (|V_{nl}|, \mathbf{r}) | \Psi_k^v \rangle.
\]

According to the relationship \( \varepsilon(\omega) = N^2 = (n + ik) \) between the complex dielectric constant \( \varepsilon(\omega) \) and the complex refractive index \( N = n + ik \), the adsorption spectrum can be obtained by

\[
\delta(\omega) = \frac{2k \omega}{c} = \frac{\omega}{c} \left\{ 2 \left[ \varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) \right]^{1/2} - 2 \varepsilon_1(\omega) \right\}^{1/2}.
\]

In the calculation of the optical properties, we used the ultrasoft pseudopotential\(^{25}\) in real space and the GGA approximation in the PBE form. The convergence threshold was \( 10^{-6} \) eV/atom, and the cutoff of the plane-wave energy was set at 300 eV. The electronic smearing was 0.1 eV in the calculations. A \( 2 \times 2 \times 3 \) Monkhorst–Pack k-point grid was used to calculate the Brillouin zone integration with 24 empty bands in the calculation of the optical properties. The 0.5 eV Gaussian broadening was used to determine the dielectric function under zero scissor operators. The lifetime broadening was set to 0.05 eV of the Drude contribution.

### III. RESULTS AND DISCUSSION

In the relaxed structure of pristine M-WS\(_2\), the distance between the adjacent W atoms is about 3.24 Å, which agrees well with experiment.\(^{17}\) The length of W-S is about 2.48 Å, which is slightly larger than reported in an early experiment (about 2.41 Å).\(^{28}\) This discrepancy is consistent with the tendency of GGA. The S-W-S angle between nearest neighbor S atoms is about 82°, which is less than previous calculations.\(^{26,27}\) The bond angle would be greater than 90° when including the hybridization of the 3s-3p orbitals of the S atoms. However, the angle of W-S-W was about 82° in our relaxed atomic structures. These data explicitly show that there is no orbital hybridization on the S atoms. According to the six unique W-S bonds of every W atom, we can conclude that the W atoms have sp\(^{2d}\) hybridization.

Our relaxation results show that the vacancy defects cause only slight geometric deformation in the M-WS\(_2\) layers. The VW defects hardly cause any visible movement of other atoms in the supercell. The atoms neighboring the VS1 defect are slightly closer to the point A. The maximum deformation appears in the VS2 model, in which the distance between three neighboring W atoms decreases to about 2.90 Å. Overall, the three types of atomic defects cause little deformation, and thus it is difficult to explore the vacancy defects by geometric deformation.

The band structures of M-WS\(_2\) with atomic vacancies are shown in Fig. 2. The direct band gap of pristine M-WS\(_2\) is about 1.85 eV, which is in good agreement with previous theoretical\(^{13}\) and experiment results. After introducing the defects, the Fermi level approaches the valence bands owing to reduction of the total number of electrons. On the other hand, the intrinsic direct gap increases about 0.1 eV in the VW model, while it is unchanged in both the VS1 and VS2 models.

As shown in Fig. 2, the four defect subbands (labeled as \( \alpha \) and \( \alpha' \)) occur around 0.63 eV and \(-0.616\) eV for spin-up/down in the VS1 and VS2 models. The energy widths of \( \alpha \) and \( \alpha' \) are about 0.03 eV, which indicates strong localization of the defect states of the vacancies. From the insert below the \( \alpha \) subbands in Fig. 2, the two \( \alpha \) defect subbands of spin-up and spin-down are slightly split in the VS1 and VS2 models. This observation shows that there are an odd number of electrons in some atoms because of charge transfers between the S and W atoms. The two \( \alpha \) subbands are about 0.5 eV lower than the lowest conductance band, and similar to acceptor doping states. In the VS1 model, the upper \( \alpha' \) subband is 0.1 eV higher than the lower subband, which is partially degenerate with the highest valence band. Furthermore, the \( \alpha \) defect subbands in the VS1 model have a larger spin splitting than those in the VS2 model, where the two \( \alpha' \) subbands are partially degenerate and...
FIG. 2. The spin-up/down band structures of WS₂ with and without defects. For comparison, the band structures of pristine WS₂ are also given and labeled as Pr. The Fermi energy is set to zero. The wave vector K ranges from Γ (0 0 0) to X (0 0.5 0) in each panel. The black arrows point to the enlargement of the corresponding α, β, γ and γ' subbands.

FIG. 3. The projected density of states (PDOS) of the WS₂ layer with defects. (a) and (b) are the semicore shells of the VS2 and VW models. The results of the VS1 model is almost the same as the VS2 model, except for some minor differences of 3s semicore shells of the S atoms in the conduction and valence bands. As a consequence, the data are not shown here. The Fermi energy is set to zero.
located above the highest valence band. In contrast to the VS1 defect, the VS2 defects have a strong influence on the valence bands, which results in an obvious decrease in degeneracy of the valence bands. The three types of defects have little influence on the conduction bands.

