The energy band alignment at the interface between mechanically exfoliated few-layer NiPS₃ nanosheets and ZnO

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Abstract
We have studied the electronic structure and interfacial properties of mechanically exfoliated few-layer NiPS₃ van der Waals crystals on ZnO/Nb: SrTiO₃ substrates using scanning photoelectron microscopy and spectroscopy. The conducting ZnO layer enhances the visibility of few-layer NiPS₃ on Nb: SrTiO₃ and prevents charging effects in photoemission. We experimentally determined a type-II band alignment at the NiPS₃/ZnO interface. The valence band offset (VBO) of few-layer NiPS₃/ZnO is 2.8 ± 0.09 eV, and the conduction band offset is 1.0 ± 0.09 eV. Moreover, we found an increase of ~0.3 eV in VBO as decreasing NiPS₃ thickness, suggesting electronic coupling or charge transfer at the NiPS₃/ZnO interface.

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1. Introduction

Recently, there has been intensive study of van der Waals (vdW) materials and their heterostructures [1,2]. Beginning with graphene, attention has now been extended to other two-dimensional (2D) atomic crystals, such as isolated monolayers and few-layer crystals of hexagonal BN, MoS₂, and other dichalcogenides. Numerous applications have been suggested, including transistors [3], photovoltaic devices [4], and light emitting diodes [5]. However, these efforts have not been extended to 2D vdW materials exhibiting magnetic orderings, which can have their potential applications for spintronic devices.

MPS₃ (M = Mn, Fe, Co, Ni) is a class of chalcogenide materials, which have magnetically-ordered ground states. The MPS₃ lattice consists of layers of covalently bonded (P₂S₆)₄⁻ bipyramids and honeycomb arrangements of transition metal ions [see Fig. 1(a)]. These materials were studied previously in bulk form due to their antiferromagnetic ordering and potential applications in lithium batteries [6,7]. However, there have been few studies on few-layer MPS₃ nanosheets [8]. Intriguingly, it has recently been theoretically predicted that 2D atomic crystals of these vdW materials could show spin-valley coupling [9], an antiferromagnetic-ferromagnetic transition [10] and a tunable electronic structure suitable to photocatalytic water splitting. Therefore, monolayer and/or few-layer MPS₃ are promising materials for future advanced electronic devices [9–11].

Among the MPS₃ series, nickel phosphorous trisulfide NiPS₃ has the highest Neel temperature (~155 K), the smallest bandgap energy (~1.6 eV), and capability of both p- and n-type doping for device applications [6,7]. Recently, we succeeded in obtaining monolayer and few-layer NiPS₃ vdW crystals on SiO₂/Si substrates by using the micromechanical exfoliation technique [12]. However, most of their physical properties in the few-layer limit, in particular electronic and magnetic properties, are still unknown. A major obstacle in this regard is that photoemission, a central tool in electronic structure studies, is not possible on standard SiO₂/Si due to charging effects. In this paper, we will show how depositing few-layer NiPS₃ on conducting ZnO/Nb: SrTiO₃ alleviates this problem.
Fig. 1. (a) Top and side view of monolayer NiPS₃. Optical images of exfoliated (b) bulk (thickness ~ 100 nm) and (c) few-layer [3 and 6 ML] NiPS₃ nanosheets on ZnO(85 nm)/Nb: SrTiO₃. The gray dashed lines mark the boundary of the few-layer nanosheets. The optical images in (b) and (c) are obtained at different illumination conditions to maximize the visibility of nanosheets. (d) Sample measurement geometry for the SPEM/S study for few-layer NiPS₃ nanosheets on ZnO/Nb: SrTiO₃.

and enables electronic structure studies using scanning photoelectron microscopy and spectroscopy (SPEM/S). In addition, we will show experimentally that the NiPS₃/ZnO interface has a type-II band alignment suitable for photovoltaic and photocatalytic applications.

2. Experiment

We fabricated the few-layer NiPS₃ nanosheets on 0.5%wt Nb: SrTiO₃ substrates coated with a ZnO layer by mechanical exfoliation. Single crystal NiPS₃ bulk samples were synthesized by vapor transfer method. The ZnO thin films were grown on Nb: SrTiO₃ substrates by pulsed laser deposition and their thicknesses were determined using a stylus profiler. The ZnO thin films were treated by O₂ plasma ashing to improve the NiPS₃ exfoliation efficiency. The adhesive residue from the tape on the sample was removed by trichloroethylene after exfoliation [13]. The thickness of few-layer NiPS₃ nanosheets was identified by atomic force microscope (see supplementary data). The NiPS₃ bulk samples are insulating, showing high crystal quality and nearly stoichiometry [14]. The bottom ZnO layer is unintentionally n-type doping [15]. In this work, we study the band alignment of few-layer NiPS₃ and n-type ZnO.

