# Low barrier height in a ZnO nanorods/ NbSe<sub>2</sub> heterostructure prepared by van der Waals epitaxy <sup>©</sup>

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Note: This paper is part of the Special Topic on Fundamentals and Applications of Mixed-Dimensional Heterostructures.

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#### ABSTRACT

Two-dimensional (2D) materials as contacts for semiconductor devices have attracted much attention due to minimizing Fermi level pinning. Schottky–Mott physics has been widely employed to design 2D material-based electrodes and to elucidate their contact behavior. In this study, we revealed that charge transfer across a 2D/semiconductor heterointerface and materials characteristics besides work function should be accounted for in fabrication of electrodes based on 2D materials. Our density functional theory (DFT) calculations predicted that charge transfer between ZnO and NbSe<sub>2</sub> lowers the barrier height at the heterojunction and that conductive surface states of ZnO provide an additional conduction channel in the ZnO/NbSe<sub>2</sub> heterostructures. Crystalline ZnO/NbSe<sub>2</sub> heterostructures were prepared by the hydrothermal method. Electrical characterizations of the ZnO/NbSe<sub>2</sub> heterostructures showed Ohmic-like behavior as predicted by the DFT calculations, opposed to the prediction based on the Schottky–Mott model.

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Electrodes are essential components interfacing functional building blocks with the environment for controlling devices. Understanding and engineering of metal/semiconductor interfaces are critical for the development of semiconductor devices. Schottky–Mott physics based on electronic band alignment is a rule of thumb to select metals as contacts to semiconductors. However, in real devices, the interfacial properties of metal/semiconductor junctions, such as trapped states and their surface density, induce Fermi level pinning, which governs the barrier height and contact resistance. A crucial issue for electrical contacts is that the interfacial properties are highly process-dependent. Postprocessings, including rapid thermal annealing and plasma treatment, have been widely used to minimize the unintentional formation of interfacial states that deteriorate device performances by increasing the contact resistance and changing the barrier height.

Recent advances in two-dimensional (2D) materials research have shed light on electrical contact formation. In ideal cases, 2D

materials do not have surface dangling bonds, which are the source of Fermi level pinning. A framework to design metallic 2D and semiconducting 2D materials heterostructures for tuning the Schottky barrier height according to Schottky-Mott physics, without hindrance from Fermi level pinning, has already been introduced.<sup>1,2</sup> Moreover, the Schottky barrier height tuning with the metallic 2D material contact has been demonstrated in various device applications.<sup>3,4</sup> Because minimizing Fermi level pinning via a 2D material contact layer depends on the fundamental physics of band alignment, incorporation of metallic 2D materials into non-2D semiconductor devices is a natural approach to improve device performances. Graphene has been intensively studied as a transparent electrode in various devices and as an insertion layer to reduce contact resistivity in Si devices by weakening Fermi level pinning.5-Additionally, metallic 2D materials can be used as flexible substrates for devices with three-dimensional (3D) architectures. Flexible lightemitting diodes (LEDs) and photodetectors with compound semiconductors/graphene heterostructures prepared by van der Waals epitaxy have been successfully demonstrated.9-11 However, in the same material combination of ZnO and graphene, graphene behaves as either Ohmic contacts (for LEDs) or Schottky contacts (photodetectors).<sup>12-16</sup> The opposite behaviors of graphene as contacts imply that designing contacts based on 2D materials requires knowledge of other aspects of interfacial properties besides Schottky-Mott physics.

The electrical properties of 2D/conventional semiconductors have been studied in a few cases, such as graphene/Ge, graphene/GaN,  $MoS_2/Ge$ , and  $MoS_2/Si$ .<sup>17–21</sup> In the reported cases, charge transfer between a 2D material and a conventional semiconductor is commonly observed. Thus, charge transfer across an interface between a metallic 2D material and a conventional semiconductor is a crucial factor to design a 2D material-based electrical contact of semiconductor devices.

