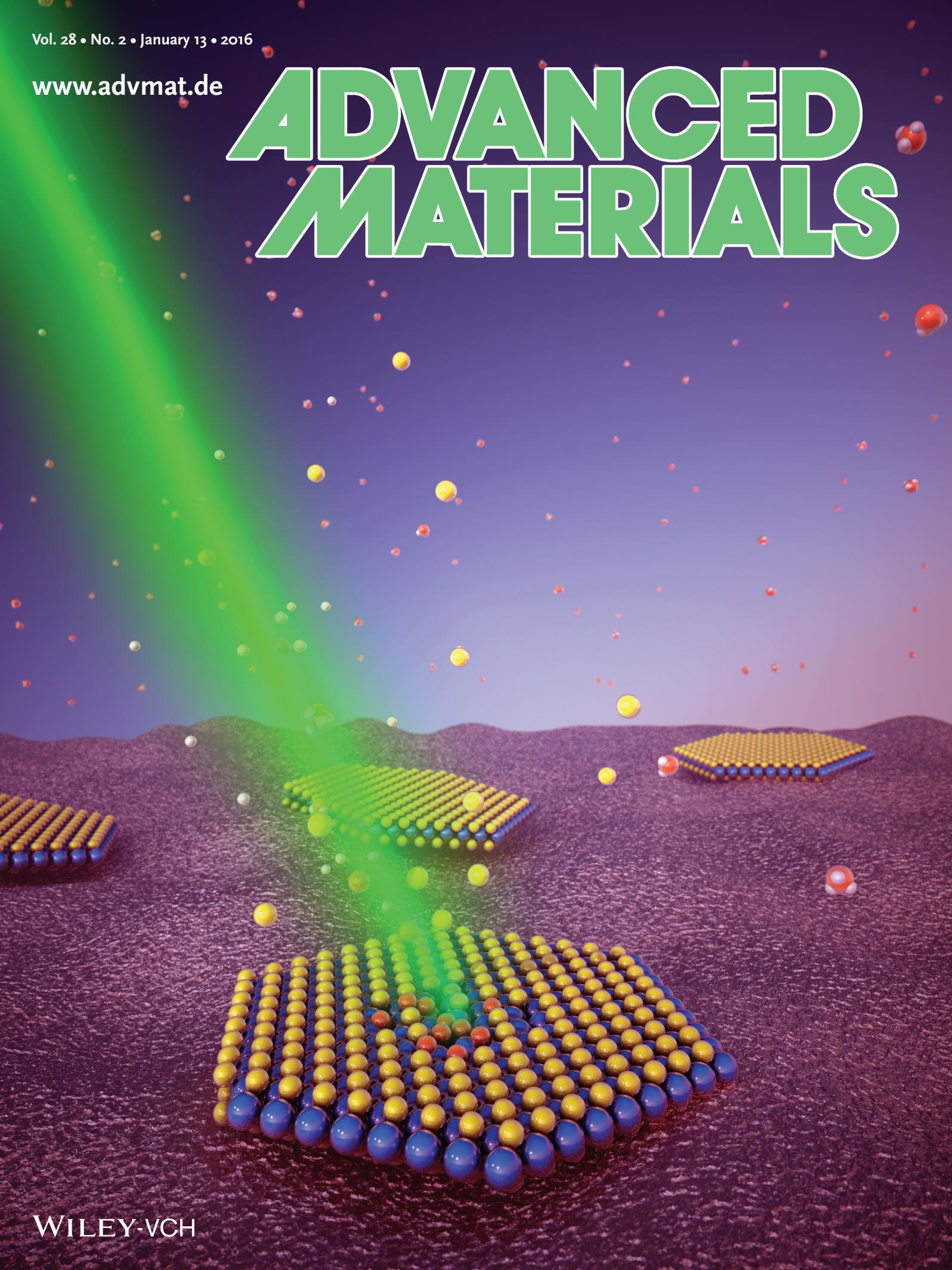


Vol. 28 • No. 2 • January 13 • 2016

www.advmat.de

ADVANCED MATERIALS



WILEY-VCH

Site Selective Doping of Ultrathin Metal Dichalcogenides by Laser-Assisted Reaction

Eunpa Kim, Changhyun Ko, Kyunghoon Kim, Yabin Chen, Joonki Suh, Sang-Gil Ryu, Kedi Wu, Xiuqing Meng, Aslihan Suslu, Sefaattin Tongay, Junqiao Wu,* and Costas P. Grigoropoulos*

2D transition metal dichalcogenide (TMDC) devices exhibit exceptional characteristics that are particularly suitable for next generation optoelectronic and electronic device applications.^[1–3] They are excellent candidate materials for transistors,^[4–6] photodetectors,^[7,8] electroluminescent devices,^[9] and sensors.^[10–14] For most of these applications, doping is needed to tune the free carrier type and density. However, previous efforts have mostly focused on doping TMDCs by means of charge transfer from adsorbed molecules,^[15–19] electrostatic,^[20,21] or physisorption gating,^[22] defect engineering,^[23,24] and substitutional doping during growth.^[25] Here we report a versatile method for widely tunable, site-specific doping of ultrathin TMDCs (MoS₂ and WSe₂) through focused laser irradiation in a phosphine environment. The p-type doping with phosphorus is localized and selective, and the doping level is widely tunable by varying the duration and intensity of laser irradiation. We show the doping tendency in both n-type and p-type TMDCs by photoluminescence mapping and device characterization. This study therefore establishes a new paradigm for digitally controlled and

air-stable doping of TMDCs for high-quality, and high-fidelity nanodevices.

Recently, TMDCs with the general chemical formula of MX₂ (M = Mo and W; X = S, Se, and Te) have attracted much interest owing to their finite direct band gaps, rich excitonic dynamics, and valley polarization (valleytronics) associated with the broken inversion symmetry. These layered semiconductors, composed of vertically stacked layers held together by van der Waals interactions, are emerging alternatives to silicon-based electronics.^[26] Despite the potential in electronics and optoelectronics, reliable and stable processing methods are needed for transition to practical applications.^[27] More specifically, controlled doping of semiconductors is vital for integration into devices. Especially, for nanoscale devices using ultrathin TMDCs as an ultrathin body in devices, in order to minimize random dopant fluctuation and ensure device performance reproducibility, site-specific doping with precise doping level control becomes essential. Our method provides a systematic approach to this problem, demonstrating superior, in situ control of the spatial distribution and doping level of TMDCs.

