Layer-Dependent Hydrazine Adsorption Properties in Few-Layer WS₂

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ABSTRACT: We have developed a lithography free technique for the fabrication of two-dimensional material based devices for electrical characterization. We fabricated few-layer and multilayer WS₂ devices using a transmission electron microscope (TEM) grid as a shadow mask, and its transport characteristics were studied by electrical measurements. WS₂ samples were synthesized by first depositing WO₃ followed by sulfurization and characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), and Raman spectroscopy. Each sample was exposed to hydrazine at varying pressures, and their electrical resistance were monitored during adsorption (exposing to hydrazine vapor) and subsequent desorption (by pumping). The WS₂ sample consisting of two layers showed a decrease of resistance upon exposure to hydrazine vapor and showed complete reversibility upon pumping. The WS₂ sample with three layers showed a decrease of resistance during exposure but showed only partial recovery during desorption. In contrast, the multilayered (12 layers) WS₂ sample showed an initial decrease followed by a continued increase of the resistance upon exposure to hydrazine with little or no reversibility upon pumping. The charge transfer from N₂H₄ to WS₂ is believed to be responsible for the decrease of the resistance. Trapping of N₂H₄ molecules within the multilayers of WS₂ causing charge redistribution and possible chemical reactions may be responsible for the increase in resistance during the adsorption and complete irreversibility of resistance during desorption. The experimental results are explained with the help of computational calculations performed by employing the density functional theory (DFT) framework, as implemented in the Vienna Ab-initio Simulation Package (VASP).

1. INTRODUCTION

The discovery of graphene has initiated a tremendous interest in other two-dimensional (2D) materials.¹ Transition metal dichalcogenides (TMDs) have generated vast attention due to the excellent performance in electronic and optoelectronic measurements.²⁻⁴ Particularly, when TMDs eventually reach few-layer dimension, a wide range of electronic and optical properties, in striking contrast to bulk samples, are detected. 2D materials offer a platform that allows creation of heterostructures with a variety of properties. One atom thick crystals now comprise a large family of these materials, collectively covering a very broad range of properties. Nguyen et al. investigated the size-dependent properties of two-dimensional MoS₂ and WS₂,⁵ which could potentially be used in optical devices, hydrogen evolution reaction catalysts, bioapplicable devices, and so on. The first material to be included was graphene, a zero-overlap semimetal.⁶ The family of 2D crystals has grown to includes metals (e.g., NbSe₂),⁷ semiconductors (e.g., MoS₂), and insulators (e.g., hexagonal boron nitide (h-BN)).⁸ Many of these materials are stable at ambient conditions, and we have come up with strategies for handling those that are not. Surprisingly, the properties of such 2D materials are often very different from those of their 3D counterparts. Furthermore, even the study of familiar phenomena (like superconductivity or ferromagnetism) in the 2D case, where there is no long-range order, raises many thought-provoking questions. The 2D materials synthesized up to now can be broadly divided into two main categories: single atom thick and single polyhedral thick materials. Graphene¹ and hexagonal boron nitride (h-BN)⁸ belong to the former category, while TMDs⁵ belong to the latter. The single atom thick materials also include silicene,¹⁰ germanene,¹¹ and...
phosphorene.\textsuperscript{12} Graphene is metallic, while h-BN is a wide band gap semiconductor, thus making them both unsuitable for electronics applications that require small and (preferably) tunable band gap materials. Even though silicone is found to be semimetal and amenable to band gap tuning, it is highly reactive and completely unstable in air.\textsuperscript{13} Phosphorene, on the other hand, reacts very strongly with oxygen and water and needs to be sandwiched between layers of other materials if it is to last longer than a few hours.\textsuperscript{14} Interestingly, neither silicone nor phosphorene has a flat surface. Although TMDs are semiconducting and stable, they are much slower conductors of electrons than silicone or phosphorene.