Here, we report the electrical contact behavior of the epitaxially grown ZnO nanorods (NRs) on NbSe<sub>2</sub> flakes. Vertically aligned hexagonal ZnO NRs were synthesized on a mechanically exfoliated NbSe<sub>2</sub> flake using a hydrothermal method. The ZnO NRs showed identical in-plane alignment, in terms of sidewall facet orientation, on a crystalline NbSe<sub>2</sub> flake. Theoretical calculations confirmed the lattice-matched heteroepitaxy of the ZnO NRs on NbSe<sub>2</sub>. Despite the 0.3–0.7 eV built-in potential of the heterojunction estimated by work functions, charge transfer across the ZnO/NbSe<sub>2</sub> interface and the metallic surface states of epitaxially grown ZnO NRs induced barrier height lowering and resulted in Ohmic behavior of the ZnO/NbSe<sub>2</sub> heterostructure. This electrical behavior is opposite to that predicted by Schottky–Mott physics.

The NbSe<sub>2</sub> flakes were prepared by exfoliating a NbSe<sub>2</sub> crystal and subsequently transferring them onto 300 nm-thick SiO<sub>2</sub>/Si substrates. Crystalline NbSe<sub>2</sub> was synthesized by the chemical vapor transport method. Details of the synthesis of NbSe<sub>2</sub> crystals can be found elsewhere.<sup>22</sup> ZnO NRs were grown on NbSe<sub>2</sub> flakes/SiO<sub>2</sub>/Si substrates by hydrothermal synthesis. Zinc nitrate hexahydrate (0.0284 g), hexamethylenetetramine (0.0525 g), and deionized water (15 ml) were employed as precursors of the hydrothermal growth. The growth temperature and time were typically 94 °C and 4 h, respectively.

Figure 1 shows scanning electron microscopy (SEM) and crosssectional transmission electron microscopy (TEM) images of ZnO



**FIG. 1.** (a) Tilted-view SEM images of ZnO nanorods (NRs) grown on an exfoliated NbSe<sub>2</sub> prepared on the SiO<sub>2</sub>/Si substrate. The inset SEM image was obtained at a higher magnification. (b) Top-view SEM image of vertically aligned ZnO NRs grown on a NbSe<sub>2</sub> flake. The arrow indicates the direction parallel to a side facet of a NR. (c) and (d) Cross-sectional TEM images of a ZnO NR grown on a NbSe<sub>2</sub> flake.

NRs grown on an exfoliated NbSe<sub>2</sub> flake/SiO<sub>2</sub>/Si substrate. Vertically aligned ZnO NRs with hexagonal cross sections were selectively grown on NbSe<sub>2</sub> flakes, as shown in Fig. 1(a). The length and diameter of the ZnO NRs were 4  $\mu$ m and 500–750 nm, respectively. In Fig. 1(b), the arrangement of the sidewall facets of neighboring ZnO NRs implies an epitaxial relationship between ZnO and NbSe<sub>2</sub>. A 500 nm-thick Pt/500 nm-thick SiO<sub>2</sub> layer was deposited to protect the ZnO NR during TEM sample preparation via focused ion beam milling. Figure 1(c) shows a crystalline ZnO NR grown on NbSe<sub>2</sub> that was vertically aligned along the [0001] direction. The high-resolution TEM (HRTEM) image in Fig. 1(d) shows that there is neither oxidized NbSe<sub>2</sub> nor distinguishable defect at the interface between the root of the ZnO NR and NbSe<sub>2</sub>.

