Optical Engineering

OpticalEngineering.SPIEDigitalLibrary.org

WS₂ film on a SiC substrate and its optical properties

Ma Yu-ke
Xu Xian-Gang

SPIE.

Ma Yu-ke, Xu Xian-Gang, "WS₂ film on a SiC substrate and its optical properties," *Opt. Eng.* **58**(9), 097110 (2019), doi: 10.1117/1.OE.58.9.097110.

WS₂ film on a SiC substrate and its optical properties

Ma Yu-ke and Xu Xian-Gang*

Shandong University, Institute of Crystal Material, Ji Nan, China

Abstract. Photoelectric functional material WS₂ thin film on SiC substrate was synthesized. Both 15 and 150 nm thickness of WS₂ film were deposited on an n-doped SiC substrate ($7.37 \times 10^{19} \text{ cm}^{-3}$) by pulsed laser deposition method. Optical properties of the WS₂/SiC material were discovered. (I) a photovoltaic effect: (1) there is a cutoff wavelength λ_c (661 nm), which means the wavelength of an incident monochromatic light must be less than λ_c in order to have the photovoltaic effect; (2) the incident light must be polarized. (3) It was found that the maximum open circuit voltage output is 6.3 V in a condition of 40 mW @ 532 nm. (II) Wavelength blueshift: when a laser of 532 nm is used in the experiment to incident perpendicularly through the thin layer WS₂/SiC film stack, which is driven by an external electric field, it is found that the 532-nm photons are blue-shifted 1.33 nm under a 30 V (DC) voltage. We also find that the blueshift of the laser wavelength is tunable with the applied voltage. Inverse Compton scattering of the photon by both electron and hole is used to explain this blueshift, the consistency of experimental results and the theoretical calculation for the wavelength blueshift was found. © The Authors. Published by SPIE under a Creative Commons Attribution 4.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI. [DOI: [10.1117/1.OE.58.9.097110](https://doi.org/10.1117/1.OE.58.9.097110)]

Keywords: WS₂ film on SiC; photovoltaic effect; tunable blue-shift of wavelength; inverse Compton scattering.

Paper 191073L received Aug. 5, 2019; accepted for publication Sep. 12, 2019; published online Sep. 30, 2019.

1 Introduction

Recent advances in two-dimensional (2-D) semiconductors, particularly monolayer transition-metal dichalcogenides (TMDs), have attracted rapidly growing scientific interests for next-generation electrical and optoelectronic device applications.^{1–11} A single layer of TMDs exhibits a totally new phenomenon, which can lead to 2-D nanoelectronic and nanophotonic applications owing to its unique physical, electrical, and optical properties.^{12–15} Chemical vaporized deposition method was used to synthesize monolayer TMDs^{16–19} mainly; however, magnetron sputtering technique can be used to produce large thin layered TMDs films or even monolayer TMDs.²⁰ Simply, a pulsed laser deposition (PLD) method was used.^{21,22} However, the size of most large stable monolayer TMDs is of several hundred micrometers scales.^{1,2} It is much easier to have a wafer size thin layer WS₂ film (tens of nm thickness or over), especially in optoelectronic device applications; it is necessary to investigate the optical natures of thin layered TMDs film.

In this study, a new photoelectric material is reported, which is a few layer WS₂ film on an n-doped SiC substrate. The 15-nm-thick WS₂/SiC film and 150-nm-thick WS₂/SiC film were superimposed by WS₂ – WS₂ face to face together to form a film stack, and both n-doped SiC substrates on each side was used as electric electrode. For this WS₂/SiC film stack, new optical properties about this material are discovered as follows: photovoltaic effect is related to a cutoff wavelength of the incident monochromatic light or laser, and the power of laser, as well as the polarization of the laser electric field. It is found that the maximum open circuit voltage output is 6.3 V with the 40 mW of a 532-nm linearly polarized laser at the present experiment.

The second new phenomenon concerning WS₂/SiC material is the wavelength of the laser beam passing through

these film stacks was blueshifted, when an external electric field was applied perpendicularly. It was well known that the laser frequency does not change any more when it passes through most of the transparent medium. However, in this paper, a tunable blueshift of laser wavelength by an electrically driven thin layered WS₂ film was reported for the first time, and a tunable blueshift by changing the driven DC voltage is also demonstrated.

To explore the mechanism of blueshift of the laser wavelength when the laser is passing through the external field driven film stack, the inverse Compton scattering model of photon by both electron and hole was used to explain this photon energy gain. Both theoretical and experimental data matches well.