The laser doping method has been demonstrated to produce superior device characteristics compared with other conventional methods such as implantation or diffusion.^[28,29] A schematic diagram of the laser-assisted doping process is shown in **Figure 1a**. The laser serves two major functions: (i) creation of sulfur vacancies in the TMDC materials and (ii) simultaneous dissociation of the dopant molecules. The released dopant molecules are then incorporated into the vacancy sites. Phosphine (PH₃) was introduced as a p-type dopant precursor for ultrathin TMDCs where phosphorus occupies sulfur sites, in contrast to its use for n-type doping of silicon. The PH₃ doping of Si has been extensively studied both experimentally and through theoretical modeling.^[30–32] Despite differences between silicon and TMDCs, it is reasonable to adopt the vacancy mechanism in the present study. Considering that the dissociation temperature of the TMDCs is in the range of 1200–1400 K, a laser power slightly below this range is enough for breaking the PH₃ molecules whose dissociation temperature is 685 K.

Figure 1b shows the optical image of mechanically exfoliated monolayer and five-layer MoS₂ flakes. The monolayer MoS₂ flake in **Figure 1c** is identified with a thickness of ≈0.7 nm.^[4] The photoluminescence (PL) map shown in **Figure 1d** is taken from the laser-irradiated region indicated in **Figure 1c**.^[33] The PL spectra of monolayer MoS₂ before and after the laser-assisted phosphorus doping are shown in **Figure 2a**. The peak PL intensity of the laser-doped area is approximately one order of magnitude greater than that of the as-exfoliated monolayer

Dr. E. Kim, Dr. S.-G. Ryu, Prof. C. P. Grigoropoulos
Laser Thermal Lab
Department of Mechanical Engineering
University of California
Berkeley, CA 94720, USA
E-mail: cgrigoro@berkeley.edu

Dr. C. Ko, Dr. Y. Chen, J. Suh,
Dr. X. Meng, Prof. J. Wu
Department of Materials Science and Engineering
University of California
Berkeley, CA 94720, USA
E-mail: wuj@berkeley.edu

Prof. K. Kim
School of Mechanical Engineering
Sungkyunkwan University
Suwon 440-746, South Korea

K. Wu, Dr. X. Meng, Dr. A. Suslu, Prof. S. Tongay
School for Engineering of Matter, Transport and Energy
Arizona State University
Tempe, AZ 85287, USA

Dr. X. Meng
Research Center for Light Emitting Diodes (LED)
Zhejiang Normal University
Jinhua 321004, P. R. China

Prof. J. Wu
Division of Materials Sciences and Engineering
Lawrence Berkeley National Laboratory
Berkeley, CA 94720, USA



DOI: 10.1002/adma.201503945

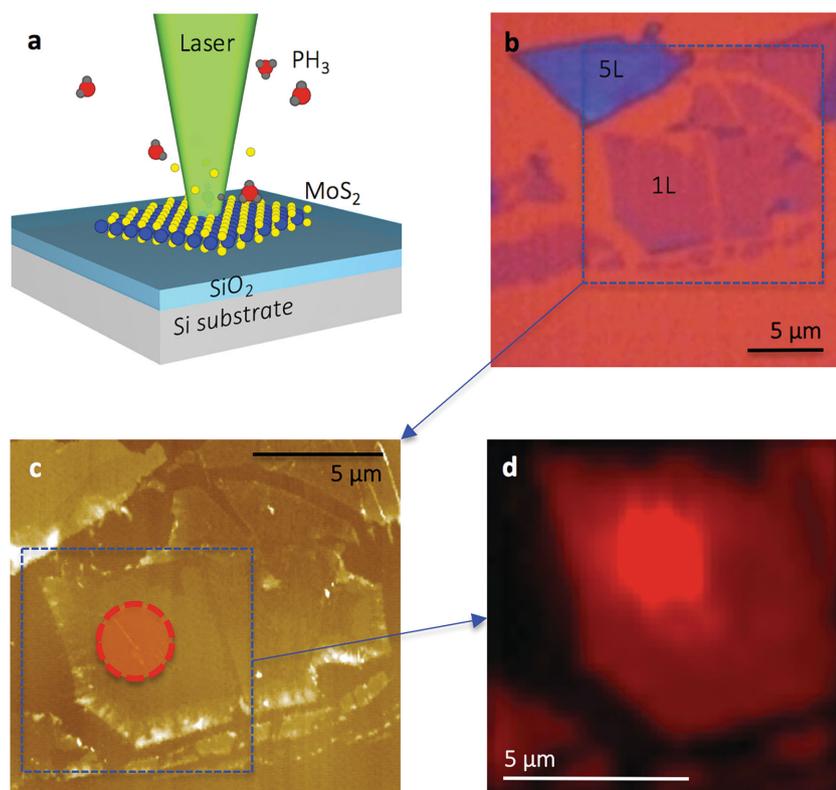


Figure 1. a) Schematic diagram of the laser-assisted doping method. b) Optical image of as-prepared monolayer MoS₂ on SiO₂/Si substrates. c) Atomic force microscopy (AFM) image of the zoomed area in (b). Its thickness is around 0.7 nm, in good agreement with the thickness of monolayer MoS₂. The circle in (c) is the laser spot area in the laser doping. d) PL mapping of the zoomed area in (c) that clearly shows the PL intensity enhancement of the laser-assisted doped area.

