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WS_2 film on a SiC substrate and its optical properties

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Abstract. Photoelectric functional material WS_2 thin film on SiC substrate was synthesized. Both 15 and 150 nm thickness of WS_2 film were deposited on an n-doped SiC substrate (7.37×10^{19} cm^{-3}) by pulsed laser deposition method. Optical properties of the WS_2/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 WS_2/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. [DOI: 10.1117/1.OE.58.9.097110]

Keywords: WS_2 film on SiC; photovoltaic effect; tunable blue-shift of wavelength; inverse Compton scattering.

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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 WS_2 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 WS_2 film on an n-doped SiC substrate. The 15-nm-thick WS_2/SiC film and 150-nm-thick WS_2/SiC film were superimposed by $WS_2 - WS_2$ 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 WS_2/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 WS_2/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 WS_2 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 WS_2/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 WS_2/SiC film. Finally, we summarize our findings and give our discussions in Sec. 5.

2 Photovoltaic Effects in WS_2/SiC Film

The photovoltaic effect experiment setup was shown as Fig. 1. The thickness of 15 nm WS_2/SiC sample and 150 nm thickness of WS_2/SiC sample were overlapped (with WS_2 surface to WS_2 surface) face-to-face tightly to form a WS_2/SiC film stack. An excitation laser beam passes through the surface of the 15-nm WS_2 film first and then through 150-nm WS_2 film perpendicularly. The beam splitter (transparency 50% @ 532 nm) was placed in front of the WS_2/SiC film stack and two optical power meters (HIOKI 3664 together with the HIOKI 9742 detector) were

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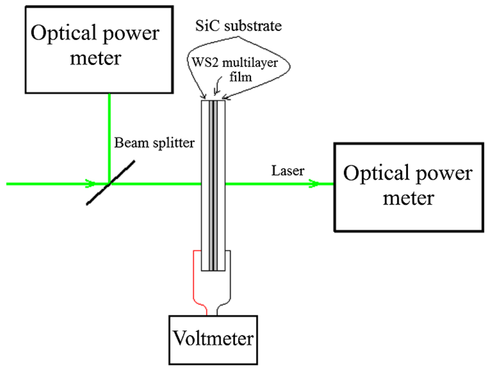

Fig. 1 Principle diagram of photovoltaic effect experiment setup.

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 WS_2/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 WS_2/SiC films stack, and the correspondent open circuit photovoltaic voltage (V_{oc}) and short-cut 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 WS_2 film and the SiC substrate or between WS_2 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 WS_2 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 cut circuit current I_{sc} is much limited by the resistance of SiC substrate.

In order to investigate influences of thickness of WS_2 film on photovoltaic effect of WS_2/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 WS_2/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

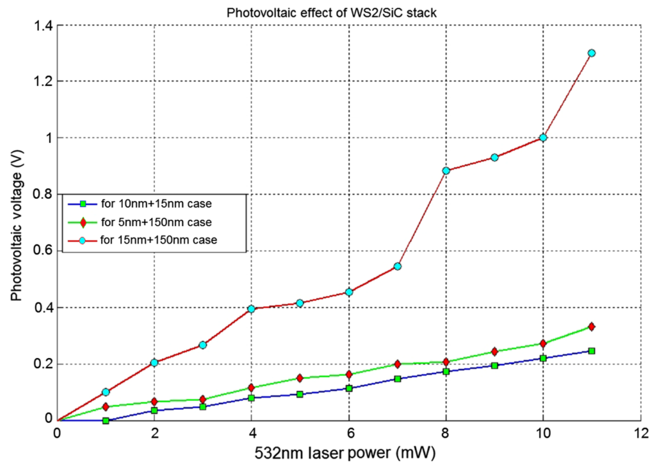

Fig. 2 Photovoltaic effects of WS_2/SiC stacks with different WS_2 film thickness configurations. The red line is for 15 + 150 nm thickness case; the green line is for 5 + 150 nm thickness case; the blue line is for 10 + 15 nm case.

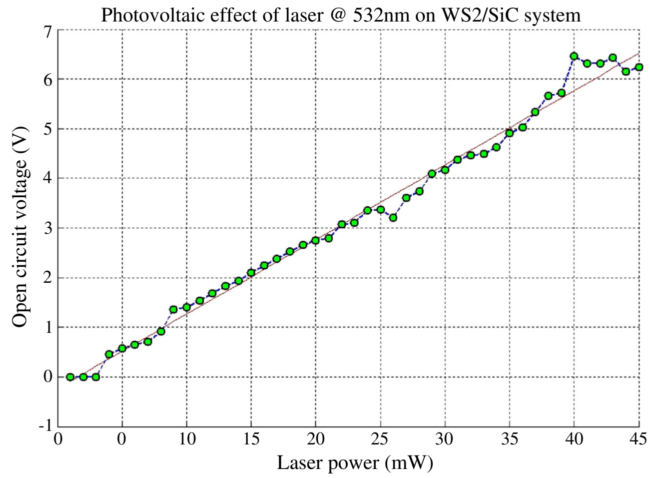

Fig. 3 Photovoltaic open circuit voltage versus laser power (@532 nm).