The article is organized as follows. In Sec. 2, we describe the photovoltaic effect of a WS₂/SiC film stack. In Sec. 3, we study the effect of transverse electric field on the wavelength blueshift of the film experimentally. It is demonstrated that the blueshift can be modified smoothly by changing the strength of applied electric field. A theoretical explanation based on the inverse Compton scattering about the blueshift changes is investigated. In Sec. 4, we briefly describe design, formation, and characterization of the WS₂/SiC film. Finally, we summarize our findings and give our discussions in Sec. 5.

2 Photovoltaic Effects in WS₂/SiC Film

The photovoltaic effect experiment setup was shown as Fig. 1. The thickness of 15 nm WS₂/SiC sample and 150 nm thickness of WS₂/SiC sample were overlapped (with WS₂ surface to WS₂ surface) face-to-face tightly to form a WS₂/SiC film stack. An excitation laser beam passes through the surface of the 15-nm WS₂ film first and then through 150-nm WS₂ film perpendicularly. The beam splitter (transparency 50% @ 532 nm) was placed in front of the WS₂/SiC film stack and two optical power meters (HIOKI 3664 together with the HIOKI 9742 detector) were

*Address all correspondence to Xu Xian-Gang, E-mail: xxu@sdu.edu.cn

Fig. 1 Principle diagram of photovoltaic effect experiment setup.

used to monitor the reflected and transparent laser powers. A HIOKI 3238 Digital Hitester was used to measure the open circuit photovoltaic voltage of stacked WS₂/SiC films under laser irradiation.

Several laser wavelengths (532, 650, 661, 780, 808, 850, 980, and 1064 nm) were utilized to investigate this photovoltaic effect. Each laser was tuned to an output power of 5 mW to incident on the WS₂/SiC films stack, and the correspondent open circuit photovoltaic voltage (V_{oc}) and short-circuit current (I_{sc}) were measured as shown in Table 1.

It is found that (1) no incident laser, no V_{oc} can be tested. (2) There must exist a cutoff wavelength λ_c (>661 nm for this film) less than which there is a photovoltaic phenomenon, otherwise, no photovoltaic effect can be observed. (3) This photovoltaic effect is much related to the polarization of the incident light. No polarization, no photovoltaic effect (refer to Sec. 5.2).

No laser no V_{oc} means that there are no junctions between the WS₂ film and the SiC substrate or between WS₂ films, and the main cause of this photovoltaic effect is supposed that a photon is absorbed to produce positive and negative charges. Therefore, λ_c must be much related to the band gap of the WS₂ film. $\lambda_c = 1240/Eg$, where Eg is the band gap. Those lasers with the wavelength less than λ_c will produce charges and thus photovoltaic phenomena happen, whereas, lasers with the wavelength greater than λ_c will not produce any charges and thus no photovoltaic phenomena can be observed.

As we used SiC substrate as the electrode, the short circuit current I_{sc} is much limited by the resistance of SiC substrate.

In order to investigate influences of thickness of WS₂ film on photovoltaic effect of WS₂/SiC stack, three stacks are combined by using 10 + 15 nm, 5 + 150 nm, and 15 + 150 nm configurations. Each configuration stack is tested and the photovoltaic output voltage is regarded as criteria for choosing the best configuration.

Table 1 Photovoltaic effect of WS₂/SiC film stack measurement.

λ (nm)	532.0	661.0	780.0	808.0	850.0	980.0	1064.0
V_{oc} (mV)	572.0	772.0	0.0	0.0	0.0	0.0	0.0
I_{sc} (μA)	6.0	7.0	0.0	0.0	0.0	0.0	0.0

Fig. 2 Photovoltaic effects of WS₂/SiC stacks with different WS₂ film thickness configurations. The red line is for 15 + 150 nm thickness case; the green line is for 5 + 150 nm thickness case; the blue line is for 10 + 15 nm case.

Fig. 3 Photovoltaic open circuit voltage versus laser power (@532 nm).

The tested results are shown in Fig. 2. It was noted that the 15 + 150 nm configuration stack presents a better performance in photovoltaic output voltage measurement.

The maximum photovoltaic output voltage measurement was conducted by applying a commercial 532-nm laser (YRL-532-100) to a WS₂/SiC film stack. The output power of the laser can be tuned from 0 to 50 mW continuously. The relation between V_{oc} and the laser output power is shown in Fig. 3. V_{oc} varies linearly with the increase of laser power, and it reaches to a maximum of 6.3 V at 40 mW.