Two-dimensional materials are desirable for sensing applications considering their high surface-to-volume ratio, wide range of chemical compositions, and the unique thickness-dependent properties.\textsuperscript{15–17} Graphene and graphene oxide have been widely utilized for chemical and biological sensing applications,\textsuperscript{18–23} and properties of molecular adsorbed graphene have been investigated in many areas.\textsuperscript{23,24} TMDs show extreme sensitivity to various gas molecules\textsuperscript{25–27} as well as layer dependence.\textsuperscript{28} High-performance TMDs are highly desirable for the development of nanosensors, piezotronics, and photo-piezotransistors.\textsuperscript{29} WS\textsubscript{2} exhibits high thermal stability and wide operation temperature range as lubricants; it shows the potential to outperform other 2D crystals in FETs applications due to its favorable band structure.\textsuperscript{30} Zhou et al. theoretically predict the possible gas sensing properties of single-layer WS\textsubscript{2}, considering the moderate interaction of the 2D materials with several gas species.\textsuperscript{31} Recently, WS\textsubscript{2} sensors in the form of thin films, multilayer photoresponsive FET, Pd-loaded nanosheets, metallic 1T-WS\textsubscript{2}, and Ag nanowire functionalized nanosheets have been tested as room temperature NH\textsubscript{3}, H\textsubscript{2}, NO\textsubscript{2}, and different vapor gas sensors.\textsuperscript{32–35} Among other 2D materials, single- or few-layer MoS\textsubscript{2} has been found to have high sensitivity in ppm to ppb levels for oxidizing agents such as NO\textsubscript{2} and reducing agents such as H\textsubscript{2} and NH\textsubscript{3}.\textsuperscript{36–39} However, only a limited number of reports are available on the gas sensing characteristics of WS\textsubscript{2}, especially in sub-ppm level detection. Furthermore, the recovery of WS\textsubscript{2} based gas sensors has been found to be poor at room temperature because of strong gas adsorption, limiting their practical applications.\textsuperscript{40} This study explores the layer-number-dependent adsorption properties of hydrazine, an even stronger reducing agent.

2. EXPERIMENTAL SECTION

In this work, WS\textsubscript{2} continuous films were fabricated by chemical vapor deposition which involves deposition of thin layers of WO\textsubscript{3} by thermal evaporation followed by sulfurization. Briefly, WO\textsubscript{3} films (1, 2, and 5 nm thick) are deposited on Si/SiO\textsubscript{2}
Figure 3. (a) Raman spectra of WS₂ samples with varying number of layers. (b) Frequency difference and peak intensity ratio between $E_{2g}^{1}(\Gamma)$ and $A_{1g}(\Gamma)$ peaks.

Figure 4. WS₂ based device fabrication scheme using a lithography free technique.

substrates by thermal evaporation of oxide powders (WO₃, Alfa Aesar, 99.99%), using a high-vacuum evaporator. After the oxide deposition, the substrates were loaded in a quartz reactor placed inside a tube furnace for a subsequent sulfurization at 700 °C for 30 min.

Figure 1 shows the SEM images of each WS₂ sample taken by an FEI Nova 600 field emission scanning electron microscope. Although this microscope can operate at accelerating voltages of up to 30 kV, the low acceleration voltage of 5 kV was used for the imaging of the WS₂ samples. This helped to enhance the surface probing capabilities and to increase the contrast difference between thin 2D layers of WS₂ and the substrate. As evident from Figure 1, the contrast difference between WS₂ regions and the substrate increases.
with the layer thickness. Furthermore, for the thickest layer (Figure 1c), the edges of the square WS$_2$ region are clearly defined.

Figure 2 shows the AFM images taken by an Asylum Research MFP-3D-Bio atomic force microscope. The AFM topography images were acquired in tapping mode in air using Si tips with a typical tip radius of 25 nm, tip length of ~240 µm, spring constant range 1.8–12.5 N/m, and frequency range 58–97 kHz (Asylum Research probe, Model ASYSELEC.01-R2). The AFM images in Figure 2 show the surface and height profile of each sample. The average thicknesses of samples were found to be 1.41, 2.46, and 9.19 nm with number of layers being 2, 3, and 12 layers, respectively.

WS$_2$ films were characterized by Raman spectroscopy with a spectral resolution better than 1 cm$^{-1}$. A Renishaw inVia spectrometer with a grating of 1800 lines/mm, a charge-coupled device (CCD) detector, and an effective resolution of 0.5 cm$^{-1}$ was used. We used 647 nm laser excitations, keeping the laser power under 0.2 mW at all times. Raman spectra show the in-plane phonon mode $E_{2g}^{1}(Γ)$ and the out-of-plane phonon mode $A_{1g}(Γ)$. The frequency difference and the intensity ratio between $E_{2g}^{1}(Γ)$ and $A_{1g}(Γ)$ peaks are key indications for determining the number of layers of WS$_2$ sample. For λ$_{exc}=647$ nm, the frequency difference between $E_{2g}^{1}(Γ)$ and $A_{1g}(Γ)$ modes, and the intensity ratio shown in Figure 3b seems to follow systematic changes with the number of layers.

