Electronic properties of hybrid WS$_2$/MoS$_2$ multilayer on flexible PET

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Abstract

Two-dimensional (2D) layered materials transition metal dichalcogenide compound (TMDC), which stack-together and form van der Waals heterostructures, have created interesting phenomena due to their interlayer interactions and their great potential for atom-scale devices. Various electrical properties have been investigated. The presence of vacancies and their related charge trappings have been reported to affect the electrical properties. In this study, we investigate the electrical properties of hybrid WS$_2$/MoS$_2$ multilayer film deposited on polyethylene terephthalate (PET). The hybrid morphology and signatures are confirmed by the scanning electron microscope image and Raman shift spectra, respectively. We observed a semiconductor like behaviour as well as the large hysteresis which indicates the vacancies inducing charge trappings. This characteristics is different with the electronic characteristics of WS$_2$ and MoS$_2$ multilayer which tend to exhibit insulating behaviours and small hysteresis. This study shows how hybrid dichalcogenide WS$_2$/MoS$_2$ multilayer might create new features for future electronic devices.

1. Introduction

The van der Waals interaction along c axis of TMDC provides the possibilities to create thin transparent flexible films which have different electrical and optical properties from the thick ones. The number of layers affect the electronic band structure [1–4]. Various studies reported the intriguing properties such as tunability of photoluminescence by strain [5, 6] and circularly polarized light [7, 8]. Those phenomena are suggested to have application in strain engineering devices [9, 10], optoelectronics [11, 12], and pseudo spin valleytronics [13, 14]. The possibility to create two dimensional materials with strong mechanical properties also trigger suggestions the exploration of TMDC deposited on flexible substrate to create flexible electronics [15, 16].

In addition to the study of the excellent pure TMDC properties, tremendous efforts have been also dedicated to investigate the properties of TMDC hybrids [17, 18] and heterostructure [19, 20]. The TMDC combination affects the electronic bandgap. For example, the WS$_2$/MoS$_2$ heterostructure has a bandgap of 1.42 eV [21], whereas the WS$_2$ and MoS$_2$ monolayer have bandgaps of 2.1 eV and 1.8 eV, respectively [1]. Lateral WS$_2$/MoS$_2$ heterostructures exhibits an intrinsic p-n junctions characteristics and a photovoltaic effect with an open-circuit voltage (Voc) of 0.15 V and a short-circuit current (Isc) of 5.2 pA [22].

The presence of hysteresis in I–V curve characteristics of hybrid TMDC has revealed various scenarios related to the presence of sulphur atom vacancies or defects in WS$_2$ and MoS$_2$ [23, 24]. The adsorbed oxygen and moisture or fabrication residues on the sample surface have been also discussed [25, 26]. The ohmic characteristics, the space charge limited current, and the trap filled limited current are suggested to be dominant factors influencing the hysteresis [27]. Despite its potential for memory devices, hysteresis influences the stability of the devices and required further investigations.

This study is aimed to explore the electronic characteristics of hybrid WS$_2$/MoS$_2$ multilayer on flexible substrate. We modified the thickness of WS$_2$ and MoS$_2$ layer by using liquid exfoliation method. A thin multilayer hybrid film is fabricated by dropping the WS$_2$ and MoS$_2$ supernatant on flexible Polyethylene terephthalate (PET) substrate. A semiconducting characteristics is shown by the I–V curve characterization. Furthermore, we elucidate three different hysteresis characteristics and discuss the possible reason behind them.
2. Experimental methods

The 1 mg ml$^{-1}$ WS$_2$ and 1 mg ml$^{-1}$ MoS$_2$ solutions were modified by liquid-phase exfoliation (LPE) [28, 29]. Detail of exfoliation process is explained in supplementary information (available online at stacks.iop.org/MRX/8/016409/mmedia). The supernatant was subsequently deposited by drop-casting on the Polyethylene

Figure 1. The typical surface morphology of (a) WS$_2$, (b) MoS$_2$, and (c) hybrid WS$_2$/MoS$_2$ multilayer.
terephthalate (PET) substrate. The sample was dried using a commercial oven (oxone OX 858) for 1–3 h at a temperature of 70 °C to remove the remaining organic solvents. The surface morphology of the hybrid WS2/MoS2 thin film was characterized using scanning electron microscopy (SEM SU3500). To confirm the presence of WS2 and MoS2, we conducted the energy dispersive x-ray spectroscopy (EDS) measurement. Furthermore, the phonon vibrations were also investigated using Raman spectroscopy measurement (XploRA ONE Horiba) with a laser spot size of ∼1 μm and a laser excitation of 532 nm. Measurement of the electrical properties was conducted using 2400 Keithley in two probes configuration. Silver paste were used as electrodes on both sides of the sample.