The surface characteristics of the exfoliated NbSe<sub>2</sub> before and after hydrothermal synthesis of ZnO NRs were investigated by x-ray photoelectron spectroscopy (XPS). Figure 2 shows the Nb 3d and Se 3d spectra before and after the growth of ZnO NRs. In Fig. 2(a), the Nb 3d spectrum of the pristine exfoliated NbSe<sub>2</sub> flake consists of two peaks at 203 and 205.9 eV, corresponding to Nb<sup>4+</sup> 3d<sub>5/2</sub> spectra, which are assigned to NbSe<sub>2</sub>.<sup>23,24</sup> After the hydrothermal synthesis of the ZnO NRs, the Nb 3d spectrum of the exfoliated NbSe<sub>2</sub> flake has multiple peaks at 203.8, 206.2, 207.6, and 210.4 eV, as shown in Fig. 2(b). The peaks at 203.8 and 206.2 eV are Nb<sup>4+</sup> 3d<sub>5/2</sub> spectra, corresponding to NbSe<sub>2</sub>.<sup>23,24</sup> The peak at 207.6 eV is assigned to Nb<sup>4+</sup> ions in NbSe<sub>2</sub>. The peak at 210.4 eV corresponds to the Nb<sup>5+</sup> 3d<sub>3/2</sub> spectrum, indicating the existence of Nb<sub>2</sub>O<sub>5</sub>.<sup>24,25</sup> The arise of



FIG. 2. XPS spectra for exfoliated NbSe<sub>2</sub> before and after the growth of ZnO. The dashed lines are fitted curves and baselines. The Nb 3d and Se 3d spectra of exfoliated NbSe<sub>2</sub> before [(a) and (c)] and after [(b) and (d)] ZnO, respectively.

the 210.4 eV peak in Fig. 2(b) reveals that  $Nb_2O_5$  and  $NbSe_2$  coexist on the surface of exfoliated NbSe2 after the hydrothermal synthesis of the ZnO NRs. Figure 2(c) shows that the Se 3d spectrum of the pristine exfoliated NbSe<sub>2</sub> flake has one dominant peak at 53.4 eV, corresponding to a Se 3d<sub>5/2</sub> spectrum.<sup>24,26</sup> After the growth of ZnO NRs, the Se 3d spectrum has two peaks at 53.6 and 54.7 eV, corresponding to Se  $3d_{5/2}$  spectra, as shown in Fig. 2(d). In the Se 3d spectra, there is no noticeable feature of oxidized states of NbSe<sub>2</sub>. The XPS studies indicate that NbSe<sub>2</sub> is partly oxidized under the ZnO synthesis condition. However, the NbSe<sub>2</sub> phase is still dominant in the NbSe<sub>2</sub> flakes after ZnO synthesis. The presence of carbon (C) atoms was assured by XPS. Tables S1 and S2 in the supplementary material show that the C surface level was higher on the surface of NbSe2 after the growth of ZnO NRs. The dominant form of C atoms was hydrocarbon. The observation of hydrocarbon on the surface of NbSe<sub>2</sub> is consistent with previous reports characterizing surfaces of 2D materials.<sup>27,28</sup> The role of hydrocarbon on the properties of NbSe<sub>2</sub> is not elucidated. However, the trapped C atoms on the surface of NbSe<sub>2</sub> and in the interfacial region of adjacent NbSe<sub>2</sub> layers induce stabilization of Se divacancies, which does not noticeably shift the Fermi level of NbSe2.28

The selective growth of vertically aligned ZnO NRs on NbSe<sub>2</sub> was elucidated by both structural compatibility and energetics of the material system. Both ZnO and 2H–NbSe<sub>2</sub> have a hexagonal inplane atom arrangement. The in-plane lattice constants of ZnO and NbSe<sub>2</sub> are 3.25 and 3.45 Å, respectively. Nucleation of ZnO on NbSe<sub>2</sub> is preferable to amorphous SiO<sub>2</sub> because NbSe<sub>2</sub> is a commensurate substrate. However, the lattice mismatch between ZnO and NbSe<sub>2</sub> is 5.79%, which is too large to ensure an epitaxial heterostructure. To augment the structural compatibility argument, we calculated the binding energies of ZnO on NbSe<sub>2</sub> and SiO<sub>2</sub> systems via density functional theory (DFT) calculations. Moreover, DFT calculations were conducted to establish the arrangement of Zn, O, Nb, Se, and Si atoms in the ZnO/NbSe<sub>2</sub> and SiO<sub>2</sub> was calculated according to the following equation:

$$E_B = (E_{\text{substrate}} + E_{\text{ZnO}} - E_{\text{ZnO/substrate}})/n, \qquad (1)$$

where  $E_{\text{substrate}}$  is the total energy of the substrate (i.e., SiO<sub>2</sub> or NbSe<sub>2</sub>),  $E_{\text{ZnO}}$  is the total energy of the ZnO NR,  $E_{\text{ZnO/substrate}}$  is the

total energy of the combined NRs/substrate system, and n is the number of Zn or O atoms at the surface of the substrate.

