Laser THz Emission Spectroscopy of Gas Adsorption-Desorption Dynamics in Tungsten Disulfide Nanosheets*

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Physically adsorbed gas molecules have dramatic effects on the inherent properties of 2D nanomaterials due to their atomic/molecular-level thinness. In this work, we applied laser THz emission spectroscopy to study the gas adsorption-desorption dynamics of tungsten disulfide (WS_2) nanosheets prepared by liquid phase exfoliation technique. We find that in low vacuum conditions, NIR irradiation promotes desorption of O_2 molecules from WS_2 nanosheets. Upon exposure to atmospheric air, results suggest slight photo-oxidation caused by NIR irradiation. Strong photo-oxidation by UV illumination is also confirmed, and we also observed subsequent O_2 desorption from WS_2 nanosheets by NIR irradiation when the UV illumination is turned off. These results are discussed using the Langmuir adsorption isotherm, which explains the variation of gas adsorption with the gas pressure.
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I. INTRODUCTION

Two-dimensional (2D) materials such as graphene [1, 2] and boron nitride [3] have recently garnered much research interests because of their very good potential for many applications. The prospects of 2D materials research have become even more promising with the discovery of another class of 2D materials [4] that are electronic complements of graphene and boron nitride, the so-called transition metal dichalcogenides (TMDs) in which tungsten disulfide (WS_2) is an example. WS_2 nanolayers/nanosheets have already been shown to be good candidates as light emitters [5, 6], FETs for light detection and gas sensing [7], and even as second harmonic generators [8]. However, because these materials are so thin, their inherent properties are easily affected by the boundary conditions such as the type of substrate used and most importantly by the adsorbed molecules on the surface [9]. Thus it is very important to elaborate on the gas adsorption-desorption dynamics of these materials. Our group has recently shown the potential of laser terahertz (THz) emission spectroscopy (LTES) for imaging adsorbed gas molecules in the surface of chemical vapor deposited - graphene [10]. In this paper, we have applied LTES for studying the gas adsorption-desorption dynamics of WS_2 nanosheets that are prepared using liquid phase exfoliation.

II. EXPERIMENTAL DETAILS

Bulk WS_2 powder obtained from Sigma Aldrich was used as starting material for the liquid phase exfoliation

method in producing the nanosheets. To remove impurities and to possibly improve the crystallinity of the starting material, the powder was annealed for 3 hours in an argon atmosphere at 300°C . The annealed powder was mixed with isopropyl alcohol to an initial concentration of ~ 10 mg/mL. The exfoliation was done (for around 4 hours) using a horn-tip ultrasonicator with power set at ~ 30 W. The vessel containing the mixture was immersed in an ice-water bath during ultrasonication to keep the solvent from evaporating. After the exfoliation process, the mixture was centrifuged at 1500 rpm for 45 minutes and then the supernatant was collected for characterization and sample preparation. Nanosheets dropped and dried on copper grids were prepared for TEM characterization while nanosheets dispersed in isopropyl alcohol was used for UV-Vis spectroscopy. The WS_2 nanosheets were then drop-casted on SI-InP substrate (heated to around $\sim 80^\circ\text{C}$) for Raman spectroscopy (excitation wavelength of 532 nm) and laser THz emission spectroscopy (LTES) measurements. For LTES, the sample was optically excited using ~ 100 fs NIR pulses of central photon energy of 1.55 eV and repetition rate of 80 MHz from a Ti:sapphire laser. The excitation beam was incident at $\sim 45^\circ$ with respect to the sample surface, with a power of 45 mW and a $(1/e)$ diameter of ~ 380 μm . The emitted THz waves were focused onto a dipole-shaped LT-GaAs photoconductive switch using a pair of off-axis parabolic mirrors. More detailed description of the LTES experimental set-up is discussed in our previous paper [10].