MoS₂. The spectral distribution of the PL also sharpens upon the laser phosphorus doping while the peak energy of the PL spectra in monolayer MoS₂ is blue-shifted by ≈32 meV. The PL peak positions are consistent with the energies of the exciton peak (X; ≈1.88 eV, e–h pair) and the negative trion peak (X⁻; ≈1.84 eV, e–e–h clusters).^[20] For the as-exfoliated monolayer, the PL contribution of the negative trion peak (X⁻) is higher than that of the exciton peak (X), demonstrating that the material is n-type in accordance with the previous reports, presumably owing to omnipresent sulfur vacancies.^[25] However, in the PL spectra of monolayer MoS₂ after phosphorus laser doping, the X peak dominates the X⁻ peak contribution, indicating addition of free holes to the system to improve parity between the densities of free electrons and holes. Hence, the blue shift of the PL spectrum is consistent with the hole doping effect of phosphorus that acts as an acceptor in MoS₂, resulting in a compensation of the originally n-type MoS₂.

In contrast to the intrinsically n-type MoS₂, WSe₂ is known to be intrinsically p-type.^[15] Such a phosphorus doping is expected to enhance the free hole density in WSe₂. Figure 2b shows the PL spectra of monolayer WSe₂, before and after the laser-assisted phosphorus doping. The as-exfoliated monolayer WSe₂ exhibits a direct band gap at 1.67 eV. The PL intensity of doped WSe₂ is drastically reduced after the laser doping. In addition, the spectral shape of the peak broadens (by 12% in full

width half maximum (FWHM)). The PL peak in monolayer WSe₂ is red-shifted by 45 meV. The PL intensity and position changes are explained by the introduction of additional free holes with the phosphorus doping. These free holes turn the original, already p-type WSe₂ flakes into more p-type, thus favoring the formation and recombination of positive trions (X⁺, e–h–h clusters) over those of excitons (X, e–h pair). Similar effects were also found in another p-type TMDC, WS₂ (see the Supporting Information). We note that the laser doping process does not cause detrimental structural damage to these TMDCs under the given conditions. To identify the structural damage after laser-assisted doping of MoS₂, we conducted Raman mapping prior to single spot Raman spectrum acquisition (Figure 2a,b, inset). The Raman and PL mapping area was ≈10 × 10 μm², corresponding to ≈400 spots separated by 0.5 μm steps per mapping image. This procedure helps confirm that point data are indeed taken from the laser reaction spot center.

We analyze the effects of different laser processing parameters (Figure 2c,d). It is known that the laser-assisted thermochemical processing provides a convenient means for systematically and rapidly accessing a wide parameter space in a single sample configuration.^[34–36] The enhancement of the PL peak intensity of monolayer MoS₂ at a fixed laser power exhibits an approximately linear dependence on the laser illumination time

(Figure 2c, inset), which implies monotonically increasing hole doping over the laser illumination time. At a fixed laser power of 200 mW and exposure times of 10, 60, and 120 s with the PL intensity was enhanced by 1.6, 5, and 10 times, respectively. On the other hand, as can be seen in Figure 2d, the enhancement of PL intensity with respect to the laser power shows a threshold behavior (Figure 2d, inset). Namely, the PL intensity greatly increases from that of the as-exfoliated sample as the laser power increases from 200 to 250 mW (from 6 to 35 times, respectively), but decreases as the laser power increases to 300 mW. This implies the existence of an optimal laser power, around 250 mW, at the fixed irradiation time of 60 s. Decomposition of the monolayer MoS₂ at the laser power of 300 mW was detected by contact-mode AFM. Presumably, irradiation with the laser at the power of 300 mW raises the local temperature in excess of the decomposition temperature of monolayer MoS₂, which should be ≈900 K at the given experimental conditions considering the substrate type, the environment gas species, and the gas pressure.

The Gaussian profile of the laser beam intensity is expected to generate a spatially varying temperature distribution at the irradiation spot. Although various reports have been published on optical and thermal properties of TMDC materials,^[37–40] there is still insufficient information to enable accurate prediction of the induced temperature in our laser doping process.