The calculations were performed with consideration of the small supercells of ZnO bonded to commensurate supercells of each substrate material (Fig. S1) to limit computational demand and approximate the binding energies without needing to consider edge effects. The total binding energies,  $E_{\rm B}$ , as defined by Eq. (1), were 365.4 and 700.4 meV for the ZnO/SiO<sub>2</sub> and ZnO/NbSe<sub>2</sub> systems, respectively. The stronger relative binding energy of Zn atoms onto NbSe<sub>2</sub> implies that nucleation of ZnO is preferred on NbSe<sub>2</sub>. Figure 3 shows the arrangement of Zn, O, Nb, and Se atoms that minimizes the total energy of ZnO/NbSe<sub>2</sub> via the ball-andstick model. These findings are in agreement with the experimental results, showing that the growth of ZnO NRs is more energetically favorable on NbSe2 than SiO2. In the atomic arrangement achieving minimum energy, the Zn, O, Nb, and Se atoms preserved an in-plane hexagonal geometry. The first layer of O atoms sits on Se atoms. However, the first layer of Zn atoms and the second layer of O atoms are displaced due to the 5.7% lattice mismatch. Nevertheless, ZnO/NbSe2 has an epitaxial relationship, which is not available for conventional planar epitaxy without the formation of structural defects, such as threading dislocations and stacking faults. The calculated atomic arrangement shown in Fig. 3(b) and the absence of structural defects shown in Fig. 1(d) indicate that the ZnO/NbSe<sub>2</sub> heterostructure was formed by van der Waals epitaxy. The crystal axes of the grown ZnO are well-aligned with those of the NbSe2, although the lattice constant varies unexpectedly through the interface shown in Fig. 3(b).

The physical properties of the ZnO/NbSe2 heterostructure were predicted by DFT. Details of the DFT calculations are described in the supplementary material. To eliminate quantum size effects from the calculations, we performed local density of states (DOS) calculations of a  $10 \times 10$  horizontal cross section of the ZnO structure, with periodic boundary conditions in the z-direction. Figure 4(a) shows the calculated total DOS of the ZnO/NbSe2 heterostructure. The absence of a bandgap in the total DOS, as represented by the Fermi level (E<sub>F</sub>) position, indicates that the heterostructure is metallic. The metallic nature of the ZnO/NbSe2 heterostructure is explained by charge transfer between ZnO and NbSe<sub>2</sub>, as reported in other conventional semiconductor and transition metal dichalcogenide (TMD) systems due to electronegativity differences. In addition to the metallic interface formation, the DFT calculations revealed a carrier transport channel along the surface of ZnO NR, as shown in Fig. 4(b). An additional analysis of the  $10 \times 10$  supercell in a horizontal plane of ZnO also indicated that the local DOS at the Fermi energy,  $\rho(E_F)$ , along an edge is higher than that at the center regardless of the length of the diagonals in a horizontal plane, as shown in Fig. 4(c). As seen in the edge  $\rho(E_F)$  curves, the ZnO surface is metallic. This accounts for the variation in  $\rho(E_F)$  magnitude at the edges. The diagonal regions also had metallic behavior at both ends, with  $\rho(E_F) \rightarrow 0$  in the middle. These results, along with those of the analysis of the vertical regions of ZnO, indicated that the heterostructure had a metallic base formed from a ZnO/NbSe<sub>2</sub> heterointerface and metallic ZnO surfaces, which should allow for conduction along the bottom, sides, and top of the material.