III. RESULTS AND DISCUSSIONS

A. TEM, UV-Vis Spectroscopy and Raman Spectroscopy

TEM images in Fig. 1 show the typical WS_2 nanosheets synthesized using the described liquid phase exfoliation technique. The lateral dimensions range from ~ 100 –2000 nm, and upon closer inspection of the edges of the

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FIG. 1. Typical TEM images of the WS₂ nanosheets prepared using liquid phase exfoliation. (A) and (B) are multilayer nanosheets while (C) and (D) are possible monolayer/bilayer nanosheets. All scale bars read 100 nm.

FIG. 2. UV-Vis absorbance spectrum of WS₂ nanosheets dispersed in isopropyl alcohol, showing the very prominent “A” exciton peak that is usually associated with the direct excitonic transition at the K point of the Brillouin zone, and also the indirect “B” excitonic transition peak.

nanosheets and of the contrast between each nanosheet and the TEM grid, we can see that mostly multilayer nanosheets (Fig. 1A and 1B) with substantial monolayer/bilayer nanosheets are produced (Fig. 1C and 1D). Figure 2 shows the UV-Vis absorbance of the WS₂ nanosheets dispersion. The well-pronounced peak at ~ 630 nm (~ 1.98 eV) is commonly assigned as the “A” exciton peak [5, 6] and is related to the direct excitonic transition at the K point of the Brillouin zone [6]. The peak associated to the indirect “B” excitonic transition (~ 525 nm, ~ 2.36 eV) can also be seen in the absorbance spectrum but is not as prominent as the “A” exciton peak. Figure 3A shows Raman spectroscopy measurements at different spots (as indicated in the optical image, Fig. 3B) in the WS₂/SI-InP surface. Since an excitation laser with $\lambda = 532$ nm was used for the Raman measurement, we observed features in the spectra (probably due to second-order Raman resonance) that are similar to the ones reported by A. Berkdemir *et al.* [11]. Using as basis their

Raman measurements of WS₂ nanolayers grown by sulfurization of tungsten trioxide, the Raman spectra from points 1 and 4 are most likely from monolayers while the spectra from points 2 and 3 are most likely from WS₂ multilayers. The Raman measurements suggest that even though the drop-casting method resulted in a non-uniform deposition of WS₂ nanosheets on the SI-InP substrate, there is no question about the sample coverage on the substrate surface which is an important concern for the laser THz emission spectroscopy measurements.

B. Laser THz emission Spectroscopy

We studied the gas adsorption-desorption dynamics of WS₂ nanosheets using laser THz emission spectroscopy (LTES). NIR pulse is used to optically excite the sample to emit THz radiation. To ensure that there are WS₂ nanosheets on the part of the substrate that is excited by the femtosecond laser, we used the largest beam diameter possible for the current LTES set-up. Figure 4A shows the THz emission from SI-InP substrate under atmospheric conditions (open chamber). Within the range of laser fluence used in the experiments, the dominant mechanism of THz emission from SI-InP is transient surge current, which is basically the movement of the photogenerated carriers under the influence of the surface depletion field in the substrate [12–14]. In addition, the polarization of the THz radiation is dependent on the direction of the surge current, whereas the amplitude is directly proportional to the time derivative of this surge current, $E_{\text{THz}}(t) \propto \frac{\partial J(t)}{\partial t}$. There is no change in time in the THz emission from SI-InP substrate which is similar to our previously reported results [10]. This implies that the direction as well as the rate of change of the surge current generated by the NIR excitation, remain almost constant over the measurement period. For the air-exposed WS₂-coated part however, we observed a reversal of the polarity of the THz waveforms (with respect to the emission from the bare substrate) as well as a gradual change in time as indicated by the arrows (Fig. 4B). Based on our previous results with CVD-graphene [10], we think that this change in polarization is caused not by the nanosheets themselves but by the adsorbed O₂ molecules in the WS₂ nanosheets as illustrated in Fig. 4C and 4D. Similar with SI-InP coated with CVD-graphene, we suspect that the band diagram for WS₂-coated SI-InP is almost the same as that of the bare substrate (Fig. 4C). But with the adsorption of O₂ molecules in the nanosheets (Fig. 4D), local electric dipoles at the SI-InP surface are formed which tend to increase the surface potential of the substrate. This causes the band to bend in the upward direction, which could cause the photogenerated carriers to accelerate in a direction opposite to that caused by the built-in surface potential alone. Depending on the degree of the upward bending (which is dependent on the amount of adsorbed O₂ molecules), the direction of the photogenerated current could change as well as the polarization of the THz radiation. The change in the THz emission from WS₂/SI-InP (indicated by the arrows in Fig. 4B) is attributed the increase in the adsorbed O₂ molecules which possibly means that slight photo-oxidation in WS₂ nanosheets is induced by NIR illumination. We then performed measurements

