Optical and electrical characterization of WS₂ multilayer on flexible PET substrate

I P Handayani, A M Utama, M Rosi, A M Rafli and A Setiawan

Engineering Physics, School of Electrical Engineering, Telkom University, Bandung, Indonesia
E-mail: iphandayani@telkomuniversity.ac.id

Keywords: WS₂, multilayer, optical properties, Raman shift, photoluminescence spectra, electrical properties, flexible substrate

1. Introduction

The flexible electronics have been widely applied in many fields [1]. These platform developments have involved various thin film material studies such as candidate materials for flexible photovoltaic solar cells [2, 3] and flexible transparent electrode [4]. The need for nano scale flexible semiconductor-based devices has also triggered tremendous studies on transition metal dichalcogenide compounds (TMDCs). A lot of TMDCs flexible devices have been reported such as flexible and transparent MoS₂ field effect transistors [5], monolayer WS₂ field transistor on thin flexible polyimide [6], and wearable sensors [7]. It is different with graphene, which is gapless, the electronic band gap of TMDCs is dependent on the number of layers [8, 9]. A transition from indirect to direct band gap is observed when the TMDC layer changes from multi-layer to single layer. Due to the intra layer covalent bond and inter layer van der Waals bond, the TMDC can be easily exfoliated along c axis to create single layer with nano scale thickness [10].

Among the TMDC, WS₂ attracts a lot interest due to its tendency to have n- or p- type semiconductor characteristics. The WS₂ has been combined with MoS₂ to create MoS₂/WS₂ heterostructure with p-n diode characteristics [11]. Furthermore, 1T metallic and 2-H semiconducting phase can be obtained by different type of exfoliation process [12]. The 2-H WS₂ bulk is indirect semiconductor with 1.3 eV band gap while the monolayer one has 2.02 eV direct band gap [13, 14]. Each W atom is bounded with three S atoms and forms hexagonal structure. The W and S composition is reported to be sensitive to high temperature above 100 °C [15]. Possessing a charge mobility of 300 cm² V⁻¹ s⁻¹ [16], a Young’s modulus of 272 GPa [17], as well as a stability under cyclic bending [18], the layered WS₂ thin film is proposed to be a good candidate for flexible electronics. The optical and electronic properties of WS₂ is also in flexile transparent electrode

© 2021 The Author(s). Published by IOP Publishing Ltd
increase the WS$_2$ work function. The NO$_2$, O$_2$, and NO molecules also change the transmission spectrum and dielectric constant.

Modification of the layer number to produce large scale monolayer WS$_2$ was reported previously [20, 21]. The liquid phase exfoliation has been reported to be the simple exfoliation method which can produce reasonable nano scale thickness as well as the quite large quantity of single layer [22–24]. In this study, the optical and electrical properties of WS$_2$ multilayer prepared by liquid phase exfoliation method are investigated. We observed a blue shift of absorption peak when a white light is transmitted through exfoliated solution. This is an indication that the band gap is changed when the WS$_2$ is exfoliated to a thinner layer. Furthermore, the SEM/EDS measurement was also confirmed the presence of WS$_2$ flakes in the sample even though the concentration is quite low. The WS$_2$ multilayer characteristics is further confirmed by Raman and photoluminescence (PL) spectroscopy. Various Raman shifts and PL spectra are observed and confirmed previous study in single layer, multilayer, as well as defect and strain affected WS$_2$. A stable current in the order of tens nA was observed when an applied voltage is varied from $-10$ to $10$ V. This current did not change significantly when mechanical stretching is applied up to 55%. This study features the richness of multilayer WS$_2$ properties which is expected to open possibility of creating a TMDC based nano scale flexible electronics.