Figures 4(b) and 4(c) clearly show that the surfaces of a ZnO NR can act as conduction channels. Figure 4(d) is a schematic illustration of a possible circuit model of the ZnO NR/NbSe<sub>2</sub> heterostructure. According to the reported work functions of ZnO (4.9–5.3 eV) and NbSe<sub>2</sub> (5.5–5.69 eV),<sup>1,29–31</sup> the barrier height (V<sub>bi</sub>) of the ZnO/NbSe<sub>2</sub> junction, estimated by the Anderson model, is in the range of 0.3 and 0.7 eV. Thus, the NbSe<sub>2</sub> can be considered as a Schottky contact to ZnO according to Schottky–Mott physics. However, the metallic interface between ZnO and NbSe<sub>2</sub>, and the electrically conductive surface of the ZnO NR, imply that the ZnO/NbSe<sub>2</sub> heterostructure has a low barrier height at the ZnO/NbSe<sub>2</sub> heterojunction.

Current–voltage (I-V) characterization was performed at room temperature to confirm the predicted electrical properties of the ZnO/NbSe<sub>2</sub> heterostructure. Heterostructures were prepared on the TiN/SiO<sub>2</sub>/Si substrates to enable measurement of the electrical signals through the junction between ZnO NRs and NbSe<sub>2</sub>. The TiN layer was used as a bottom electrical contact pad. To make top electrical contacts for ZnO NRs, the NbSe<sub>2</sub> surface was spin-coated with poly(methyl methacrylate) (PMMA, 950K A4) at 1000 rpm and baked at 180 °C. Then, a Ti/Au layer was deposited on the tips of the ZnO NRs, which were uncovered by the PMMA layer. Two electrical probes were used to make electrical contacts with the TiN bottom electrode and Au/Ti top electrode. The electrical measurements were performed by a probe station equipped with a B1500 semiconductor parameter analyzer at room temperature.

Figure 5 shows the I-V curve of the ZnO NRs/NbSe<sub>2</sub> heterostructure. The linear shape of the I-V curve indicates Ohmic behavior, opposite to that predicted by the Schottky–Mott model. Charge transfer across the ZnO/NbSe<sub>2</sub> interface and subsequent current movement along the surfaces of ZnO NRs can explain the Ohmic-like behavior. There was decreasing resistance represented by the steeper slope of the I-V curve, at 0.8 V, which is close to the highest value of the estimated barrier height of the ZnO/NbSe<sub>2</sub> junction of 0.7 eV. The emergence of lower resistance is attributed to the



FIG. 3. (a) A schematic of atomic arrangements calculated by DFT at the interface between a ZnO NR and a NbSe<sub>2</sub> layer. (b) Top-view of the calculated atomic arrangement in a unit cell composed of a monolayer NbSe<sub>2</sub> and a unit cell of ZnO.



FIG. 4. (a) Density of states (DOS) of a supercell of the ZnO/NbSe<sub>2</sub> heterostructure. (b) The corresponding DOSs at the Fermi energy,  $\rho(E_F)$ , of the core (blue and solid circles) and the surface (red and hollow circles) regions of a ZnO NR along the longitudinal (z) direction. (c) The corresponding DOSs at the Fermi energy,  $\rho(E_F)$ , in the horizontal plane of a 10 × 10 cell of ZnO. "a" and "b" indicate different directions in a horizontal plane. (d) A scheme of the predicted electrical circuit at the interface between ZnO and NbSe<sub>2</sub>.

formation of another conduction channel in the center regions of the ZnO NRs, in turn, due to electron transport under forward bias.