FIG. 3. Raman spectra (A) taken at different points indicated in the optical image (B) of the $\text{WS}_2/\text{SI-InP}$ sample. Spectrum from bare SI-InP is also included for comparison.

FIG. 4. THz emission from (A) bare SI-InP and from (B) $\text{WS}_2/\text{SI-InP}$ measured at 2-min intervals under continuous optical excitation by NIR laser pulses. Waveform from WS_2 -coated part shows changes with time (indicated by arrows) under NIR irradiation, probably due to O_2 adsorption in WS_2 nanosheets. (C) Proposed band diagram for pristine WS_2 nanosheets on SI-InP (figure adapted from [10]). The photogenerated carriers flow towards the substrate under the influence of the built-in surface potential. (D) Proposed band diagram for WS_2 nanosheets on SI-InP with adsorbed O_2 molecules (figure adapted from [10]). The induced local electric dipoles modify the band bending, accelerating the photogenerated carriers in a direction opposite to that caused by the built-in surface potential alone.

under vacuum conditions to further understand the O_2 adsorption-desorption dynamics in WS_2 nanosheets. Figure 5A shows the THz emission from $\text{WS}_2/\text{SI-InP}$ under vacuum conditions ($\sim 5 \times 10^{-1}$ Pa). The waveform is qualitatively the same to that of the emission from bare substrate (Fig. 4A), which supports the hypothesis that the WS_2 nanosheets themselves have no significant effect on the THz radiation from SI-InP. We also observed an increase in the peak at ~ 2.0 ps, which we attribute to the removal (by NIR irradiation) of the physically adsorbed O_2 molecules that were not removed by the vacuum pumping. Immediately after flooding the chamber with atmospheric air, the intensity of the peak at ~ 2.0 ps starts to decrease (Fig. 5B), which means that O_2 molecules are being adsorbed in the nanosheets right

after exposure to air. This is different from our previous results with CVD-graphene, where there was no noticeable change in the waveforms right after exposure to air/ O_2 under NIR irradiation [10]. Also, we did not observe saturation of the waveform within the measurement time frame which probably means that O_2 molecules are still being adsorbed. After exposing the sample to atmospheric air for more than 12 hours, we observed two peaks with opposite polarities (one at ~ 2.1 ps and one at ~ 2.6 ps in Fig. 5C) which means that substantial amount of O_2 molecules are already adsorbed in the WS_2 nanosheets. This reverses the original direction of the surge current and consequently the THz radiation. Under continuous NIR irradiation, the peaks changed in the direction indicated by the arrows which indicates further

FIG. 5. THz emission from WS₂/SI-InP measured at 2-min intervals at different conditions. (A) At $\sim 5 \times 10^{-1}$ Pa, increase in intensity of the peak at ~ 2.0 ps due to removal of adsorbed O₂ molecules from WS₂ nanosheets by NIR irradiation. (B) Right after exposure to atmospheric air, the ~ 2.0 ps peak decreases in intensity due to adsorption of O₂ molecules. (C) After more than 12 hours exposure to air, more O₂ molecules are adsorbed (indicated by the two peaks with opposite polarities, the ~ 2.1 ps peak and the ~ 2.6 ps peak). These two peaks changes in the direction indicated by the arrows which may be due to photo-oxidation induced by NIR irradiation. (D) Measurements in air, showing the fast photo-oxidation by UV illumination (blue arrows) and the subsequent O₂ desorption from WS₂ nanosheets by NIR irradiation when the UV illumination is turned off.