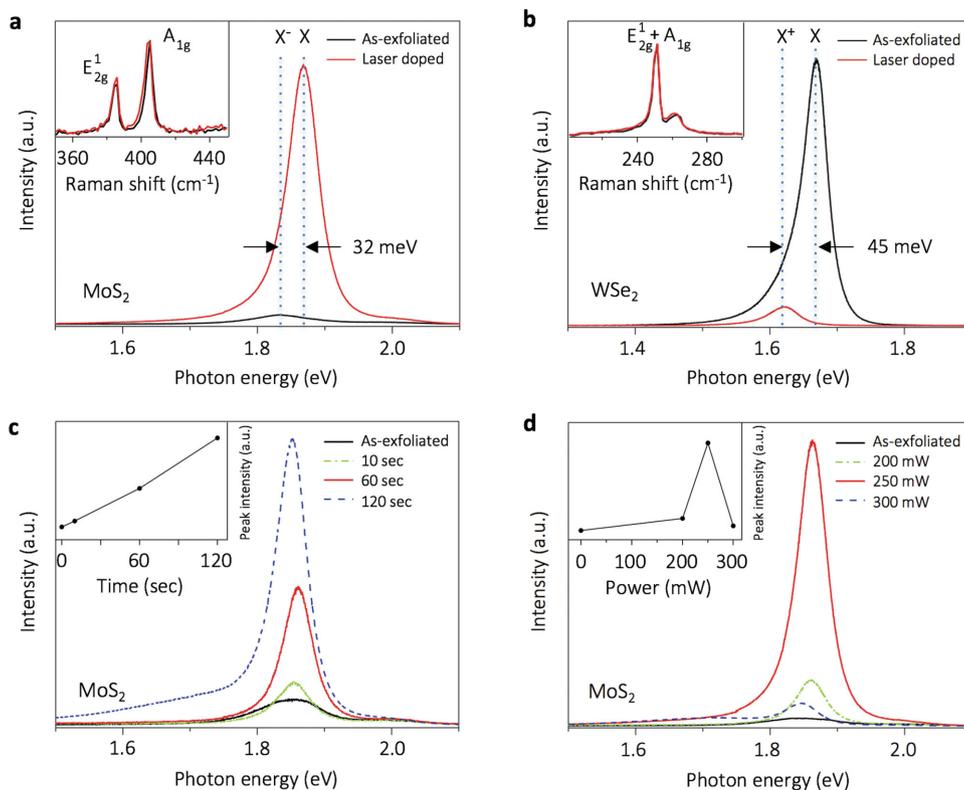


Figure 2. a) PL spectra of as-exfoliated and optimally (250 mW for 60 s, laser-doped spot center) laser-doped monolayer MoS₂. Inset: Raman spectrum of as-exfoliated and laser-doped monolayer MoS₂. b) The same spectra for monolayer WSe₂ (optimal condition is 150 mW for 60 s). c) PL change of monolayer MoS₂ with different laser doping time at a fixed laser power of 200 mW. The inset shows the peak PL intensity values as a function of the laser doping time. d) PL spectra of monolayer MoS₂ with different laser doping power at a fixed laser doping time of 60 s. The inset shows the peak PL intensity values as a function of the laser power.

The maximum PL intensities across the laser-doped regions in the monolayers MoS₂ (Figure 3a, inset) and WSe₂ (Figure 3b, inset) are plotted in Figure 3a,b. These distributions could be fitted to a Gaussian profile, suggesting that the hole doping concentration increases with doping temperature, which maximizes at the center of the laser reaction spot. The FWHM of the PL intensity profile was $\approx 2.5 \mu\text{m}$, which is in agreement with the focal spot size of $\approx 2.3 \mu\text{m}$, considering the 10 \times with a numerical aperture (NA) of 0.28 objective lens and the 532 nm laser light wavelength. Figure 3c, inset, shows that for MoS₂, the PL gradually shifts weight from X⁻ to X emission as the reaction spot is scanned from the edge to the center. In contrast, the WSe₂ shows a transition from X to X⁺ (Figure 3d, inset).

Reliable performance of devices requires stable doping of the active materials. Indeed, previous studies have already achieved both n-type and p-type dopings by surface charge transfer mechanisms, mostly through chemical physisorption.^[15] However, physisorption doping is unstable and decays almost completely within an hour,^[17] or is retained for longer periods only if the doping environment is maintained or protected.^[22] Among the various doping methods, substitutional doping of foreign elements is an effective and stable doping strategy for TMDCs.^[25] In our work, the laser was used to create sulfur vacancies and locally heat up the material to crack the precursor molecules, enabling the substitution of sulfur with phosphorus. The PL data in Figure 4a show that the laser-assisted

doping is irreversible and stable, even after exposure in air for a month. In order to test the doping stability, we also studied the effect of pure laser annealing. In this case, the monolayer MoS₂ was laser irradiated in the absence of the dopant gas at the laser power of 250 mW and an exposure time of 60 s (i.e., exactly the same conditions used for doping). As shown in Figure 4b, the PL intensity of monolayer MoS₂ increased right after the laser annealing to a level higher by an order of magnitude than the incurred by laser doping, possibly due to suppression of nonradiative recombination of excitons at defect sites created by the laser annealing.^[24] However, the PL intensity drastically dropped after one week. Within two weeks, the PL intensity receded to the original level prior to laser annealing, indicating instability of the laser annealing effect. Presence of the PH₃ molecules is, therefore, needed for stable doping.

In parallel to strong modification of the luminescent properties, the laser-assisted doping also causes drastic effects on electrical properties of the ultrathin TMDCs. This was investigated using field-effect transistor (FET) devices incorporating the locally doped TMDC layers as current channels. As displayed in Figure 5a,d, multiple electrodes were patterned onto TMDC bilayer flakes, covering both pristine and laser-doped regions. A voltage applied through the back gate provided additional modulation of carrier density in the TMDC channel. In the undoped regions, n-type (p-type) FET behavior was observed with on-off ratio exceeding five orders of magnitude from the MoS₂ (WSe₂)

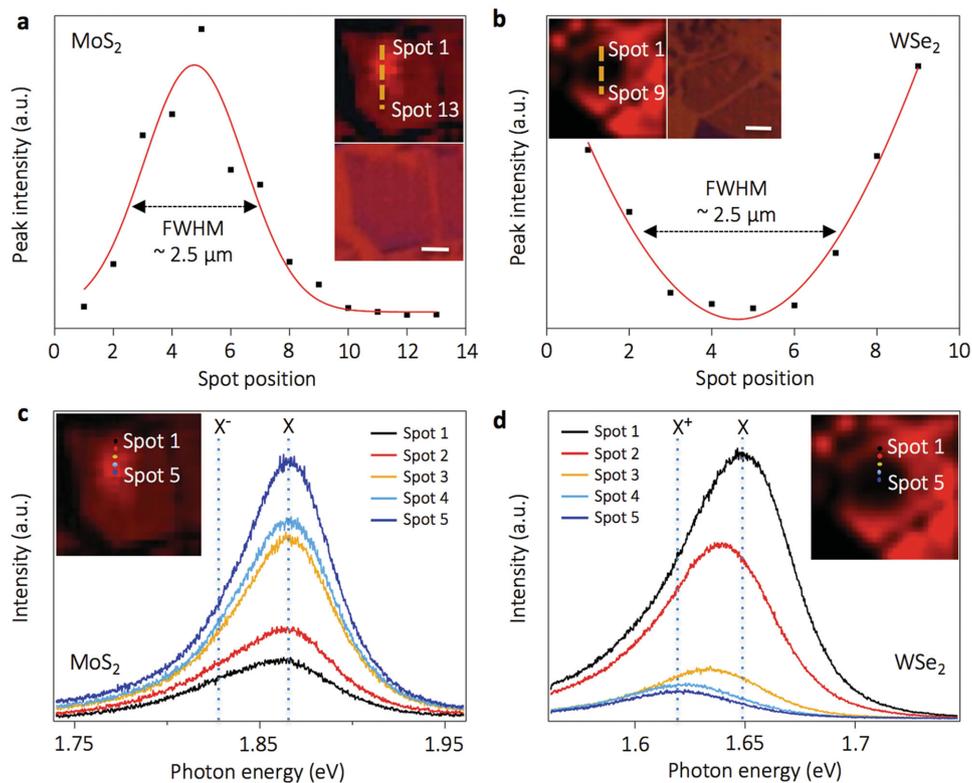


Figure 3. The PL peak intensity line profile of laser-assisted doping monolayer a) MoS₂ and b) WSe₂ at the reaction spot. Inset images show the PL peak intensity-mapping image and optical microscopy image of the laser-doped region. Scale bars are 2 and 5 μm, respectively. Variation of the PL intensity within the single spot of laser-doped monolayers c) MoS₂ and d) WSe₂. The inset shows the PL mapping image. The spacing between each spot is 500 nm.