2. Experimental methods

The sample preparation is begun by mixing 1 mg/ml WS2 in N-Methyl-2-pyrrolidone (NMP) with 2 mg NaOH intercalator. Afterward, the solution was sonicated using Elma Ultrasonic Cleaner S10. After 60 h sonication process, the solution is centrifuged for 30 min in 2500 rpm to separate the WS$_2$ supernatant with the heavier sediment. The solution is further checked optically by transmitting white light from HL2000 halogen lamp. The transmitted light is analysed using AvaSpec-ULS2048CL-EVO spectrometer to study the difference between supernatant and non-exfoliated WS$_2$ solutions. In order to study the electronic properties and the effect of mechanical stretching, the WS$_2$ supernatant is subsequently drop casted on Polyethylene terephthalate (PET). After 3 h drying process in 70 °C commercial oven, silver paste electrodes were applied to both side of the sample. The morphology and the composition of the dried supernatant sample on top of ITO/PET is investigated using Scanning Electron Microscope/Energy Dispersive x-ray Spectroscopy (SEM/EDS) SU3500. Moreover, Raman modes and photoluminescence (PL) spectra were observed using LabRAM HR Evolution.
Horiba spectrometer with 532 nm laser excitation. The characteristic I-V curve were subsequently observed using Keithley 2400. The mechanical stretching effect is tested using home-made mechanical stretching device [25].

3. Results and discussion

Figure 1 shows a typical evolution of WS₂ solution during sonication process. The solution changed from (a) black into (b) reddish black after sonication. The centrifugation process separated the supernatant from the heavier sediment (figure 1 (c)). Finally, the reddish-brown supernatant was obtained after the sediment removal (figure 1 (d)).

In order to check the optical properties, a white light coming from halogen lamp was transmitted through the WS₂ supernatant, non-exfoliated WS₂ solution, and NMP. The absorption spectra of supernatant and non-exfoliated WS₂ solution is presented in figure 1(e). Detail of transmission spectra extraction into absorption spectra is given in supplementary information (available online at stacks.iop.org/MRX/8/026405/mmedia). We interpreted the spectra in figure 1(e) as the absorption (negative value) and emission (positive value) spectra. The WS₂ non-exfoliated solution has two absorption valleys at 564 nm and 663 nm as well as a peak of broad emission at 885 nm. These absorption valleys and emission peak are blue shifted to 528 nm, 641 nm, and 747 nm, respectively. The absorption valleys at 528 nm and 641 nm are close to A and B exciton energies of WS₂, respectively, which experience blue shifts when the number of layers is changed [26] as indicated by * and ** in figure 1(e).

The morphology of WS₂ supernatant thin film on PET substrate is displayed in figure 2(a). Different shape of WS₂ flakes in the order of micrometre present and are randomly stacked in the sample. From the EDS scanning measurement, we observed the percentage of W and S elements are only about 3 and 4%, respectively. It was found that the element of C, N, Na, and O from the NMP solvent and the NaOH intercalator contribution were
Figure 3. (a) The Raman shift and (b) the PL spectra of WS$_2$ multilayer. Various colour peaks are fits of the Lorentzian (for Raman peaks) and Gaussian (for PL spectra) functions.

Figure 4. The I-V characteristics of multilayer WS$_2$ deposited on PET and SiO$_2$ substrate.
still dominating the sample even though the sample was dried up to 70°C for 3 h. Currently it is not possible to dried up at higher temperature and longer time due to the softening of the PET substrate.

The WS₂ characteristics was confirmed using Raman and PL spectroscopy. The observed Raman shifts are presented in figure 3 (a). The Raman shifts at 175, 232, 269, 298, 323, 351, 355, and 421 cm⁻¹ are match to LA(M), A₁g(M)-LA(M), 2LA(M)-3E₂g(M), E₁g(M), 2LA(M), E₂g(Γ), and A₁g(Γ) modes of previously reported WS₂ Raman spectra, respectively [27]. The 128 and 280 cm⁻¹ are not currently assigned. Following previous assignments, the two modes cannot be attributed to NaOH intercalator which the active Raman modes are above 3000 cm⁻¹ [28]. Even though each NMP solvent and PET substrate possess Raman mode around 200 cm⁻¹, that mode was not assigned as the main Raman characteristics of NMP solvent [29] and PET substrate [30]. Hence, we do not specifically assign the 128 and 280 cm⁻¹ as the contribution of either NaOH, NMP, or PET. Furthermore, the position of 2LA(M), E₂g(Γ) and A₁g(Γ) modes suggests that our WS₂ film is a multilayer [27].