Figure 4 shows the sequential processes of fabricating WS$_2$-based device. First, a square TEM grid WO$_3$ (∼1, 2, and 5 nm) was deposited by thermal evaporation followed by sulfurization. To define the electrical contacts on each sample, a customized straight TEM grid was carefully aligned so that WS$_2$ layers are exposed after gold deposition as masked by the bar.

Figure 5 shows the $I–V$ characteristics of WS$_2$ samples with varying thicknesses. The resistance of the thickest sample is several orders of magnitude lower than that of other two samples as expected. The $I–V$ for the two few-layer samples are also shown in an expanded scale as an inset. All three samples show linear ohmic behavior in the measured voltage range.

Figure 6 shows the resistive response of each sample when exposed to hydrazine at room temperature. The downward arrows in each figure indicate where hydrazine was introduced for the specified pressure while the upward arrows indicate when the hydrazine was pumped out. Figure 6a shows the time dependence of the resistance of the WS$_2$ sample with two layers during adsorption and desorption of hydrazine. When hydrazine was admitted to a pressure of 12 Torr, the resistance is seen to decrease from the initial value of ∼760 MΩ down to ∼460 MΩ. Upon pumping, the resistance recovers to the original value. Next, when hydrazine was admitted to a pressure of 13 Torr, the resistance dropped to a lower value of ∼160 MΩ and again recovers back upon pumping. Finally, admission of hydrazine to a pressure of 14 Torr causes the resistance to a much lower value of ∼30 MΩ yet recovers back to the initial value upon pumping. The decrease of resistance due to hydrazine exposure can be explained as due to the charge transfer process from the adsorbed N$_2$H$_4$ molecules to the WS$_2$. The full recovery of the resistance during the pumping suggests that for the two layer thick WS$_2$ hydrazine can be completely desorbed at room temperature. Such perfect recovery feature may come from the fact that WO$_3$ in the WS$_2$ has a larger radius, causing less bonding ability to hydrazine. Figure 6b shows the time dependence of the resistance of the WS$_2$ sample with 3–4 layers during adsorption and desorption of hydrazine. When hydrazine was admitted to a pressure of 12 Torr, the resistance is seen to decrease from the initial value of ∼8.2 MΩ down to ∼6 MΩ. Interestingly, the resistance value does not recover back to the initial value upon pumping and saturates at a lower value at ∼7.8 MΩ. Further exposure to hydrazine to higher pressure causes a higher decrease of resistance but only recovers to a lower value upon pumping. The partial recovery of the resistance during the pumping suggests that for 3–4 layer thick WS$_2$ hydrazine can only be partially desorbed at room temperature. This partial recovery behavior may come from the trapping of N$_2$H$_4$ molecules when the layer number increases. This is further confirmed by the result from multilayered WS$_2$ sample. Figure 6c shows completely different behavior of resistance when the multilayered WS$_2$ sample was exposed to hydrazine. When hydrazine was admitted to a pressure of 12 Torr, the resistance shows a sudden decrease as in the first two samples but then starts to increase. When pumping was introduced at that point, the resistance does not show any significant change. Next when hydrazine was introduced to a pressure of 13 Torr, again the
resistance shows an initial decrease followed by an eventual increase. Again, pumping has a minimal effect on the resistance value. A similar trend continues for the hydrazine exposure to a pressure of 14 Torr. The results suggest initial charge transfer from N₂H₄ to WS₂, causing the resistance to drop, but the trapping of N₂H₄ molecules within the multilayers of WS₂ causes charge redistribution, and possible chemical reactions may be responsible for the increase in resistance during the adsorption and complete irreversibility of resistance during desorption.