bilayers. The FET characteristics, i.e., source–drain current (I_{SD}) versus back gate voltage (V_G) curves, of devices fabricated at different distances from the center of the laser-doped region change in a manner consistent with the spatial variation of PL across the same region, as summarized in Figure 5b,e. The phosphorus doping suppresses the n-type characteristics of the MoS₂ and enhances the p-type characteristics of the WSe₂, with increase in conductance as well as shift of threshold voltage. The hysteresis features of FET loops are likely due to water molecule absorption on the surface of the TMDCs, considering that all electrical measurements were conducted under ambient

conditions.^[41] In addition, the I_{SD} versus source–drain voltage (V_{SD}) curves obtained from the MoS₂ and WSe₂ channels in Figure 5c,f, respectively, further confirm introduction of acceptors by the laser treatment.

In summary, laser-assisted phosphorus doping was demonstrated on ultrathin (monolayer and bilayer) TMDCs including n-type MoS₂ and p-type WSe₂. This approach effectively introduces electronically active phosphorus atoms into the TMDCs. The precise level, temporal and spatial controls of the doping are achieved by varying the laser irradiation power and time, demonstrating wide tunability and high site selectivity. Future

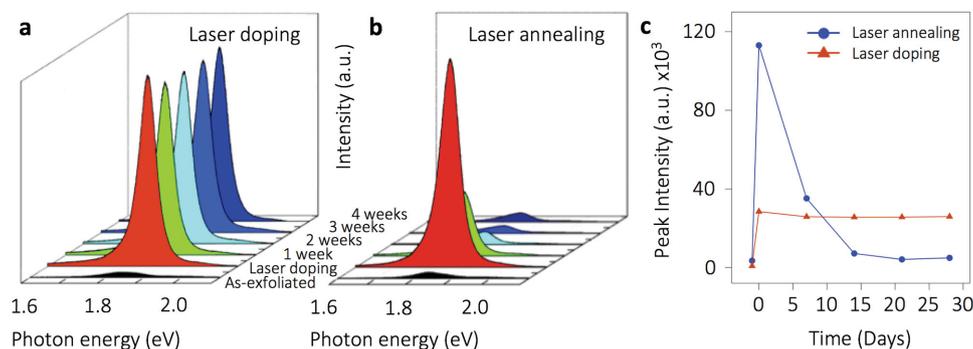


Figure 4. Long-term room-temperature stability of laser-doped monolayer MoS₂. a) PL spectra demonstrating the stability of the monolayer MoS₂ laser-assisted doped with phosphorus and b) laser annealed with the same laser power and time but under exposure to oxygen and water molecules in ambient air. c) The peak PL intensity of the laser-doped and laser-annealed monolayer MoS₂ varying over time in ambient.

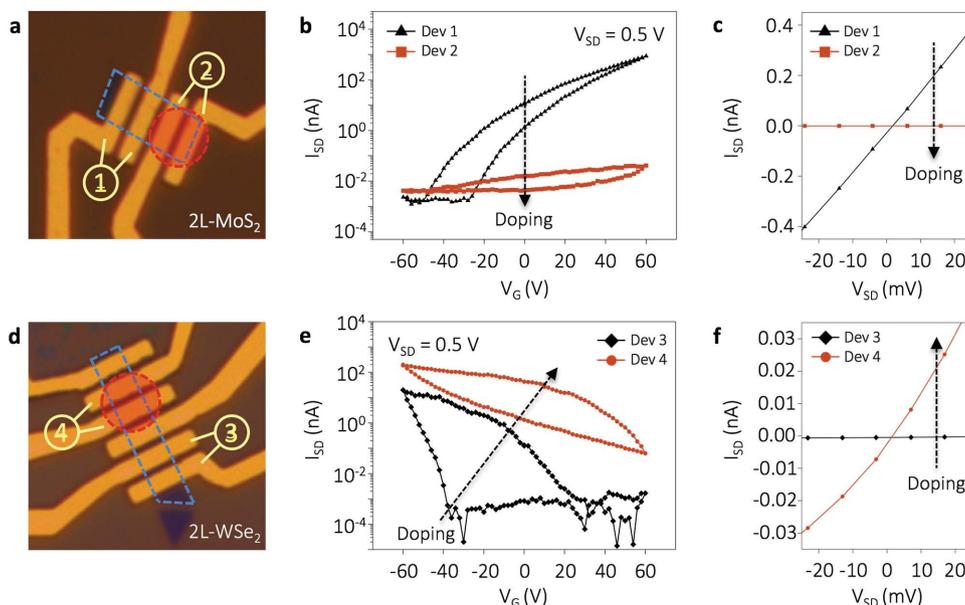


Figure 5. a,d) Bilayer MoS₂ and WSe₂ FET devices. The flakes are outlined by the blue dashed boxes and the laser-irradiated areas are denoted by the red dashed circles. b,e) Source–drain current (I_{SD}) versus back gate voltage (V_G) curves recorded from the devices in panels (a) and (d) with a bias voltage of 500 mV. c,f) Source–drain current (I_{SD}) versus source–drain voltage (V_{SD}) curves recorded from the doped (Dev 2, 4) and undoped (Dev 1, 3) devices.

investigation of the choice of dopant, the dopant concentration, and the contact engineering should be conducted. The high stability and effectiveness of the laser-assisted doping method combined with the site selectivity and tunability demonstrated here may enable a new avenue for functionalizing TMDCs for customized nanodevice applications.