The PL spectra are displayed at figure 3 (b) showing broaden peak from 600–700 nm. Three main Gaussian functions are well fitted to the experimental data which indicates that the broad PL spectrum consists of three main spectra at 640, 630, and 675 nm. Four narrow Gaussian functions should also be added to fit narrow peaks at 629, 631, 632, and 635 nm. Following the interpretation on [31], the PL at 640 nm is attributed to A exciton while the 660 nm PL is due to the defect-bound neutral exciton (XD) which the intensity increases with the increasing of the defect concentration. The 675 nm was previously assigned as local strain activated indirect PL (I) [32]. Both defect induced small-sized nano crystallites [31] and local strain [32] were previously reported to broaden the PL spectra.
The electrical characteristics of multilayer WS$_2$ is presented in figure 4 showing the insulating behaviour of multilayer WS$_2$ when deposited on top of PET substrate. This is in contrast with the one deposited on top of SiO$_2$ substrate which tends to exhibit semiconducting characteristics. The current value in PET substrate is also lower about two order of magnitude than in SiO$_2$ substrate. To understand the difference of WS$_2$ current on SiO$_2$ and PET substrates, we adopt information in [33] which explained that the dielectric screening, the lattice disorder, and charge trappings influence the charge transport on WS$_2$ thin film-substrate interface. In our case, the crystalline SiO$_2$ and PET substrates most likely induce different electronic environments to WS$_2$ multilayer interface. The dielectric screening induced by PET substrate might create larger WS$_2$ exciton binding energy which together with the lattice disorder as well as charge trapping subsequently create lower current. Similar case has been reported in [34–36] which studied the different effect of SiO$_2$ and Boron Nitride substrates to the electronic properties of TMDCs.

Regarding the semiconducting behaviour on SiO$_2$ and ohmic characteristics on PET substrates, we consider the different Fermi energy of SiO$_2$ and PET substrates which might create different characteristics of charge carrier in the framework of variable range hopping model [16, 35]. We should also note several studies in thin film [37–39] reporting the effect of substrate roughness, resistivity, and strain to the electronic characteristics of the thin films.

Figure 5 displays the I-V characteristics of multilayer WS$_2$ on PET substrate under influence of mechanical strain. When the applied voltages were varied from ~10 to 10 V, the multilayer WS$_2$ has a tens nA current while the non-exfoliated one exhibits about 10 μA currents. The multilayer WS$_2$ was observed to be robust again the mechanical stretching. There was no significant change of current when the mechanical stretching was applied up to 55% strain. It is different with the non-exfoliated one which was very sensitive to mechanical stretching. The current decrease from 18 μA (without strain) to 9 μA when 50% strain was applied. Adopting the explanation in [40], we suspect various nano or microscale cracks might present in non-exfoliated thin film and subsequently decrease the current. The cracks apparently can be eliminated in multilayer WS$_2$ and the currents are not significantly affected by the applied strain up to 55%.

4. Conclusion

The optical properties of multilayer WS$_2$, which is modified by liquid phase exfoliation method and deposited on top of flexible PET substrate, are abundant and signify the contribution of W-S vibrations, A-exciton, defect bound neutral exciton, defect induced nano crystallites, as well as strain activated indirect transition. Furthermore, the electrical characterization evidences that the multilayer film is robust against the mechanical strain up to 55% strain. This finding is expected to give valuable information for future application of WS$_2$ multilayer on defect and strain engineering devices as well as on opto- and flexible electronics. Further investigation on cyclic strain measurement as well as light induced electronic properties will enrich the information.

Acknowledgments

This work is financially supported by Direktorat Riset dan Pengabdian Masyarakat Direktorat Jendral Pendidikan Tinggi (DRPM Kemenristek/BRIN) No. 7/E/KPT/2019; 226/SP2H/LT/DRPM/2019; 2879/L4/PP/12019/062/PNLT2/PPM/12019.