adsorption of O₂ molecules in the WS₂ nanosheets. The waveforms observed in Fig. 5B and 5C seem to indicate photo-oxidation of WS₂ nanosheets by NIR irradiation. However, the present data are still not enough to conclusively support this hypothesis. We also exposed the samples to UV ($\lambda = 365$ nm, ~ 400 mW power and ~ 8 mm diameter) light because the previous data for CVD-graphene indicates strong photo-oxidation by UV illumination [10]. Figure 5D shows the THz waveform with UV exposure. Initially, there are no significant changes in the waveforms under NIR irradiation, which indicates that the amount of O₂ molecules adsorbed has already reached saturation level. However with UV exposure, there is abrupt and significant change in the waveforms (in the direction indicated by the blue arrows) emitted from WS₂/SI-InP which is due to fast photo-oxidation of WS₂ by UV irradiation. When the UV illumination is turned off, the waveforms (under NIR irradiation) seem to go back to the initial form (indicated by the red arrows) which means that the adsorbed O₂ molecules (due to UV exposure) are slowly being released back to the surrounding air. These results can be understood using the Langmuir adsorption isotherm, which explains the variation of adsorption with pressure [15]. According to this theory, dynamic equilibrium exists between the adsorbed gaseous oxygen and the free gaseous oxygen (in air) according to the equation:

where O_{2(g)} is the free gaseous oxygen, S* is the ad-

sorption site at the surface and O₂ · S is the adsorbed oxygen molecule at the surface. The rate at which desorption occurs is mainly dependent on the number of sites on the surface that are covered with the gas molecules (θ). Specifically, if θ is large, the rate of desorption is expected to be fast. On the other hand, the rate at which the forward reaction (gas adsorption) progresses is dependent upon two factors: the fraction of adsorption sites available on the surface ($1 - \theta$) and the pressure (P). With many adsorption sites available and higher gas pressure, adsorption rate is also fast. We have previously shown that NIR irradiation can remove adsorbed O₂ molecules from the surface of CVD-graphene [10], and we also observed the same effect in vacuum conditions in our current experiments (Fig. 5A). When atmospheric air is introduced into the chamber, the gas pressure increased which makes the forward reaction (adsorption) in Eq. (1) the favorable process (Fig. 5B and 5C). Also, the portion of the surface without adsorbed molecules ($1 - \theta$) is initially large because the sample has been kept in vacuum, further favoring the adsorption process. The noticeable change in the waveforms right after exposing the WS₂ nanosheets to air means a faster rate of adsorption in the case of WS₂ nanosheets as compared to CVD-graphene. This can be explained by the fact that the number of adsorption sites (S*) for WS₂ nanosheets is larger due to its surface morphology. The non-changing waveforms before UV exposure (Fig. 5D) means that equilibrium has been reached. Upon UV illumination, fast photo-oxidation occurred making θ (portion of the surface with adsorbed molecules) larger. The large value of θ and the fact that NIR irradiation also removes O₂ molecules, make the rate of desorption faster (favoring the backward reaction in

Eq. (1)) when the UV illumination is turned off (red arrows in Fig. 5D).

IV. CONCLUSIONS

We have applied laser THz emission spectroscopy to study the gas adsorption-desorption dynamics of WS₂ nanosheets deposited on SI-InP substrate. Different from our previous results with CVD-graphene, we find that the THz emission from WS₂-coated SI-InP changes noticeably with NIR irradiation under atmospheric conditions. This change indicates adsorption of O₂ molecules, which imply that NIR irradiation induces photo-oxidation in WS₂ nanosheets. However, more experimental evidence is needed to support this hypothesis. We have also confirmed strong photo-oxidation of WS₂ nanosheets

upon UV illumination. Furthermore, the results from the LTES measurements in vacuum and atmospheric air conditions indicate that O₂ gas adsorption-desorption dynamics in WS₂ nanosheets is consistent with the Langmuir adsorption isotherm. These findings are very important when considering WS₂ nanosheets for device applications since their properties are highly affected by the adsorbed molecules.

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