3. THEORETICAL CALCULATIONS

To explain the observed resistive responses during adsorption and desorption of hydrazine on WS₂ samples with varying number of layers, theoretical calculations and modeling were performed using the density functional theory (DFT) as implemented in the Vienna Ab-initio Simulation Package (VASP). Figure 7 shows the fully relaxed monolayer (Figure 7a), the double-layer (Figure 7b), and the multilayer WS₂ (Figure 7c) exposed to the N₂H₄ molecule. The shortest distances (~3.5 Å) of N₂H₄ to the WS₂ layers clearly show a physical adsorption nature. The corresponding adsorption energy per N₂H₄ gas molecule is listed in Table 1. They are in the range of −0.009 to −0.47 eV, confirming their physical adsorption. In particular, the adsorption energy in the case of the multilayer with optimized separation distance of 8 Å (~0.4713 eV) is almost 4 times lower than that in the case of the monolayer (~0.0977 eV). This indicates that it will need more energy to remove N₂H₄ molecules from multilayer WS₂ than from monolayer WS₂, consistent with our experimental observation that the change of the resistance during the pumping/degassing processes depends on the number of WS₂ layers (see Figure 6a,b). Furthermore, it is also found that the optimized separation distance between WS₂ layers after exposure to N₂H₄ molecule is 9.37 Å in the double layer, about 1.37 Å larger than that in the multilayers. In particular, if the multilayer WS₂ with the separation distance is close to that of bulk WS₂ (~6–7 Å), the N₂H₄ molecules strongly interact with WS₂ layers. They either form chemical bonds with S atoms or break W–S bonds, leading to a distortion in WS₂ layers and therefore a change in the electronic structures, which might explain our experimental observation for resistance changes in the sample with the thickness of 9.19 nm (see Figure 6c).

Figure 8 shows the calculated electronic band structures for the pristine WS₂ monolayer (Figure 8a), the monolayer WS₂ exposed to N₂H₄ gas molecules (Figure 8b), the double-layer WS₂ exposed to N₂H₄ (Figure 8c), and the multilayer WS₂ exposed to N₂H₄ (Figure 8d). Upon comparison to the pristine WS₂, there is an impurity state (indicated by the red line) associated with N₂H₄ molecules pinning into the band gap, independent of the number of WS₂ layers. Because this state is below the Fermi level, it clearly exhibits an n-type behavior, which can generate more electrons jumping to the empty conduction bands and reduce the resistance. These results demonstrate that the electronic band structures of WS₂ near the Fermi level are very sensitive to the explosion of N₂H₄ gas molecules, in agreement with the experimental observation that a reduduction of the resistance occurred after the WS₂ layers are exposed to N₂H₄ gas molecules (Figure 6).

4. CONCLUSIONS

In conclusion, few-layer and multilayer WS₂ devices fabricated using a simple lithography free technique were exposed to hydrazine at varying pressures, and their electrical resistances were monitored during adsorption and subsequent desorption. The WS₂ sample consisting of 2 layers showed a decrease of resistance upon exposure to hydrazine vapor and showed complete reversibility upon pumping. The WS₂ sample with 3–4 layers showed decrease of resistance during exposure but showed only partial recovery during desorption. In contrast, the multilayered (12 layers) WS₂ sample showed an initial decrease followed by a continued increase of the resistance upon exposure to hydrazine with little or no reversibility upon pumping. The charge transfer from N₂H₄ to WS₂ is believed to be responsible for the decrease of the resistance. Trapping of N₂H₄ molecules within the multilayers of WS₂ causing charge

<table>
<thead>
<tr>
<th>System</th>
<th>Eₘ (eV)</th>
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<tr>
<td>monolayer WS₂ exposed to N₂H₄ molecules</td>
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</tr>
<tr>
<td>double-layer WS₂ exposed to N₂H₄ molecules</td>
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</tr>
<tr>
<td>multilayer WS₂ exposed to N₂H₄ molecules</td>
<td>−0.4713</td>
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redistribution and possible chemical reactions may be responsible for the increase in resistance during the adsorption and complete irreversibility of resistance during desorption. The experimental results are further supported by the computational calculations performed by employing the density functional theory (DFT) framework, as implemented in the Vienna Ab-initio Simulation Package (VASP). It was found to exist an impurity state in the band structure of WS₂ associated with NH₃ molecules below the Fermi level exhibiting an n-type behavior. The adsorption energy per NH₃ gas molecule conforms the physical adsorption nature of NH₃ in WS₂, and the optimized separation distance between layers in multilayers is almost 4 times lower than that in the case of the monolayer, indicating it requires more energy to remove NH₃ molecules from multilayer WS₂ than from monolayer WS₂.

Figure 8. Band structures of the pristine 3 × 3 WS₂ monolayer (a), the monolayer WS₂ with NH₃ (b), the double-layer WS₂ with NH₃ (c), and multilayer with NH₃ (d). The red lines are the impurity states associated with the NH₃ molecule.

[Image of the figure showing band structures]

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Notes
The authors declare no competing financial interest.

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