ORCID iDs

I P Handayani  Ⓡ  https://orcid.org/0000-0002-7949-225X

References

[1] Nathan A et al 2012 Flexible electronics: the next ubiquitous platform Proc. IEEE 100
[2] Zhao B, He Z, Cheng X, Qin D, Yun M, Wang M, Huang X, Wu J, Wu H and Cao Y 2014 Flexible polymer solar cells with power conversion efficiency of 8.7% Mater. Chem. C 2 5077–82
[3] Rodriguez-Rosales K et al 2017 Nanocrystalline-CdS thin films grown on flexible PET-substrates by chemical bath deposition Mater. Res. Express 4 075904
[4] Rowell M W, Topinka M A, McGeheea M D, Prall H J, Dennler G, Sariciftci N S, Hu L and Gruner G 2006 Organic solar cells with carbon nanotube network electrodes Appl. Phys. Lett. 88 233506
[5] Lee G-H et al 2013 Flexible and transparent MoS$_2$ field effect transistors on hexagonal boron nitride–graphene heterostructures ACS Nano 7 7931–6
[6] Gong Y, Carozo V, Li H, Terrones M and Jackson T N 2016 High flex cycle testing of CVD monolayer WS2 TFTs on thin flexible polyimide 2D Mater. 3 021008

[7] Donarelli M and Ottaviano L 2018 2D Materials for gas sensing applications: a review on graphene oxide, MoS2, WS2, and phosphorene Sensors 2018 18 3638

[8] Zhao W, Ghorannevis Z, Chu L, Toh M, Kloc C, Tan P-H and Eda G 2013 Evolution of electronic structure in atomically thin sheets of WS2 and WSe2 ACS Nano 7 7971–79

[9] Roldán R, Silva-Guillen J A, Pilar López-Sancho M, Guainea F, Cappelluti E and Ordejón P 2014 Electronic properties of single-layer and multilayer transition metal dichalcogenides MX2 (M = Mo, W and X = S, Se) Ann. Phys. 526 347–57

[10] Choi W, Choudhary N, Hee Han G, Park I, Akinci D and Hee Lee Y 2017 Recent development of two-dimensional transition metal dichalcogenides and their applications Mater. Today 20 117

[11] Chen K, Wan X, Wen J, Xie W, Kang Z, Zeng X, Chen H and Xu J-B 2015 Electronic properties of MoS2–WS2 heterostructures synthesized with two-step lateral epitaxial strategy ACS Nano 9 8686–78

[12] Chou S S et al 2015 Controlling the metal to semiconductor transition of MoS2 and WS2 in solution J. Am. Chem. Soc. 137 1742–5

[13] Kuc A, Zibouche N and Heine 2011 Influence of quantum confinement on the electronic structure of the transition metal sulfide Phys. Rev. B 83 245213

[14] Laura Elias A et al 2013 Controlled synthesis and transfer of large-area WS2 sheets: from single layer to few layers ACS Nano 7 5235–42

[15] Perrozzia F, Emamjomeh S M, Paolucci V, Taglieri G, Ottaviano L and Cantalini C 2017 Thermal stability of WS2 flakes and gas sensing properties of WS2/WO3 composite to H2, NH3, and NO2 Sensors Actuators B 243 812–22 2016

[16] Ovchinnikov D, Allain A, Huang Y-S, Dumencio D and Kis A 2014 Liquid-phas exfoliation of graphite towards solubilized graphenes Small 5 1841–5

[17] O’Neill A, Khan U and Coleman J N 2012 Preparation of high concentration dispersions of exfoliated MoS2 with increased flake size Chem. Mater. 24 2414–21

[18] Nguyen P F, Carey B J, Daeneke T, Zhen Ou J, Latham K, Zhuiykov S and Kalantar-Zadeh K 2014 Chemistry of Materials Investigation of two-solvent grinding-assisted liquid phase exfoliation of layered MoS2, MoS2, and WSe2 ACS Nano 2017 57 2753–9