The insertion of the ZnO layer between NiPS₃ nanosheets and Nb: SrTiO₃ substrates has several advantages for electronic structure studies. (1) Few-layer NiPS₃ nanosheets can be prepared on ZnO by exfoliation. (2) The unintentional n-type conductivity leads to the conducting ZnO layer, which allows for the photoelectron spectroscopic study. (3) The exfoliated NiPS₃ flakes on ZnO are optically visible, so it can be easily located in an optical microscope. For our study, we chose a 85-nm-thick ZnO layer since it can lead to a high visibility enhancement of few-layer NiPS₃ nanosheets. A multilayer optical model clearly shows that the insertion of ZnO layer can enhance the optical contrast of monolayer NiPS₃ by a factor of about 4 (See Fig. S2 in the supplementary data) [16].

Fig. 1(b) and (c) show the optical images of exfoliated bulk and few-layer NiPS₃ nanosheets on ZnO(85 nm)/Nb: SrTiO₃. As shown in Fig. 1(c), both 3 and 6 monolayer (ML) NiPS₃ nanosheets are visible with an optical microscope. In contrast, the exfoliated 4 ML NiPS₃ flakes on bare Nb: SrTiO₃ are nearly transparent, meaning they are difficult to locate using an optical microscope (see Fig. S3 in the supplementary data).

To investigate the electronic properties of our samples, we performed SPEM/S experiments with a synchrotron radiation soft x-ray light. As displayed in Fig. 1(c) and (d), NiPS₃ flakes were quite small with a flat surface with a general size of several μm. The beam was focused down to 100 nm with a Fresnel zone plate, which allowed the SPEM/S measurements on small NiPS₃ flakes [17]. The samples were in situ annealed in ultra-high vacuum to remove the surface contaminants and then transferred into the main chamber for SPEM measurements. The cleanliness of the NiPS₃ surfaces was monitored by the intensity of C 1s core level peak to be near the background level after in situ annealing. We found that the dissociation of NiPS₃ began when the annealing temperature was higher than 300 °C. The samples were annealed at 240 °C for 30 min to reveal a clean surface and to prevent from dissociation. As schematically shown in Fig. 1(d), we could investigate the local electronic properties of exfoliated few-layer NiPS₃ flakes by using SPEM/S, including core level chemical mappings and micro-beam photoelectron spectroscopy (μ-PES). We used the core level chemical mappings to find the few-layer flakes, and then obtained the photoelectron spectra of exfoliated NiPS₃ nanosheets on ZnO by μ-PES. The photon energy for the SPEM/S measurement was 380 eV with energy resolution of 100 meV. The photon energy was calibrated using the Au 4f core level of a gold reference, prior to measure the exfoliated NiPS₃ samples.

3. Result and discussion

Fig. 2(a) and (b) show the Zn 3d and S 2p chemical maps of exfoliated bulk NiPS₃ sheets, corresponding to the optical image in Fig. 1(b). And Fig. 2(c) and (d) show the similar maps of exfoliated few-layer NiPS₃ nanosheets shown in Fig. 1(c). The maps look quite similar to the optical images. Fig. 2(e) shows the μ-PES spectra of exfoliated bulk NiPS₃ flakes, 3 ML NiPS₃ flakes, and the ZnO substrate. These spectra do not contain any intermixing signal from other sample portions due to the high spatial resolution of μ-PES measurements.

Our measurements demonstrate the high quality of the exfoliated NiPS₃ flakes. Note that the core level peak positions (e.g. Ni 3p, P 2p₃/₂, and S 2p₃/₂, and 2p₃/₂) can be used for investigating the chemical states of the exfoliated NiPS₃. The μ-PES spectra of few-layer NiPS₃/ZnO show the photoelectron signals (S 2p and Zn 3d) for both NiPS₃ and ZnO. In order to rule out the surface or interface effects, we studied the energy difference of core level peaks. Regardless of NiPS₃ thickness (from few-layer to bulk), the energy difference between E(S 2p₃/₂) and E(Ni 3p) is 94.8 eV, and that between E(S 2p₃/₂) and E(P 2p₃/₂) is 30.4 eV. These values are consistent with the values reported for bulk NiPS₃ in situ cleaved in a He-filled glove box [18]. This indicates that the exfoliated NiPS₃ on ZnO is chemically stable with negligible aging or oxidizing effects even for
thicknesses down to 3 ML.