Experimental Section

TMDCs Sample Preparation, MoS₂: Single and bilayer MoS₂ flakes were mechanically exfoliated from commercially available crystals of MoS₂ (SPI).

WS₂ and WSe₂: Single crystals of WX₂ were grown by vapor transport technique using iodine as the transport agent to facilitate material growth using a two-step process. In the first step, polycrystalline WSe₂ (WS₂) powders were synthesized at 1065 °C (1110 °C) for 3 d in a single-zone furnace using tungsten and selenium (sulfur) high-purity (99.995%) powders (–325 mesh) with a molar ratio of 1:2.02 ± 0.01 in evacuated quartz tubes. Samples were cooled down to room temperature at 50 °C h^{–1}. About 2.5 g of the WSe₂ (WS₂) and I₂ granule (3 mg cc^{–1}) were introduced into the quartz tubes. The quartz tube was evacuated to 2 × 10^{–6} Torr and sealed. Tubes were placed in a three-zone furnace and the furnace was heated to 1030 °C, 1000 °C, and 940 °C (1070 °C, 1030 °C, and 980 °C), respectively. Powders were located in the hot zone ($T_{\text{precursor}} = 1030$ °C and 1070 °C for WS₂) and synthesized crystals were collected in the cold zone ($T_{\text{growth}} = 940$ °C and 980 °C for WS₂). The total duration of the growth was set to 3–4 weeks and eventually cooled down to room temperature at the rate of 50 °C h^{–1}.

Laser Doping System: The laser-assisted doping experiments were carried out in a dedicated apparatus. The system is equipped with a multichannel gas panel for doping gas supply (10 sccm of 1% PH₃) with 400 sccm Ar dilution gas and is equipped with vacuum chambers pumped to 10^{–4} Torr by a dry pump before the total pressure of 400 Torr for laser doping reaction. The laser source already in place was a highly stable continuous wave 532 nm laser (diode-pumped solid state laser, 5 W, Sprout-DTM, Lighthouse photonics) focused onto the sample in the vacuum reaction chamber, which was placed on high precision XY

stage (Aerotech), by a 10× objective lens (Mitutoyo, 0.28 NA) for laser delivery.

Micro-Raman/PL Measurements: A commercially available micro-PL and Raman measurement system (Renishaw) was equipped with an Ar-ion laser (488 nm) and 1200, 2400 l mm^{–1} grating for PL and Raman, respectively. A 100× objective lens (0.95 NA) was used, and the focused laser spot size on the sample was around 0.5 μm. Typical excitation laser power was around 25 μW to avoid heating, damaging, and nonlinear optical effects. Typical measurement integration time was 10 s. All measurements were performed at room temperature.

Nano-Auger Electron Spectroscopy (Nano-AES): Nano-AES was conducted to investigate the chemical properties of locally laser-assisted doped regions using an Oxford/Omicron system where a field emission gun is equipped enabling a spatial resolution of ≈10 nm at an ultrahigh vacuum of pressure ≈10^{–10} mbar.

Device Fabrication and Electrical Characterization: Exfoliated 2D crystals were patterned into rectangular patches by XeF₂ etching subsequent to standard electron beam lithography (EBL). Then, after local laser doping, polymethylmethacrylate resist masks generated by EBL were used to deposit metal electrode channels of Pt/Au and Ti/Au (10 nm/70 nm) on the WSe₂ and MoS₂ layers, respectively, by e-beam evaporation followed by the lift-off process. Back-gated FET experiments were conducted on the probes station equipped with two Keithley 617 programmable electrometers, an NI BNC-2090 A/D board, and a current amplifier, under the ambient conditions.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

C.K. and K.K. contributed equally to this work. The authors thank Taeyun Park for his assistance in sample preparation. Support from the US Air Force Office of Scientific Research AFOSR/AOARD under

grant FA2386-13-4123 is gratefully acknowledged. This work was also partially supported by the National Science Foundation under Grant No. DMR-1306601. Nano-Auger experiment at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The laser-induced doping was conducted on the LACVD apparatus in the UC Berkeley Marvell Nanofabrication Laboratory.