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 WS_2/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 WS_2/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 7.37×10^{19} cm^{-3}, tested with PHYS TECH RH-2035) 4H-SiC[23] substrate (2 in. in diameter, 4 deg tilt cutting) with a thickness of (300 μm) was used, it was coated

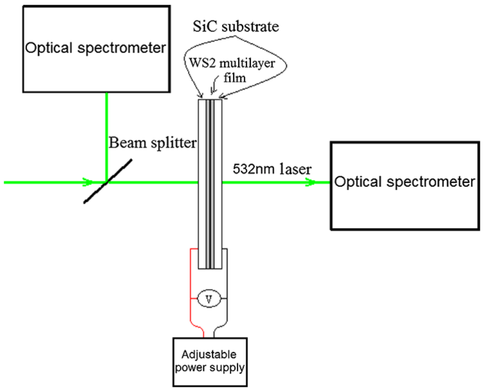

Fig. 4 Principle diagram of blueshift of laser wavelength measurement.

of 15-nm thickness thin layer WS_2 film with a WS_2 ceramic bulk material (99.9% purity) as a target by using the PLD technique. The substrate deposited with WS_2 was cut into a size of 10×10 mm^2 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 WS_2 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 WS_2/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 WS_2 film and the correspondent spectrum peak behind the WS_2 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 is[24]

$$\left\langle \frac{\Delta_i}{\omega_0} \right\rangle = \frac{4KT_i - \hbar\omega_0}{m^i_{\mathrm{eff}}C^2}, \qquad i = e, h, \tag{1}$$

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^i_{eff}, $[i = e, h]$ is the electron (hole) effective mass in WS_2 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

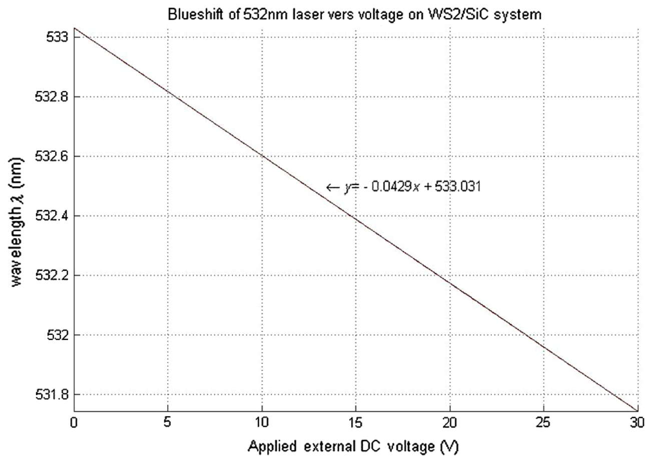

Fig. 5 The blueshift of 532-nm laser wavelength versus external electric DC voltage.

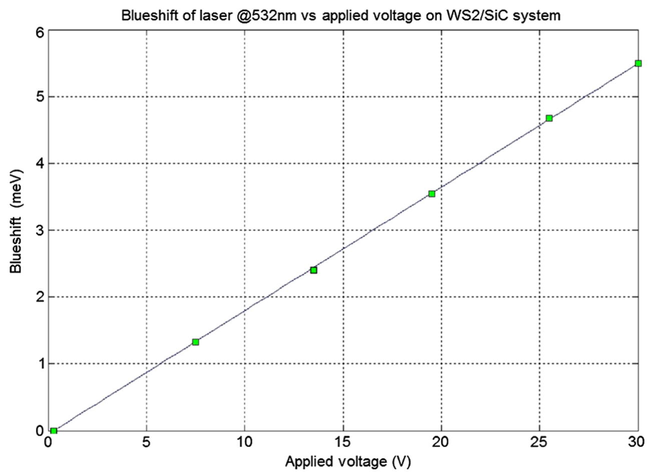

Fig. 6 532-nm photon blueshift versus applied voltage.

$0.5KT_i = eU_0$, where U_0 was the voltage applied to the WS_2 film. So Eq. (1) was modified as

$$\left\langle \frac{\Delta}{\omega_0} \right\rangle = \frac{8eU_0 - \hbar\omega_0}{m_{\mathrm{eff}}C^2}, \tag{2}$$

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

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 WS_2/SiC Film

Thin layer WS_2 film has been formed by the PLD method. The thickness of WS_2 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 WS_2 film was cut in into a size of 10×10 mm^2.