In the VW model, six W-S bands are broken by the W vacancy, which makes every S atom around the vacancy accept one non-bonding electron in the 3p orbitals. $\beta$, $\beta'$, $\gamma$ and $\gamma'$ are the corresponding defect subbands. The double degeneracy of the subbands at 1.2 eV and $-0.6$ eV is partially broken by the VW defect. Similar to the $\alpha$ subbands, the enlarged panels on the left-hand side of Fig. 2 show that the $\beta$, $\gamma$ and $\gamma'$ subbands are also spin-split. Arrow 1 in Fig. 3(a) shows that the 5d orbitals of the W atoms contribute more states to the projected density of states (PDOS) than the 3s orbitals of the S atoms in the $\alpha$ subbands. For the $\beta$ and $\gamma$ subbands, arrows 3 and 4 in Fig. 3(b) indicate that the defect states from the 3s orbitals of the S atoms are almost equal to those from the 5d orbitals of the W atoms. In the case of the $\gamma'$ subbands, however, the defect states primarily originate from the 3s orbitals of the S atoms, as shown by arrow 2 in Fig. 3(b).

To further understand the split of the spin subbands, the charge density difference of the spin-up and spin-down bands are shown in Figs. 4(a)–4(c). Obviously, spin polarization takes place for these atomic vacancies. Although the geometric structures of the three types of vacancy defects have C3 symmetry, the central symmetry of the spin polarization distribution remains only in the VW model. It can be seen from Fig. 4(a) that the nearest neighbor W atoms of the vacancy have excess spin-up charge, while the second neighbor W atoms have excess spin-down charge. In the VW model, the spin polarization orientation of the W atoms changes periodically from the center to the edge, implying that the spin polarization assumes certain non-local attributes. However, for the S atoms, spin polarization is absent, except for the six nearest neighbor S atoms.
Comparing the charge density of the VS1 and VS2 models in Figs. 4(b) and 4(c), there is little variation except for the spin orientation of the W atoms at the lower-right corner of the vacancy. Obviously, the spin polarization is mainly localized at the vacancies. In addition, Fig. 4(d) shows the charge density of the W-S bonds, in which the central charge density is smaller than the outer charge density because of the use of the pseudopotential for the inner-shell electrons. Only a few electrons reside in the region between the W and S atoms. This feature indicates that the S-W bonds are strongly ionic, which is consistent with a previous report. The ionic characteristics are believed to be the foundation of the wide charge transfer in WS2. The non-local attributes of the VW model are because of the ionic nature of the bonds. Also, the charge distribution is the underlying factor for the charge transfer, which results in the localization of the VS1 and VS2 models.

Considering the special geometric structure and the narrow band gap of M-WS2, we have calculated its optical properties. It is worth noting that the vibration and rotation of the molecules are not considered in the optical calculations, because no phonon contribution is taken into account. Consequently, the absorption peak in the infrared region is not observed. As shown in Fig. 5, the pristine model has three intrinsic peaks at 89.2 nm, 208.3 nm and 418.7 nm. The atomic defects affect both the intensity and position of the absorption peaks. The intensity of the main peak at 418.7 nm increases in the VS1 model, while it decreases slightly in the VS2 and VW models, accompanied by an obvious red shift. The intensity of the peak at 89.2 nm in the pristine system increases for the three types of vacancies. In the VW model, a new peak occurs at 98.8 nm. In addition, introduction of vacancies results in a small red shift at 208.3 nm accompanied by the increase of the absorption intensity. The defect subbands (such as \(\alpha', \beta'\) in Fig. 2) decrease the energy gap of electronic transition, which causes the red shift of the three intrinsic peaks. Furthermore, the smaller transition energy gap increases the transition probabilities, which further increases optical absorption. Note that in the VW model, the decrease of the wavelength of the peak at 418.7 nm can be attributed to the defect subbands, which inhibit direct transition from the valence to conduction bands.

![Absorption spectra of M-WS2 with and without atomic defects. The curve of pristine WS2 is also given for comparison. The inset is an enlargement of the absorption spectrum around 100 nm. The results are calculated based on unpolarized incident light perpendicular to the M-WS2 plane. The dashed line indicates the peak position of the pristine layer.](image-url)
IV. CONCLUSION

In summary, the effects of three types of atomic defects on the electronic and optical properties of M-WS$_2$ have been investigated by DFT calculations. We found that the geometrical structure of M-WS$_2$ only changes slightly after introducing the vacancies. Several new subbands of the vacancies appear in the forbidden bands, although the systems still retain their semiconducting characteristics. The atomic vacancies give rise to spin polarization around the corresponding defects. The strong ionic characteristics of the W-S bonds result in the charge transfer of the non-bonding electrons, which is the key factor for the spin polarization around the vacancies. The spin polarization is strongly localized in the VS1 and VS2 models, but is slightly delocalized in the VW model. We believe that the spin polarization could form scattering in the spin transport process. Further study is required on how to diminish or use the effect of the polarization. The absorption spectrum is obviously influenced by the defect states, which is important for photovoltaic devices based on the WS$_2$ absorber.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant Nos. 11204391, 11104364, 11047176 and 10947161) and the Scientific Research Start-up Foundation of Chongqing University of Technology (No. 2008EDJ01), and partially by the Research Foundation of the Education Bureau of Hubei Province of China (Grant No. Q20111305) and by the Natural Science Foundation Project of Chongqing (Grant No. cstc2012jjA00019).