Letter

Optics Letters

Second-harmonic generation divergence—a method for domain size evaluation of 2D materials

JINGWEN DENG,¹ ZIHAN XU,² ZHIHAO YU,^{1,3} AND JUNRONG ZHENG^{1,4}

¹ College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China ²SixCarbon Technology, Youmagang Industry Park, Shenzhen 518106, China ³e-mail: zhihaoyu@pku.edu.cn ⁴e-mail: junrong@pku.edu.cn

Received 9 September 2020; revised 23 November 2020; accepted 24 November 2020; posted 24 November 2020 (Doc. ID 409642); published 18 December 2020

Single-atomic-layered materials are important for future electronics. They allow optoelectronic devices to be fabricated at the single-atomic layer level. A singleatomic-layered two-dimensional (2D) transition metal dichalcogenide (TMD) film is usually composed of randomly orientated single-crystalline domains, and the size distribution of the domains on a large-area film has a significant impact on the applications of the film, but the impact is difficult to characterize. We report an approach to evaluate the size of the single-crystalline domains by measuring the second-harmonic generation divergence caused by the domains of different orientations. Using this method, domain size mapping on an $8 \times 8 \text{ mm}^2$ region of a continuous MoS₂ film is achieved. This method provides a fast and efficient way of domain size characterization across a large area in a non-destructive and transfer-free manner for single-atomic-layered TMD films. © 2020 Optical Society of America

https://doi.org/10.1364/OL.409642

Two-dimensional (2D) transition metal dichalcogenides (TMDs), special types of materials with extraordinary physical properties that can be manipulated at the level of single-atomic layer, have drawn extensive attention in the field of photoelectric devices [1]. Different types of single-atomic-layered TMDs are used in device fabrications, including discrete single crystals [2] and large-area thin films composed of single-crystalline domains with random orientations [3]. It is well known that the existence of grain boundaries (GBs) between single-crystalline domains has a significant impact on electronic properties [4], and different types of devices made of single-layered TMDs films have specific requirements for single-crystalline domains within GBs. For example, devices requiring high conductivity demand large-area crystal domains [5], while smaller domains are ideal for devices requiring multiple active sites [6]. Therefore, the characterization of the crystalline domain sizes in a film is crucial for device fabrication.

Determining domain sizes in a TMD film sample is not an easy task. For a sample with discrete single crystals, the boundaries can be easily observed by conventional topographical characterization methods such as optical microscopy (OM), scanning electron microscopy, and atomic force microscopy [7]. However, in a continuous film, single-crystalline domains interconnect, the GBs are fairly flat [7], making them difficult to be observed with the methods mentioned above. Aberrationcorrected annular dark-field scanning transmission electron microscopy [8,9] can achieve atomic resolution of GBs, but only a very small region of the sample can be detected, and it is not suitable for the determination of domain sizes in a large film. Dark-field transmission electron microscopy can clearly show the boundaries in a larger region, but it still requires transferring the sample onto special substrates [4]. Optical methods, including the second-harmonic generation (SHG) image, and Raman and photoluminescence (PL) mapping, have the advantage of few requirements of the substrate and little damage to the sample, making them more practical for quick characterization [10,11]. Among them, SHG microscopy is sensitive to the symmetry and electronic structure of materials, and suitable for observing the lattice orientation of 2D materials [12,13] and the twisting angles of heterojunctions [14]. However, the characterization process is time-consuming due to the scanning nature of the technology. Therefore, for large films, the domain size characterization across the entire film can only be represented by discrete small regions. With the improvement of TMD films growing technology, continuous films with larger sizes can now be fabricated [15]. Accordingly, demands for characterization of larger area are rapidly increasing. There are several methods to visualize GBs such as heating the sample to increase the width of GBs [16] or anchoring silver nanoparticles on defect sites [17] by which GBs are detectable using OM. These methods are feasible for any substrate and can be achieved on a relatively larger scale compared to SHG microscopy, but the treating process inevitably alters the sample.

Herein, we report a noninvasive method for fast evaluation of the single-crystalline domain size distribution in large-area



Fig. 1. Principle of the divergence of SHG beam produced by (a) a uniform nonlinear material and (b) 2D materials composed of randomly oriented crystals. The brightness of patterns in (b) represents the relative intensity of the SHG signal resulting from different crystal orientations in a specific polarization. The brighter the pattern, the stronger the intensity. The red light indicates the excitation light, while the blue light represents the produced SHG light. The dark red arrows show the direction of light propagation.