The effects of crystal imperfections, such as vacancies, atomic ledges, and grain boundaries, on the electrical properties can be considered to interpret the I-V curve of the ZnO NRs/NbSe<sub>2</sub>



**FIG. 5.** A typical current–voltage (I-V) characteristic curve of the ZnO NRs/NbSe<sub>2</sub> heterostructure prepared onto the TiN thin film. The upper inset shows the schematic of the I-V measurement. The lower inset is a scheme of the electronic band alignment of ZnO/NbSe<sub>2</sub> without consideration of charge transfer between ZnO and NbSe<sub>2</sub>.

heterostructure. Nb and Se vacancies, which are common defects in NbSe<sub>2</sub>, are known as crucial constituents affecting magnetic, superconducting, and charge-density-wave (CDW) characteristics at cryogenic temperatures.<sup>28,32,33</sup> However, the vacancy effect on the I-V curve of the ZnO NRs/NbSe<sub>2</sub> heterostructure can be negligible because NbSe2 at room temperature behaves as a normal metal regardless of vacancy concentration according to the phase diagram of the CDW and the superconducting states in 2H-NbSe<sub>2</sub>.<sup>34</sup> Other line and planar defects, such as dislocations and grain boundaries in NbSe<sub>2</sub>, can change the electrical conductivity of NbSe<sub>2</sub> because the defects act as conduction channels of charge carriers or reflection points in a material. Nevertheless, there is no clear evidence indicating that dislocations and grain boundaries shift the Fermi level of metallic TMD, such as NbSe<sub>2</sub>. Furthermore, the NbSe<sub>2</sub> flakes, used in the research, are prepared by exfoliation of the highly crystalline NbSe<sub>2</sub> crystal. Thus, the effects of line and planar defects on the electrical properties of NbSe<sub>2</sub> at room temperature are not seriously incorporated to explain the electrical characteristic shown in Fig. 5.

The oxidized NbSe<sub>2</sub> as shown in Fig. 2 may affect the electrical characteristics of the ZnO/NbSe<sub>2</sub> heterostructures. According to the XPS results, the oxidized form of NbSe<sub>2</sub> is niobium pentoxide (Nb<sub>2</sub>O<sub>5</sub>). Due to the abundance of NbSe<sub>2</sub> in the NbSe<sub>2</sub> flakes as substrates of ZnO, the Nb<sub>2</sub>O<sub>5</sub> can be considered as islands surrounded by NbSe<sub>2</sub>. The reported bandgap of Nb<sub>2</sub>O<sub>5</sub> varies from 3.1 to 5.3 eV along different phases.<sup>35</sup> The conduction band minimum and the valence band maximum of Nb<sub>2</sub>O<sub>5</sub> are close to those of ZnO.<sup>36,37</sup>

The large bandgap and band alignment of Nb<sub>2</sub>O<sub>5</sub> indicate that Nb<sub>2</sub>O<sub>5</sub> acts as either a blocking layer between ZnO and NbSe<sub>2</sub> in the case of the bandgap of Nb<sub>2</sub>O<sub>5</sub> larger than 3.3 eV or an extended ZnO layer making a heterojunction to NbSe<sub>2</sub>. Thus, the charge transfer behavior in the mixed structure composed of ZnO/NbSe<sub>2</sub> and ZnO/Nb<sub>2</sub>O<sub>5</sub>/NbSe<sub>2</sub> is not significantly affected by the presence of Nb<sub>2</sub>O<sub>5</sub>.

In summary, we prepared and characterized crystalline ZnO NRs/NbSe<sub>2</sub> heterostructures with an epitaxial relationship based on in-plane hexagonal atomic arrangements and van der Waals interactions. The DFT calculations predicted the metallic surface states of ZnO NRs and charge transfer across the interface between ZnO and NbSe<sub>2</sub>. The formation of an electrically conducting channel in the ZnO/NbSe<sub>2</sub> heterostructure lowered the barrier height at the heterojunction and resulted in Ohmic behavior, as opposed to Schottky behavior predicted by the Schottky–Mott model. The discrepancy between Schottky–Mott physics and the observed electrical characteristics indicates that studies of 2D materials as contacts in semiconductor devices should consider interfacial phenomena. This study should facilitate exploration of architectures composed of 3D nanostructures and metallic TMDs with potential device applications.

#### SUPPLEMENTARY MATERIAL

See the supplementary material for density functional theory calculation details.

#### ACKNOWLEDGMENTS

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Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

# DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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