We also used the μ-PES spectroscopy to determine the band alignments of the NiPS3/ZnO heterojunction. Kraut et al. developed the photoelectron spectroscopic method which can directly determine the heterojunction band alignments, namely the valence and conduction band offsets, with a precision better than 0.1 eV [19]. This method has been widely applied to numerous heterojunction systems [19–23]. Following this method, we can determine the valence band offset (VBO, $\Delta E_V$) at NiPS3/ZnO interface from the following equation:

$$
\Delta E_V = \left[ E(S\, 2p_{3/2})^{NiPS3} - E(VBM)^{NiPS3} \right] - [E(Zn\, 3d) - E(VBM)^{ZnO}] - \Delta E_{CL}
$$

(1)

where $E(VBM)$ is the energy position of the valence band maximum (VBM), $E(A)$ is the peak position of the core level A, and $\Delta E_{CL}$ is the energy difference between $S\, 2p_{3/2}$ and Zn 3d core level peaks in the few-layer NiPS3/ZnO regions. The first two terms of Eq. (1) are material constants, whose values can be measured in the bulk NiPS3 and ZnO regions. The third term $\Delta E_{CL}$ can be obtained from the few-layer NiPS3/ZnO regions, providing information on the properties of the interface between NiPS3 and ZnO.

We fitted all of experimental $S\, 2p$ and Zn 3d core level peaks using the standard Voigt line shapes and a Shirley background. We could find quite good fitting curves (the solid lines) to the experimental data. Fig. 3(a) shows the Zn 3d core level peak spectrum (left) and the valence band spectrum (right) for the bulk ZnO. Fig. 3(b) shows $S\, 2p$ core level peak spectrum (left) and the valence band spectrum (right) for the bulk NiPS3. Note that the $S\, 2p$ core level peak spectrum shows a double peak structure due to spin–orbit coupling [18]. The left and right sides of Fig. 3(c) show the $S\, 2p$ and Zn 3d core level peak spectra in the 3 ML NiPS3/ZnO interface region, whose detailed positions should be closely related to the band offset, as shown in Eq. (1).

There are thickness dependences of both $S\, 2p_{3/2}$ and Zn 3d core level peaks. Fig. 4(a) shows the energy positions of the $S\, 2p_{3/2}$ and Zn 3d core level peaks as a function of NiPS3 layer number. The energy positions of the $S\, 2p_{3/2}$ core level peaks in 3 ML NiPS3/ZnO, as shown in Fig. 4(a), are shifted to lower binding energy by ~0.2 eV from the $E(S\, 2p_{3/2})$ of bulk NiPS3 (blue dashed line). When the NiPS3 layer number increases to 13 ML, $E(S\, 2p_{3/2})$ value is close to the bulk NiPS3 value. The ~0.2 eV shift of $S\, 2p_{3/2}$ core level peaks in 3 and 6 ML NiPS3 provides the evidence of additional interface charge transfer between the few-layer NiPS3/ZnO interface compared to bulk NiPS3. The negligible difference in $E(S\, 2p_{3/2})$ value for 3 and 6 ML NiPS3 indicates little charge transfer difference between them, similar to the case of bilayer and multilayer graphene [24,25]. Moreover, combining the shifts of $S\, 2p_{3/2}$ and Zn 3d core level peaks, we can conclude the interfacial electronic properties of few-layer NiPS3 on n-type ZnO. The Zn 3d core levels have a similar behavior of peak shift but in the opposite direction. In thinner NiPS3 region (3 and 6 ML), the energy position of $E(Zn\, 3d)$ is shifted to higher binding energy by ~0.1 eV with respect to the bulk ZnO value (red dashed line), indicating a downward band bending in ZnO. In the thicker (13 ML) NiPS3 region, the shift of the Zn 3d core level peak is negligible. The observation of peak shifts in both Zn 3d (+0.1 eV) and $S\, 2p_{3/2}$ (~0.2 eV) core levels indicates the existence of electronic coupling or charge transfer at the interface between few-layer NiPS3 and ZnO. The phenomenon of interfacial coupling and/or charge transfer is also observed at the interface between other vdW materials and semiconductors, such as graphene [24,25] and MoS2 [26]. The net shift of ~0.3 eV leads to the change in VBO as decreasing NiPS3 thickness.

From this data, we determined the thickness-dependent VBOs for the NiPS3 nanosheets. By taking the difference between the peak positions of $S\, 2p_{3/2}$ and Zn 3d in Fig. 4(a), we estimated the experimental $\Delta E_{CL}$ values for 3, 6, and 13 ML to be $151.0 \pm 0.02$, $151.2 \pm 0.06$, and $151.2 \pm 0.02$ eV, respectively. From Fig. 3(a) and (b), we also estimated $[E(S\, 2p_{3/2}) - E(VBM)]^{NiPS3}$ is $161.6 \pm 0.06$ eV and that $E(Zn\, 3d) - E(VBM)^{ZnO}$ is $7.8 \pm 0.06$ eV. The $[E(Zn\, 3d) - E(VBM)]^{ZnO}$ value in this work is consistent to that reported by Singh et al. [22], and lies within the range of other reported ones, in a range of 7.3–7.81 eV [21–23]. The slight variation of values may result from surface conditions, such as surface stoichiometry and/or contaminants, of ZnO thin films cleaned by various surface cleaning methods and recipes.