3 Wavelength Blueshift and the Inverse Compton Scattering in WS₂/SiC Film

3.1 Experiment Setup of the Blueshift of Laser Wavelength Measurement

Figure 4 shows the principle diagram of blueshift of laser wavelength measurement setup. A self made n-doped (doping density of $7.37 \times 10^{19} \text{ cm}^{-3}$, tested with PHYS TECH RH-2035) 4H-SiC²³ substrate (2 in. in diameter, 4 deg tilt cutting) with a thickness of (300 μm) was used, it was coated

Fig. 4 Principle diagram of blueshift of laser wavelength measurement.

of 15-nm thickness thin layer WS₂ film with a WS₂ ceramic bulk material (99.9% purity) as a target by using the PLD technique. The substrate deposited with WS₂ was cut into a size of 10 × 10 mm² square. An adjustable DC power supply (KXN-305D) with a voltage output range from 0 to 30 V was used as an external electric supply. N-doped SiC substrate was used as a transparent electrode to which the external DC supply voltage was applied. The DC voltage applied between the two SiC substrates was measured by a microammeter (HIOKI 3238 Digital Hitester). The commercial 532-nm laser that utilizes a second harmonic generation technique was used as a monochromatic light source. The laser is linearly polarized. The optical output powers were set to be 1.5 mW. The laser beam direction is perpendicular to the surface of the thin layer WS₂ film. Two optical spectrometers (Ocean 2000 plus from Ocean Optics with a spectra resolution of 0.2 nm) were used to monitor the laser wavelength changes. The wavelength of the laser in front of and behind the WS₂/SiC film stack can be measured simultaneously. The wavelength shift of the laser is defined as the difference of the spectrum peak in front of the WS₂ film and the correspondent spectrum peak behind the WS₂ film.

It was found that, for 532-nm laser, the wavelength is shifted linearly from 532.99 to 531.66 nm when the external DC electrical supply is tuned from 0 to 30 V. A 1.33-nm blueshift of laser wavelength was observed.

Figure 5 showed the blueshift of the laser wavelength changes for 532-nm laser. The relation between the blueshift of the wavelength and the driven DC voltage was linear.

3.2 Theory

The inverse Compton scattering effect was used to explain our experiment results. The average energy change of the photon per Compton scattering is²⁴

$$\left\langle \frac{\Delta_i}{\omega_0} \right\rangle = \frac{4KT_i - \hbar\omega_0}{m_{\text{eff}}^i C^2}, \quad i = e, h, \quad (1)$$

where $[\Delta_i, i = e, h]$ is the frequency shift of an incident photon with a photon energy of by an electron or a hole, respectively. C is the light speed in vacuum, m_{eff}^i , $[i = e, h]$ is the electron (hole) effective mass in WS₂ film, T_i , $[i = e, h]$ is the accelerated electron (hole) temperature, and K is the Boltzmann constant. Here, $0.5KT_i$ was the energy of an electron (hole) accelerated by an external electric field E , or

Fig. 5 The blueshift of 532-nm laser wavelength versus external electric DC voltage.

Fig. 6 532-nm photon blueshift versus applied voltage.

$0.5KT_i = eU_0$, where U_0 was the voltage applied to the WS₂ film. So Eq. (1) was modified as

$$\left\langle \frac{\Delta}{\omega_0} \right\rangle = \frac{8eU_0 - \hbar\omega_0}{m_{\text{eff}} C^2}, \quad (2)$$

where $\Delta = \Delta_e + \Delta_h$ was the total frequency shift contributed by both electron and hole. And $1/m_{\text{eff}} = 1/m_{\text{eff}}^e + 1/m_{\text{eff}}^h$ was the reduced effective mass of the electron and hole pair. Take $m_{\text{eff}}^e = 0.39m_0$ and $m_{\text{eff}}^h = 0.4m_0$, here m_0 was the static mass of an electron.²⁵ This results in a reduced mass $m_{\text{eff}} = 0.197m_0$.

The calculated photon energy gain and measured wavelength blueshift were shown in Fig. 6. Good coincidence between experiment and the theory was found.

4 Design and Characterization of a Thin Layered WS₂/SiC Film

Thin layer WS₂ film has been formed by the PLD method. The thickness of WS₂ film, which was formed on the n-doped SiC substrate of 2 in. in diameter and thickness of 400 μm, is about 15 and 150 nm, respectively, in our experiment. The WS₂ film was cut in into a size of 10 × 10 mm².