Received: August 13, 2015

Revised: September 21, 2015

Published online: November 16, 2015

- [1] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano, *Nat. Nanotechnol.* **2012**, *7*, 699.
- [2] D. Jariwala, V. K. Sangwan, L. J. Lauhon, T. J. Marks, M. C. Hersam, *ACS Nano* **2014**, *8*, 1102.
- [3] R. Ganatra, Q. Zhang, *ACS Nano* **2014**, *8*, 4074.
- [4] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, *Nat. Nanotechnol.* **2011**, *6*, 147.
- [5] H. Wang, L. L. Yu, Y. H. Lee, Y. M. Shi, A. Hsu, M. L. Chin, L. J. Li, M. Dubey, J. Kong, T. Palacios, *Nano Lett.* **2012**, *12*, 4674.
- [6] S. Kim, A. Konar, W. S. Hwang, J. H. Lee, J. Lee, J. Yang, C. Jung, H. Kim, J. B. Yoo, J. Y. Choi, Y. W. Jin, S. Y. Lee, D. Jena, W. Choi, K. Kim, *Nat. Commun.* **2012**, *3*, 1011.
- [7] O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic, A. Kis, *Nat. Nanotechnol.* **2013**, *8*, 497.
- [8] Z. Yin, H. Li, H. Li, L. Jiang, Y. Shi, Y. Sun, G. Lu, Q. Zhang, X. Chen, H. Zhang, *ACS Nano* **2012**, *6*, 74.
- [9] J. S. Ross, P. Klement, A. M. Jones, N. J. Ghimire, J. Yan, D. G. Mandrus, T. Taniguchi, K. Watanabe, K. Kitamura, W. Yao, D. H. Cobden, X. Xu, *Nat. Nanotechnol.* **2014**, *9*, 268.
- [10] Q. Y. He, Z. Y. Zeng, Z. Y. Yin, H. Li, S. X. Wu, X. Huang, H. Zhang, *Small* **2012**, *8*, 2994.
- [11] H. Li, Z. Y. Yin, Q. Y. He, H. Li, X. Huang, G. Lu, D. W. H. Fam, A. I. Y. Tok, Q. Zhang, H. Zhang, *Small* **2012**, *8*, 63.
- [12] B. Cho, M. G. Hahm, M. Choi, J. Yoon, A. R. Kim, Y. J. Lee, S. G. Park, J. D. Kwon, C. S. Kim, M. Song, Y. Jeong, K. S. Nam, S. Lee, T. J. Yoo, C. G. Kang, B. H. Lee, H. C. Ko, P. M. Ajayan, D. H. Kim, *Sci. Rep.* **2015**, *5*, 8052.
- [13] B. Cho, A. R. Kim, Y. Park, J. Yoon, Y. J. Lee, S. Lee, T. J. Yoo, C. G. Kang, B. H. Lee, H. C. Ko, D. H. Kim, M. G. Hahm, *ACS Appl. Mater. Interfaces* **2015**, *7*, 2952.
- [14] B. Cho, J. Yoon, S. K. Lim, A. R. Kim, D. H. Kim, S. G. Park, J. D. Kwon, Y. J. Lee, K. H. Lee, B. H. Lee, H. C. Ko, M. G. Hahm, *ACS Appl. Mater. Interfaces* **2015**, *7*, 16775.
- [15] S. Mouri, Y. Miyauchi, K. Matsuda, *Nano Lett.* **2013**, *13*, 5944.
- [16] H. Fang, S. Chuang, T. C. Chang, K. Takei, T. Takahashi, A. Javey, *Nano Lett.* **2012**, *12*, 3788.
- [17] H. Fang, M. Tosun, G. Seol, T. C. Chang, K. Takei, J. Guo, A. Javey, *Nano Lett.* **2013**, *13*, 1991.
- [18] P. D. Zhao, D. Kiriya, A. Azcatl, C. X. Zhang, M. Tosun, Y. S. Liu, M. Hettick, J. S. Kang, S. McDonnell, K. C. Santosh, J. H. Guo, K. Cho, R. M. Wallace, A. Javey, *ACS Nano* **2014**, *8*, 10808.
- [19] A. Tarasov, S. Y. Zhang, M. Y. Tsai, P. M. Campbell, S. Graham, S. Barlow, S. R. Marder, E. M. Vogel, *Adv. Mater.* **2015**, *27*, 1175.
- [20] K. F. Mak, K. L. He, C. Lee, G. H. Lee, J. Hone, T. F. Heinz, J. Shan, *Nat. Mater.* **2013**, *12*, 207.
- [21] B. Radisavljevic, A. Kis, *Nat. Mater.* **2013**, *12*, 815.
- [22] S. Tongay, J. Zhou, C. Ataca, J. Liu, J. S. Kang, T. S. Matthews, L. You, J. B. Li, J. C. Grossman, J. Q. Wu, *Nano Lett.* **2013**, *13*, 2831.
- [23] S. Tongay, J. Suh, C. Ataca, W. Fan, A. Luce, J. S. Kang, J. Liu, C. Ko, R. Raghunathanan, J. Zhou, F. Ogletree, J. B. Li, J. C. Grossman, J. Q. Wu, *Sci. Rep.* **2013**, *3*, 2657.
- [24] H. Y. Nan, Z. L. Wang, W. H. Wang, Z. Liang, Y. Lu, Q. Chen, D. W. He, P. H. Tan, F. Miao, X. R. Wang, J. L. Wang, Z. H. Ni, *ACS Nano* **2014**, *8*, 5738.
- [25] J. Suh, T. E. Park, D. Y. Lin, D. Fu, J. Park, H. J. Jung, Y. Chen, C. Ko, C. Jang, Y. Sun, R. Sinclair, J. Chang, S. Tongay, J. Wu, *Nano Lett.* **2014**, *14*, 6976.
- [26] A. K. Geim, I. V. Grigorieva, *Nature* **2013**, *499*, 419.
- [27] S. Z. Butler, S. M. Hollen, L. Y. Cao, Y. Cui, J. A. Gupta, H. R. Gutierrez, T. F. Heinz, S. S. Hong, J. X. Huang, A. F. Ismach, E. Johnston-Halperin, M. Kuno, V. V. Plashnitsa, R. D. Robinson, R. S. Ruoff, S. Salahuddin, J. Shan, L. Shi, M. G. Spencer, M. Terrones, W. Windl, J. E. Goldberger, *ACS Nano* **2013**, *7*, 2898.
- [28] T. Sameshima, S. Usui, H. Tomita, *Jpn. J. Appl. Phys.* **1987**, *26*, L1678.
- [29] D. J. Ehrlich, R. M. Osgood, T. F. Deutsch, *Appl. Phys. Lett.* **1980**, *36*, 916.
- [30] P. A. Taylor, R. M. Wallace, W. J. Choyke, J. T. Yates, *Surf. Sci.* **1990**, *238*, 1.
- [31] P. J. Chen, M. L. Colaizzi, R. M. Wallace, J. T. Yates, *Surf. Sci.* **1991**, *244*, 177.
- [32] H. F. Wilson, O. Warschkow, N. A. Marks, N. J. Curson, S. R. Schofield, T. C. G. Reusch, M. W. Radny, P. V. Smith, D. R. McKenzie, M. Y. Simmons, *Phys. Rev. B: Condens. Matter* **2006**, *74*, 195310.
- [33] A. Splendiani, L. Sun, Y. B. Zhang, T. S. Li, J. Kim, C. Y. Chim, G. Galli, F. Wang, *Nano Lett.* **2010**, *10*, 1271.
- [34] D. J. Hwang, S. G. Ryu, C. P. Grigoropoulos, *Nanotechnology* **2011**, *22*, 385303.
- [35] D. J. Hwang, S. G. Ryu, E. Kim, C. P. Grigoropoulos, C. Carraro, *Appl. Phys. Lett.* **2011**, *99*, 123109.
- [36] S. G. Ryu, E. Kim, J. H. Yoo, D. J. Hwang, B. Xiang, O. D. Dubon, A. M. Minor, C. P. Grigoropoulos, *ACS Nano* **2013**, *7*, 2090.
- [37] C. Y. Yim, M. O'Brien, N. McEvoy, S. Winters, I. Mirza, J. G. Lunney, G. S. Duesberg, *Appl. Phys. Lett.* **2014**, *104*, 103114.
- [38] X. J. Liu, G. Zhang, Q. X. Pei, Y. W. Zhang, *Appl. Phys. Lett.* **2013**, *103*, 133113.
- [39] C. Muratore, V. Varshney, J. J. Gengler, J. J. Hu, J. E. Bultman, A. K. Roy, B. L. Farmer, A. A. Voevodin, *Phys. Chem. Chem. Phys.* **2014**, *16*, 1008.
- [40] R. S. Yan, J. R. Simpson, S. Bertolazzi, J. Brivio, M. Watson, X. F. Wu, A. Kis, T. F. Luo, A. R. H. Walker, H. G. Xing, *ACS Nano* **2014**, *8*, 986.
- [41] D. J. Late, B. Liu, H. S. S. R. Matte, V. P. Dravid, C. N. R. Rao, *ACS Nano* **2012**, *6*, 5635.