[19] Bermal M M, Álvarez L, Giovaneli E, Arnáiz A, Ruiz-González L, Casado S, Granados D, Piaggio A M, Castellanos-Gomez A and Pérez E M 2016 Luminescent transition metal dichalcogenide nanosheets through one-step liquid phase exfoliation 2D Mater. 3 035014

[20] Kristena C S, Handayani I P and Chandra I 2019 Rancang Bangun Alat Uji Tarik Untuk Karakterisasi Sifat Mekanik Dan Listrik Pada Material Konduktif Fleksibel e-Processing of Engineering 6 1275

[21] Frey G L, Eliani S, Homynier M, Feldman Y and Tennen R 1998 Optical–absorption spectra of inorganic fullerene-like MS2 (M = Mo, W) Phys. Rev. B 57 4666

[22] Berkdemir A et al Identification of individual and few layers of WS2 using Raman spectroscopy Sci. Rep. 3 1755

[23] Li F, Li Z, Wang S, Li S, Men Z, Ouyang S and Sun C 2017 Structure of water molecules from Raman measurements of different concentrations of NaOH solutions Spectrochim. Acta, Part A 183 425–30

[24] Ogilvie S P, Large M J, Fratta G, Meloni M, Canton-Vitoria R, Tagmatarchis N, Massuyeau F, Ewels C P, King A A K and Dalton A B 2017 Considerations for spectroscopy of liquid-exfoliated 2D materials: emerging photoluminescence of Nmethyl-2-pyrrolidone Scientific Report 7 16706

[25] Suhbani Z, Amin M A, Naidu R, Megharaj M and Fang C 2019 Identification and visualisation of microplastics by Raman mapping Anal. Chim. Acta 1077 191–9

[26] Shi W, Lin M-L, Tan Q-H, Qiao X-F, Zhang J and Tan P-H 2016 Raman and photoluminescence spectra of two-dimensional nanocrystallites of monolayer WS2 and WSe2 2D Mater. 3 035016

[27] Cong C, Shang J, Wang Y and Yu T 2017 Adv. Optical Mater. 6 1700767

[28] Rold an R, Silva-Guill en J A, Pilar Lopes-Sancho M, Guainea F, Cappelluti E and Ordej on P 2014 Electronic properties of single-layer and multilayer transition metal dichalcogenides MX2 (M = Mo, W and X = S, Se) Ann. Phys. (Berlin) 526 347–57

[29] Ghatak S, Pal N and Ghosh A 2011 Nature of electronic states in atomically thin MoS2 field-effect transistors ACS Nano 5 7707–12

[30] Lee G-H, Yu Y-J, Lee C, Dean C, Shepherd K L, Kim P and Hone J 2011 Electron tunneling through atomically flat and ultrathin hexagonal boron nitride Appl. Phys. Lett. 99 243114

[31] Withers F, Bointon T H, Hudson D C, Cracium M F and Russo S 2014 Electron transport of WS2 transistors in a hexagonal boron nitride dielectric environment Sci. Rep. 4 4967

[32] Thakur M K et al 2016 Effect of substrate on the structural and electrical properties of Mo thin films Adv. Mater. Lett. 7 525–32

[33] Shui Y et al 2012 Substrate effect on the resistive switching in BiFeO3 thin films J. Appl. Phys. 111 07D906

[34] Jang S Y, Nakagawa N, Moon S J, Susaki T, Kim K W, Lee Y S, Hwang H Y and Myung-Whune K 2009 Effect of substrate strain on lattice structure, electrical resistivity, and optical conductivity of Nd0.5Sr0.5MnO3 thin films grown on SrTiO3 Solid State Commun. 149 1760–4

[35] Benson E E, Ha M-A, Gregg B A, van de Lagemaat J, Neale N R and Svedruzic D 2019 Dynamic tuning of a thin film electrocatalyst by tensile strain Sci. Rep. 9 15906