Raman scattering data, atomic force microscopy data of the thin layer film, and STEM were used to characterize the material, which was revealed that the thin layer WS₂ film on the n-doped SiC substrate is a fine WS₂ film,²⁶ the details of the film formation and the correspondent characterization data can be found in SPIE-PLD/TFPA 2019 (Qingdao, China, May 19 to 22, 2019).

5 Conclusions and Discussions

5.1 Conclusions

To summarize, the thin layer WS₂ film was formed on SiC substrate with PLD technique. It was clearly observed that the energy of the photon that passes through the thin layer WS₂ film can be tuned upward continuously by an adjustable DC voltage across two SiC substrate electrodes. This phenomenon can be interpreted successfully with the inverse Compton scattering model. Meanwhile, new photovoltaic

effects were also discovered in this WS₂/SiC material. The cutoff wavelength λ_c for photovoltaic effect in this material, λ_c must be much related to the band gap of the WS₂ film. Those lasers with the wavelength less than λ_c will produce charges and thus photovoltaic phenomena will occur, whereas, lasers with the wavelength greater than λ_c cannot produce charges and thus no photovoltaic phenomena will be observed.

5.2 Discussions

Several points of view were addressed as follows:

- (1) The photovoltaic effect reported in this study is quite different from the traditional solar cell or photodetectors in which there is a p-n junction. There is no junction in this WS₂/SiC film stack. No laser irradiation on the film, no photovoltaic voltage detected. This

Fig. 7 Behaviors of blue-shift of a 532-nm laser reflected and transmitted with the change of DC voltage applied on WS₂/SiC film stack. (a)–(e) The applied voltage of 4, 11, 16, 22, and 30 V, respectively.

confirms our conclusion that no junction exists in WS₂/SiC film stack.

- (2) A hypothesis is assumed that the polarized laser electric field plays an impotent role in this new kind of photovoltaic effect, i.e., laser photons initiate the electrons and holes, and then laser electric field separates the positive and negative charges, which results in an open circuit voltage output formation. To verify this hypothesis, an ordinary white light source—a halogen lamp with a 10-W output light (conducted by a coupled optical fiber bundle) was used to illuminate the WS₂/SiC film stack, the measured voltage by HIOKI 3238 Digital Hitester is almost zero. However, when a polarizer was placed in front of the WS₂/SiC film stack, a voltage of about 100 mV was detected.
- (3) Two optical spectrometers were utilized to observe the changes of the laser spectrum peak in front of the WS₂ film and behind the WS₂ film. This arrangement permits that the reflected and transmitted laser beams be measured simultaneously. The wavelength blueshift is defined by the difference of the peak positions as shown in Fig. 7.

In Fig. 7, the red curve is the laser spectrum in front of the WS₂/SiC film stack, and the green one is the laser spectrum behind the WS₂/SiC film stack. Figures 7(a)–7(e) clearly show that the red peaks keep unchanged no matter how the applied voltage changes, but the green peak changes along with the applied voltage.

- (4) The inverse Compton scattering model can explain the blueshift behavior. From Eq. (2), it may conclude that in order to increase the photon energy gain, a higher voltage may play an important role. But the maximum voltage is limited because of a breakdown of the film. Another way to increase this blueshift is to find a small reduced effective mass of electron–hole pair, this will be our next effort.²⁷
- (5) Our discoveries in this study reveal a clue that an external tunable blueshift material is of great importance in the optoelectronic device application field.

Acknowledgments

Many helpful discussions with Professor Chen Xiufang, Professor Hu Xiaobo, Professor Peng Yan from Institute of Crystal Materials; Professor Chen Yanxue, and Professor Mei Liangmo from School of Physics, Shandong University, and Professor Miao Xiangshui from Wuhan National Laboratory for Optoelectronics, School of Optical and Electronic Information, Huazhong University of Science and Technology, are much appreciated. The authors declare there

are no conflicts of interest regarding the publication of this paper.