TMD films based on SHG signal divergence: the singlecrystalline domains of different sizes in TMDs cause different divergences of the SHG signal, and the correlation between the divergence and the domain size is quantitative. An optical system was built to measure the angular distribution of the SHG signal of TMD samples, and an analytical algorithm was developed to extract the average domain size from the experimental data. The method was tested with three different TMD samples, molybdenum disulfide on a sapphire substrate (MoS_2/Al_2O_3), tungsten disulfide on sapphire and fused quartz substrates $(WS_2/Al_2O_3 \text{ and } WS_2/SiO_2)$, with discrete crystal domains for validation. It was then applied to map the domain size distribution within an $8 \times 8 \text{ mm}^2$ region of a continuous single-layer MoS_2 film. This approach takes advantage of the non-invasive nature of spectroscopy and does not require specific substrates (only if the SHG signal from the substrate is small, compared to that of TMDs); therefore, transferring is not needed.

The divergence of the SHG signal generated from 2D TMDs compared with that from a conventional SHG crystal is illustrated in Fig. 1. When the excitation light (red) passes through a uniform crystal, it generates the SHG (blue) signal along the propagation direction [Fig. 1(a)]. When the light passes through a film of many randomly orientated small crystals, the SHG signal is still along the propagation direction, but it diverges [Fig. 1(b)]. In the crystal, the SHG efficiencies of all wave sources are identical, so the wavefront of the SHG beam is parallel with the fundamental beam. In contrast, the polarization of the SHG signal of the TMD monolayer is related to the angle between the polarization of the excitation light and the crystal axis [12,18]. Therefore, single crystals with various orientations irradiated by the excitation light with a specific polarization produce SHG with different polarizations, breaking the uniformity of the SHG wavefront and leading to beam divergence. The larger the single-crystal domains are, the less broken the SHG wavefront is, and the less divergence is in the SHG signal. Thus, the diverging angle of the SHG beam is directly correlated to the averaged domain size of the 2D material within the region.



Fig. 2. Acquiring the angular distribution of the SHG signal. (a) Schematic of the experimental apparatus. The red arrow indicates the direction of light propagation, and the white arrows represent the direction of fiber movement. The inset is the diagram of angle calculation. (b) SHG spectrum for MoS_2/Al_2O_3 (blue) and the excitation laser spectrum (red). The Al_2O_3 substrate has no SHG signal (green). (c) Normalized angular distributions of the excitation light (red) and the SHG light produced by z-cut quartz (blue) and MoS_2/Al_2O_3 (green), respectively.

We designed an optical system to measure the angular distribution of the SHG beam. Due to the symmetry of the beam, measuring the intensity distribution along one direction is sufficient to evaluate the beam divergence [Fig. 2(a)]. The wavelength of the excitation light used is 856 nm for MoS₂ and 878 nm for WS_2 . The excitation light passes through the sample as a parallel beam to generate SHG light. An aspherical lens is used to convert the angular distribution at infinity to the spatial position distribution on its back focal plane [19]. The beam diverging angle α and the spatial position at the focal plane are converted by the focal length f, which is 20 mm. We defined the distance between the position of light and the center position on the back focal plane as d. (One side is positive, and the other side is negative.) [Fig. 2(a), inset]. α can be calculated by $\alpha = \arctan(d/f)$. A fiber scans on the back focal plane of the lens, collecting the SHG light at different d positions. The fiber is connected to a spectrometer for spectroscopy measurement. The filter in the experiment eliminates the near-IR excitation light. The diameter of the excitation beam is 1.6 mm, which can be adjusted via a telescope, ranging from sub-millimeter to centimeter level. By adjusting the diameter of the excitation beam, the spatial resolution of the domain size measurement can be controlled. The detailed instrumentation information and parameters are described in Supplement 1, Section 1.

The spectra of the excitation light (red) and the SHG light of the MoS_2/Al_2O_3 sample (blue) are shown in Fig. 2(b). The center wavelength of the excitation light is at 856 nm, and the SHG light is centered at 428 nm. In contrast, the Al_2O_3 substrate has no detectable SHG signal [green line in Fig. 2(b)]. The angledependent integrated intensity of the SHG spectra at each angle is plotted in Fig. 2(c). As a reference, the SHG light produced



Fig. 3. Experiments with different samples. (a) OM images of MoS_2/Al_2O_3 , WS_2/Al_2O_3 , and WS_2/SiO_2 . (b) Histogram of the sizes of the single crystals on three samples. (The number counted ~100 per sample. Aggregation pieces of single-crystalline domains are not included due to the limitation of data processing software.) The black dotted line reflects the corresponding mean size in (c). (c) Experimental angular distributions (black points) and corresponding fitting results of the MoS_2/Al_2O_3 , WS_2/Al_2O_3 , and WS_2/SiO_2 samples.

by a z-cut quartz with a thickness of 1 mm (blue), which is commonly used as an SHG reference plate, is also shown. The beam divergence of the quartz SHG light agrees with the excitation light, indicating no diverging introduced. The setup shown here is a transmission design for transparent substrates, which can be easily modified into a reflection system for samples on opaque substrates. Compared to existing techniques, this method does not require high flatness of the substrate, so it is also suitable for TMDs grown on ordinary substrates such as glass [20].