By using Eq. (1), we determined that the VBO values of 3 and 6 ML NiPS3/ZnO are 2.8 ± 0.09 eV. For 13 ML NiPS3/ZnO, the VBO...
value is 2.6 ± 0.09 eV. For comparison, we determined the VBO value of bulk NiPS₃/ZnO from \( \Delta E_{\text{CL}} \) between bulk NiPS₃ and ZnO values by assuming that the core level peaks of ZnO substrate and NiPS₃ overlayers do not shift [20]. Then the resulting VBO of bulk NiPS₃/ZnO is 2.5 ± 0.09 eV. This shows that the VBO increases with decreasing NiPS₃ thickness. Our experimental observations are summarized schematically in Fig. 4(b), where we show the band alignment of few-layer and bulk NiPS₃/ZnO. As mentioned earlier, an increase of 0.3 eV in VBO for few-layer NiPS₃ is attributed to the interfacial electronic coupling or charge transfer from ZnO to NiPS₃.

In addition, the conduction band offset (CBO, \( \Delta E_C \)) of NiPS₃/ZnO can be calculated through the following equation:

\[
\Delta E_C = \Delta E_V + E_g(\text{NiPS}_3) - E_g(\text{ZnO})
\]

(2)

where \( E_g(\text{NiPS}_3) \) is the bandgap energy of NiPS₃, and \( E_g(\text{ZnO}) \) is the bandgap energy of ZnO. One can find from Eq. (2) that the CBO values of NiPS₃/ZnO are affected by the values of VBO and the bandgap energy for both NiPS₃ and ZnO. \( E_g(\text{ZnO}) \) is constant since no localized change in the bottom ZnO layer. In the contrary, the layer number of the top NiPS₃ can vary, and it might be useful to discuss the possible evolution of bandgap energy in few-layer NiPS₃. In the case of MoS₂, the bandgap energy varies significantly between mono- and bi-layer, and gradually decreases to be close to the bulk value while layer number increases from 3 to 6 ML [27]. One may expect that the bandgap energy of few-layer NiPS₃ might vary as a function of layer number. The bulk NiPS₃ has been determined to be an indirect-gap semiconductor with the bandgap energy of 1.6 eV according to the optical absorption [28] and photoelectrochemical measurement [14]. For an indirect-gap material, bandgap photoluminescence (PL) is a weak phonon-assisted process and has negligible quantum yield [27]. Our previous work in the optical investigation of exfoliated NiPS₃ nanosheets on SiO₂/Si substrates shows that for few-layer (2–7 ML) and bulk NiPS₃ sheets, photoluminescence is absent [12]. It indicates that the quantum yield is still negligible even the thickness of NiPS₃ decreases from bulk to 2 ML, and hence no direct–indirect bandgap transition is found, which is different from the case of MoS₂ [27], and the exact values of indirect bandgap energy are still unclear for few-layer NiPS₃ sheets. Further experimental results and theoretical calculations on the bandgap energy in few-layer NiPS₃ are desirable in the future.

Due to the lack of evidence of the bandgap variation, we assume...
that the bandgap energies of 3, 6, and 13 ML NiPS3 flakes would be close to the bulk values and estimate the CBO values. Note that the VBO values are directly determined by SPEM/S measurement, which is free of influence by \( E_\text{g}(\text{NiPS3}) \) in few-layer NiPS3. The CBO values could be revised through Eq. (2) if \( E_\text{g}(\text{NiPS3}) \) is experimentally proved to vary as function of thickness in the future. Considering that the bandgap energy of bulk ZnO, \( E_\text{g}(\text{ZnO}) \), is 3.4 eV [29] and that of bulk NiPS3, \( E_\text{g}(\text{NiPS3}) \), is 1.6 eV [7,14,28], the CBO value of bulk NiPS3/ZnO is about 0.7 ± 0.09 eV and that of few-layer (3 and 6 ML) NiPS3/ZnO is estimated to be about 1.0 ± 0.09 eV.

Together with the changes of VBO, we can argue that a type-II band alignment will occur at the NiPS3/ZnO heterointerface. The type-II band alignment corresponds to a staggered gap type heterojunction, suitable for photovoltaic [30] and photocatalytic [31] applications. Under light irradiation, electrons in the conduction band minimum (CBM) of NiPS3 can transfer to that of ZnO because the CBM of ZnO is lower than that of NiPS3. Similarly, holes in the VBM of ZnO can transfer to that of NiPS3 due to the lower VBM of NiPS3. The band alignments of few-layer (3, 6, and 13 ML) NiPS3/ZnO is estimated to be about 0.9 ± 0.7 eV.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.cap.2016.01.001.

References