3. Results and discussion

Figure 1 shows the typical surface morphology of (a) WS2, (b) MoS2, and (c) hybrid WS2/MoS2 multilayers, respectively. Clear well separated micro-size features are observed for WS2 sample. The individual flakes are stacked vertically on top of each other. The MoS2 flakes are observed to have smaller micro-size and vertically stacked forming a dense multilayer. Based on the characteristics of WS2 and MoS2 morphology, we interpret that the hybrid WS2/MoS2 multilayer morphology shows various micro-size WS2 flakes on top of MoS2 background. The EDS scanning confirmed the presence of W and Mo atoms in hybrid sample.

Raman shifts of WS2, MoS2, and hybrid WS2/MoS2 multilayers are presented in figures 2(a)–(c), respectively. Two characteristic vibrational modes of WS2 sample were observed at 353 (E_{2g} (Γ)) and 418.6 cm⁻¹ (A_{1g} (Γ)) (figure 2(a)). The modes have 65.6 cm⁻¹ difference indicating the formation of multilayer [30]. Figure 2(b) presents two characteristic modes of the MoS2 observed at 379.9 and 404.4 cm⁻¹, which correspond to the vibration modes of E_{2g} (Γ) and A_{1g} (Γ) [30, 31]. The 24.5 cm⁻¹ difference also indicates that the MoS2 sample is multilayer rather than bulk [20, 30]. Figure 2(c) shows that hybrid WS2/MoS2 multilayer consists of the summation of characteristic modes belonging to the WS2 and MoS2. The E_{2g} (Γ) and A_{1g} (Γ) modes of WS2 experience a blue shift and appear at 353.8 and 419.9 cm⁻¹, similar to the ones reported in nanocomposite WS2 [20]. The modes narrowing was also observed.
which might due to the three dimensional (3D) nature of hybrid multilayer. Meanwhile, the $E_{2g}^1(\Gamma)$ and $A_{1g}(\Gamma)$ of MoS$_2$ appear as broad peaks at 374 and 406 cm$^{-1}$. They undergo redshift and peak broadening compared to ones observed in pure MoS$_2$. These phenomena can be caused by interlayer interactions, charge transfers, and changes in the interface lattice that occur in the hybrid WS$_2$/MoS$_2$\cite{32, 33}.

The I–V curve characteristics of WS$_2$, MoS$_2$, and hybrid WS$_2$/MoS$_2$ are presented in figures 3(a)–(c), respectively. The red dots and black squares were observed when the voltages were varied from $-5$ to $5$ V and

Figure 3. The I–V curve characteristics of (a) WS$_2$, (b) MoS$_2$, and (c) hybrid WS$_2$/MoS$_2$. Red and black arrows indicate the direction of voltage variation. Black solid lines at (c) are guide for eyes to show the slope variations.
vice versa, as indicating by red and black arrows, respectively. The WS₂ and MoS₂ exhibit insulating behavior whereas the hybrid WS₂/MoS₂ tends to have semiconductor characteristics. Our result is different with the one reported by Choudhary et al which shows rectifying p–n junction behavior in heterostructure MoS₂/WS₂ [20]. The mixed WS₂/MoS₂ flakes could be the reason behind the non rectifying behavior of our sample.

We also observed a clear hysteresis when the voltage polarity was varied. The suspected intrinsic factors behind the hysteresis were the presence of sulphur atom vacancies or defects in WS₂ and MoS₂ [23, 24]. Besides, there might be also extrinsic factors such as adsorbed oxygen and moisture or fabrication residues on the sample surface [25, 26]. Both intrinsic and extrinsic factors can cause charge trapings. Following the discussion at [27], the current characteristics at our hybrid sample can be divided into three regions which are (1) the linear ohmic, (2) the large slope nonlinear, and (3) the small slope nonlinear characteristic. The linear ohmic behaviour indicates that the thermally generated carriers are dominating the system below 2 V. For applied voltage larger than 2 V, the injected carriers are more dominant. The large and small slopes at nonlinear regions might due to abrupt and gradual distribution of injected carriers in the sample, respectively. The wider hysteresis at negative voltage polarity indicates the positive trapped charges are more dominant influencing the electronic characteristics. We should note that smaller sample is more sensitive to any fluctuation or disturbance in electronic system such as trap states from edge defect or mismatched layer stacking which affects charge transport. This sensitivity might generate more visible hysteresis in I–V curve which was not observed in previous study [20].

4. Conclusions

We conclude that the hybrid WS₂/MoS₂ multilayer thin film deposited on PET flexible substrate exhibits semiconducting electronic properties. It is different from the MoS₂ and WS₂ ones which tend to have insulating properties. The hysteresis are also observed more clearly in the hybrid sample. Three different characteristics of I–V curve suggest various charge carrier distributions mechanism. The wider hysteresis curve at negative voltage polarity indicates that positive trapped charges are more dominant in the sample. Further investigation to control the hysteresis will be useful for memory application.

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