With the method, we explored the size dependence of SHG beam divergence with three samples of different domain sizes and shapes, which are MoS_2/Al_2O_3 , WS_2/Al_2O_3 , and WS_2/SiO_2 . The OM images of the three samples are shown in Fig. 3(a). Using the contrast between the single crystals and the substrate in OM image, we obtained the area *s* of multiple discrete single crystals (number $N \sim 100$ per sample) in the samples. The mean size is defined as the square root of *s*. The statistical results of the size distributions of the samples are shown in Fig. 3(b). The statistical results are used as a reference for comparing the experimental results and the actual sample size.

The SHG signal angular distributions of the three samples are displayed in Fig. 3(c). To obtain the domain size distribution from the data, we developed an analytical model by considering various factors such as the size, orientation, and number of the single crystals. The SHG electric fields of all these sources are calculated. After a Fourier transform, which is equivalent to the conversion of the lens [19], the 2D SHG electric field distribution on the back focal plane can be calculated. More details can be found in Supplement 1, Section 2. We evaluated the influences of N and domain shapes in the calculation, concluding that neither of them has a noticeable impact on the fitting results (as shown in Fig. S1 and S2).

The calculated results (lines) are displayed in Fig. 3(c). With N = 100 on a total area of $S = 1 \times 1 \text{ mm}^2$, the best fitted mean sizes of the MoS₂/Al₂O₃, WS₂/Al₂O₃, and WS₂/SiO₂ samples are 12.5, 25.0, and 14.5 µm, respectively. Compared to the statistical results of three samples as the black dotted line in Fig. 3(b), the fitted mean sizes of MoS₂/Al₂O₃ sample are slightly larger, while the WS₂/Al₂O₃ and WS₂/SiO₂ samples are smaller. The possible reason of the difference is the error in feature counting on microscopic images. The area counted is limited to parts of the sample, which is smaller than the area measured with SHG diverging method. Moreover, aggregated single-crystal domains are counted as one domain, due to the lack of ability to distinguish them under an optical microscope. Differences in shapes of the samples could also affect the results. Taking these factors into consideration, the experimental and fitting results of the three samples are in fairly good agreement.

With the method verified, we then used it to map the crystalline domain size distribution of an $8 \times 8 \text{ mm}^2$ continuous



Fig. 4. Domain size mapping of a continuous single-layered MoS_2 film. (a) OM image of a MoS_2 film. (b) Domain size mapping of (a). Original data contains 5×5 pixels, and (b) is obtained by interpolation.

 MoS_2 film on a glass substrate ($MoS_2/glass$). It is worth noting that with a beam diameter of 1.6 mm, a 25-point mapping is sufficient to cover the entire area. Figure 4(a) is the OM image of the film, which contains no observable features or contrast differences that can be used to identify crystalline domains. The OM images of MoS_2 film at different magnifications are shown in Fig. S3. However, the SHG divergence mapping reveals significant domain size variation within the tested region, ranging from 4 to 8 μ m [Fig. 4(b)]. The original angular distributions and the fitting sizes are shown in Fig. S4. To verify the accuracy of the result, we scanned the PL mapping on an area randomly selected on the MoS_2 film. As shown in Fig. S5, PL images show the same size in this region as Fig. 4(b).

In the fabrication of TMDs, a lower nucleus density leads to a larger domain size of single crystals but, under such conditions, it is difficult to form continuous films. A higher nucleus density is conducive to the growth of continuous films, but the size of the single-crystal domain is reduced [21]. For this reason, the size of large single crystals can reach hundreds of microns [5,22], while the single-crystal domains in continuous films are mainly at the micron level [9]. Besides, the non-uniform growth conditions result in the non-uniformity of the size distribution of the domain size of TMDs [4]. The size resolution of the method presented here is limited by diffraction ~ 1 micron, which is sufficient to characterize TMD films.

In summary, an optical method is introduced to obtain the average size of the single-crystalline domains in TMD film based on SHG divergence measurements. This fast characterization method has several practical advantages, e.g., no contacting, no damaging to the sample, no requirement of transferring, and high tolerance on types and flatness of the substrate. The method can be improved with a 2D image sensor to increase the data acquisition rate. With the capability of quickly mapping the domain size distribution on the substrate where the 2D materials are originally grown, this method will be useful when large-area TMD film are applied in new device fabrication: for the 2D material manufacturers, it can help quickly characterize the products and improve the material growing process accordingly; for users, it will be a convenient tool to quickly find the most suitable region for their applications. **Funding.** National Natural Science Foundation of China (21627805, 21673004, 21804004, 21821004); Ministry of Science and Technology (2017YFA0204702).