References

1. Y. Yue et al., “Two-dimensional high-quality monolayered triangular WS₂ flakes for field-effect transistors,” *Appl. Mater. Interfaces* **10**, 26 (2018).
2. Y. Yue et al., “Two-dimensional large-scale bandgap-tunable monolayer MoS₂(1-x)Se_{2x}/graphene heterostructures for phototransistors,” *J. Mater. Chem. C* **5**, 5887–5896 (2017).
3. C. Cong et al., “Synthesis and optical properties of large-area single-crystalline 2D semiconductor WS₂ monolayer from chemical vapor deposition,” *Adv. Optical Mater.* **2**, 131–136 (2014).
4. W. Yang et al., “Electrically tunable valley-light emitting diode (vLED) based on CVD-grown monolayer WS₂,” *Nano Lett.* **16**, 1560–1567 (2016).
5. J. Shang et al., “Room-temperature 2D semiconductor activated vertical-cavity surface-emitting lasers,” *Nat. Commun.* **8**, 543 (2017).
6. F. Wang et al., “Tuning coupling behavior of stacked heterostructures based on MoS₂, WS₂, and WSe₂,” *Sci. Rep.* **7**, 44712 (2017).
7. Q. H. Wang et al., “Electronics and optoelectronics of two-dimensional transition metal dichalcogenides,” *Nat. Nanotechnol.* **7**, 699–712 (2012).
8. B. S. Kim et al., “Possible electric field induced indirect to direct band gap transition in MoSe₂,” *Sci. Rep.* **7**, 5206 (2017).
9. D. Mao et al., “WS₂ mode-locked ultrafast fiber laser,” *Sci. Rep.* **5**, 7965 (2015).
10. J. D. Caldwell et al., “Atomic-scale photonic hybrids for mid-infrared and terahertz nanophotonics,” *Nat. Nanotechnol.* **11**, 9–15 (2016).
11. C. F. Zhu et al., “Single-layer MoS₂-based nanoprobe for homogeneous detection of biomolecules,” *J. Am. Chem. Soc.* **135**, 5998–6001 (2013).
12. H. Q. Wang et al., “Electronics and optoelectronics of two-dimensional transition metal dichalcogenides,” *Nat. Nanotechnol.* **7**, 699–712 (2012).
13. D. Akinwande, N. Petrone, and J. Hone, “Two-dimensional flexible nanoelectronics,” *Nat. Commun.* **5**, 5678 (2014).
14. F. Bonaccorso et al., “Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage,” *Science* **347**(6217), 1246501 (2015).
15. M. Chhowalla et al., “The chemistry of ultra-thin transition metal dichalcogenide nanosheets,” *Nat. Chem.* **5**, 263–275 (2013).
16. C. H. Naylor et al., “Large-area synthesis of high-quality monolayer 1T'-WTe₂ flakes,” *2D Mater.* **4**, 021008 (2017).
17. Y.-H. Lee et al., “Synthesis of large-area MoS₂ atomic layers with chemical vapor deposition,” *Adv. Mater.* **24**, 2320–2325 (2012).
18. Y.-H. Lee et al., “Synthesis and transfer of single-layer transition metal disulfides on diverse surfaces,” *J. Nano Lett.* **13**, 1852–1857 (2013).
19. H. R. Gutierrez et al., “Extraordinary room-temperature photoluminescence in triangular WS₂ monolayers,” *Nano Lett.* **13**, 3447–3454 (2013).
20. J. Tao et al., “Growth of wafer-scale MoS₂ monolayer by magnetron sputtering,” *Nanoscale* **7**, 2497–2503 (2014).
21. G. Siegel et al., “Growth of centimeter-scale atomically thin MoS₂ films by pulsed laser deposition,” *APL Mater.* **3**, 056103 (2015).
22. T. A. J. Loh et al., “One-step synthesis of few-layer WS₂ by pulsed laser deposition,” *Sci. Rep.* **5**, 18116 (2015).
23. Y.-M. Wang et al., “Characterization of foreign grain on 6H-SiC facet,” *J. Central South Univ. Technol.* **16**(3), 344–348 (2009).
24. M. Sampoorna, “Compton scattering in astrophysics,” 2003, <http://www.iucaa.in/~dipankar/ph217/contrib/compton.pdf> (2009).
25. O. D. Restrepo et al., “A first principles method to simulate electron mobilities in 2D materials,” *New J. Phys.* **16**, 105009 (2014).
26. Y. Ma and X. Xu, “Investigation on tuning of WS₂/SiC band gap with an external electric field,” *Proc. SPIE* **11064**, 1106407 (2019).
27. C. Cong et al., “Optical properties of 2D semiconductor WS₂,” *Adv. Opt. Mater.* **4**, 1700767 (2017).

Biographies of the authors are not available.