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 WS_2 film on the n-doped SiC substrate is a fine WS_2 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 WS_2 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 WS_2 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 WS_2/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 WS_2 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 WS_2/SiC film stack. No laser irradiation on the film, no photovoltaic voltage detected. This

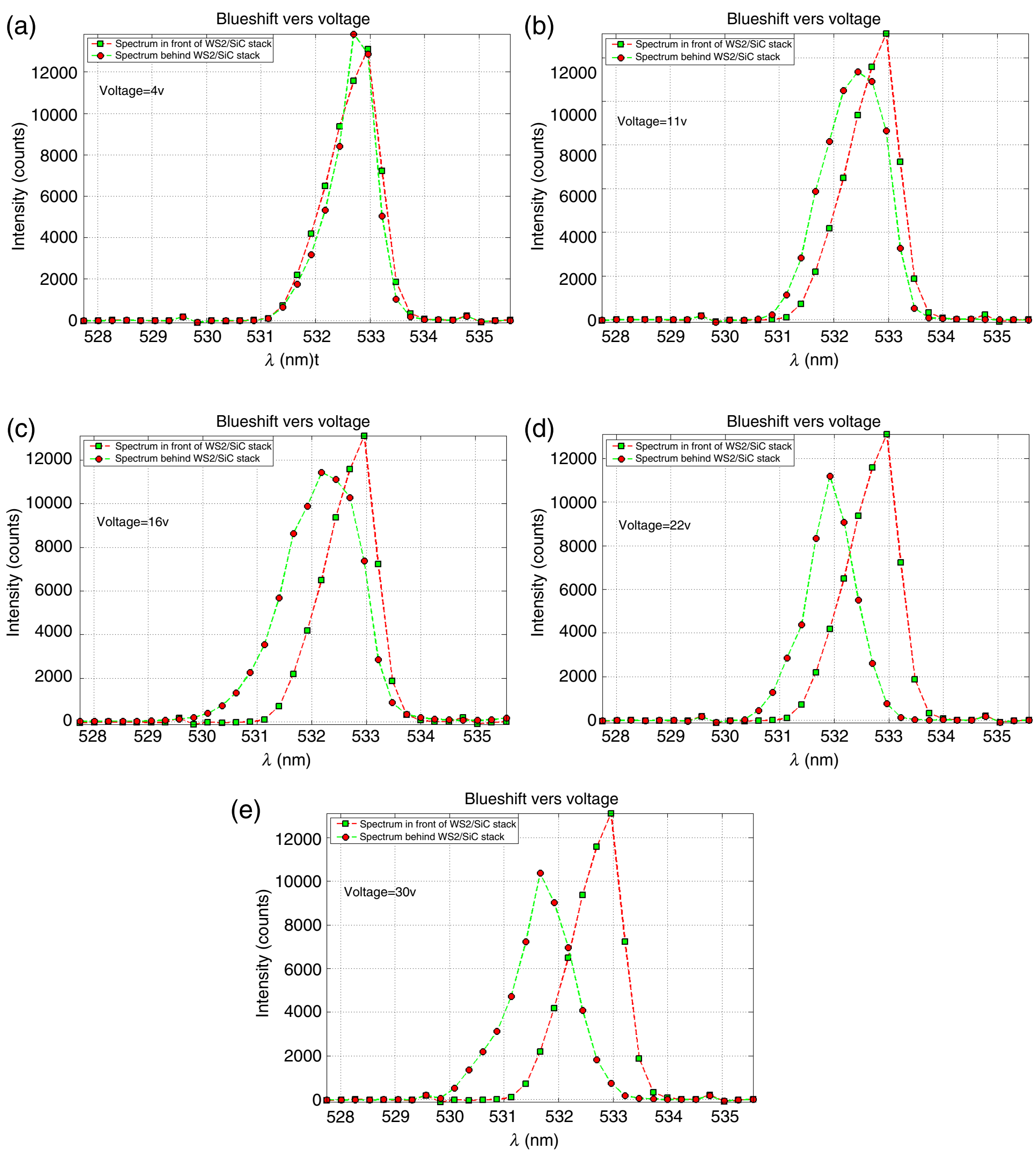

Fig. 7 Behaviors of blue-shift of a 532-nm laser reflected and transmitted with the change of DC voltage applied on WS_2/SiC film stack. (a)–(e) The applied voltage of 4, 11,16,22, and 30 V, respectively.

confirms our conclusion that no junction exists in WS_2/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 WS_2/SiC film stack, the measured voltage by HIOKI 3238 Digital Hitester is almost zero. However, when a polarizer was placed in front of the WS_2/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 WS_2 film and behind the WS_2 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 WS_2/SiC film stack, and the green one is the laser spectrum behind the WS_2/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.

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Biographies of the authors are not available.