Acknowledgment. The authors thank Yan Zhao from Peking University for assistance with the PL mapping measurement.

Disclosures. The authors declare no conflicts of interest.

See Supplement 1 for supporting content.

REFERENCES

- Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, Nat. Nanotechnol. 7, 699 (2012).
- F. K. Perkins, A. L. Friedman, E. Cobas, P. Campbell, G. Jernigan, and B. T. Jonker, Nano Lett. 13, 668 (2013).
- W. Park, J. Baik, T. Y. Kim, K. Cho, W. K. Hong, H. J. Shin, and T. Lee, ACS Nano 8, 4961 (2014).
- A. M. Van Der Zande, P. Y. Huang, D. A. Chenet, T. C. Berkelbach, Y. You, G.-H. Lee, T. F. Heinz, D. R. Reichman, D. A. Muller, and J. C. Hone, Nat. Mater. 12, 554 (2013).
- Y. J. Gong, G. L. Ye, S. D. Lei, G. Shi, Y. M. He, J. H. Lin, X. Zhang, R. Vajtai, S. T. Pantelides, W. Zhou, B. Li, and P. M. Ajayan, Adv. Funct. Mater. 26, 2009 (2016).
- C. Lan, D. Li, Z. Zhou, S. Yip, H. Zhang, L. Shu, R. Wei, R. Dong, and J. C. Ho, Small Methods 3, 1800245 (2019).
- 7. O. V. Yazyev and Y. P. Chen, Nat. Nanotechnol. 9, 755 (2014).
- W. Zhou, X. Zou, S. Najmaei, Z. Liu, Y. Shi, J. Kong, J. Lou, P. M. Ajayan, B. Yakobson, I, and J.-C. Idrobo, Nano Lett. **13**, 2615 (2013).
- K. Kang, S. Xie, L. Huang, Y. Han, P. Y. Huang, K. F. Mak, C.-J. Kim, D. Muller, and J. Park, Nature 520, 656 (2015).
- Z. Liu, M. Amani, S. Najmaei, Q. Xu, X. Zou, W. Zhou, T. Yu, C. Qiu, A. G. Birdwell, and F. J. Crowne, Nat. Commun. 5, 5246 (2014).
- L. Karvonen, A. Säynätjoki, M. J. Huttunen, A. Autere, B. Amirsolaimani, S. Li, R. A. Norwood, N. Peyghambarian, H. Lipsanen, and G. Eda, Nat. Commun. 8, 15714 (2017).
- 12. L. M. Malard, T. V. Alencar, A. P. M. Barboza, K. F. Mak, and A. M. De Paula, Phys. Rev. B 87, 201401 (2013).
- X. Yin, Z. Ye, D. A. Chenet, Y. Ye, K. O'Brien, J. C. Hone, and X. Zhang, Science **344**, 488 (2014).
- W. T. Hsu, Z. A. Zhao, L. J. Li, C. H. Chen, M. H. Chiu, P. S. Chang, Y. C. Chou, and W. H. Chang, ACS Nano 8, 2951 (2014).
- J. Zhu, H. Xu, G. Zou, W. Zhang, R. Chai, J. Choi, J. Wu, H. Liu, G. Shen, and H. Fan, J. Am. Chem. Soc. **141**, 5392 (2019).
- Y. Rong, K. He, M. Pacios, A. W. Robertson, H. Bhaskaran, and J. H. Warner, ACS Nano 9, 3695 (2015).
- H. Y. Jeong, S. Y. Lee, T. H. Ly, G. H. Han, H. Kim, H. Nam, Z. Jiong, B. G. Shin, S. J. Yun, and J. Kim, ACS Nano 10, 770 (2015).
- S. Psilodimitrakopoulos, L. Mouchliadis, I. Paradisanos, A. Lemonis, G. Kioseoglou, and E. Stratakis, Light Sci. Appl. 7, 18005 (2018).
- 19. E. Hecht, Optics (Pearson, 2017), p. 546.
- P. Yang, X. Zou, Z. Zhang, M. Hong, J. Shi, S. Chen, J. Shu, L. Zhao, S. Jiang, and X. Zhou, Nat. Commun. 9, 979 (2018).
- L. Tao, K. Chen, Z. F. Chen, W. J. Chen, X. C. Gui, H. J. Chen, X. M. Li, and J. B. Xu, ACS Appl. Mater. Interfaces 9, 12073 (2017).
- Y. Gao, Y. L. Hong, L. C. Yin, Z. T. Wu, Z. Q. Yang, M. L. Chen, Z. B. Liu, T. Ma, D. M. Sun, Z. H. Ni, X. L. Ma, H. M. Cheng, and W. C. Ren, Adv. Mater. 29, 1700990 (2017).