ADVANCED MATERIALS

Supporting Information

for *Adv. Mater.*, DOI: 10.1002/adma.201503945

Site Selective Doping of Ultrathin Metal Dichalcogenides by
Laser-Assisted Reaction

*Eunpa Kim, Changhyun Ko, Kyunghoon Kim, Yabin
Chen, Joonki Suh, Sang-Gil Ryu, Kedi Wu, Xiuqing Meng,
Aslihan Suslu, Sefaattin Tongay, Junqiao Wu,* and Costas P.
Grigoropoulos**

DOI: 10.1002/adma.201503945

Article type: Communication

Supporting Information

Site selective doping of ultra-thin metal dichalcogenides by laser-assisted reaction

Eunpa Kim, Changhyun Ko, Kyunghoon Kim, Yabin Chen, Joonki Suh, Sang-gil Ryu, Kedi Wu, Xiuqing Meng, Aslihan Suslu, Sefaattin Tongay, Junqiao Wu and Costas P. Grigoropoulos**

Dr. E. Kim, Dr. S.-G. Ryu, Prof. C.P. Grigoropoulos
Laser Thermal Lab.
Department of Mechanical Engineering
University of California, Berkeley
Berkeley, CA 94720-1740, USA
E-mail: cgrigoro@berkeley.edu

Dr. C. Ko^[+], Dr. Y. Chen, J. Suh, Dr. X. Meng, Prof. J. Wu
Department of Materials Science and Engineering
University of California, Berkeley
Berkeley, CA 94720-1760, USA
E-mail: wuj@berkeley.edu

Prof. K. Kim^[+]
School of Mechanical Engineering
Sungkyunkwan University
Suwon-si, Gyeonggi-do 440-746, Korea

K. Wu, Dr. X. Meng, Dr A. Suslu, Prof. S. Tongay
School for Engineering of Matter, Transport and Energy
Arizona State University
Tempe, AZ 85287, USA

Dr. X. Meng
Research Center for Light Emitting Diodes (LED)
Zhejiang Normal University
Jinhua 321004, P. R. China

Prof. J. Wu
Division of Materials Sciences and Engineering
Lawrence Berkeley National Laboratory
Berkeley, California 94720, USA

^[+]These authors contributed equally to this work.

Keywords: 2D materials, transition metal dichalcogenide, site selective, laser assisted doping, field-effect transistors

Supporting Information

1. Nano-Auger Electron Spectroscopy

To study the mechanisms of the laser-assisted doping process, nano-Auger electron spectroscopy (nano-AES) which enables local chemical analysis using focused electron beam of ~ 10 nm spot size at ultra-high vacuum of base pressure $\sim 10^{-10}$ mbar (Oxford/Omicron system) was performed on pristine and laser-doped regions of MoS₂ crystals at various doping conditions such as irradiation time, doping gas composition, and laser power. Considering that AES reflects in the chemical properties of the material surface within a depth of few atomic layers, multilayer and tri-layer MoS₂ flakes were chosen as model structures analogous to monolayers to explore the role of laser heating during doping process.

In Figure S1 (a), the S/Mo Auger signal ratio of the multilayer MoS₂ layer is slightly reduced by 10 sec and 30 sec irradiation implying that chalcogen vacancies are created at low density, while it can be clearly shown that the S/Mo ratio decreases significantly and the Auger transitions of P atoms are shown up after 60 sec irradiation. The drastic changes in Auger spectra occurred between 30 sec and 60 sec. Therefore, it is presumable that the phosphorous atoms were directly deposited on the MoS₂ surface after 30 sec laser irradiation via the dissociation of PH₃ dopant molecules accelerated by the heat accumulation. Surface roughness change after irradiation for 60 sec was also confirmed by AFM scanning. Also, Figure S1 (b) clearly shows that as the concentration of the PH₃ dopant gas that is balanced with Ar is higher (i.e., Ar flow rate is set lower), the S/Mo ratio of the multilayer MoS₂ flake is decreased more after laser irradiation.

Further, the laser-assisted doping reaction in the 2D regime has been analyzed quantitatively by performing nano-AES on MoS₂ tri-layers as summarized in Figure S1 (c). The P doping level, $[P]/([P]+[S])$, was estimated to be 4.68 at.% and 56.04 at.% from the tri-layers that were laser-doped at 180 mW and 200 mW respectively, while the doping duration time was set as 60 sec for both cases. In the case of 200 mW process, P atoms seem

to be deposited on the MoS₂ surface excessively, which gives a very similar result with the cases where either the laser power or gas composition are set higher than threshold values as described in Figures S1 (a) and (b).

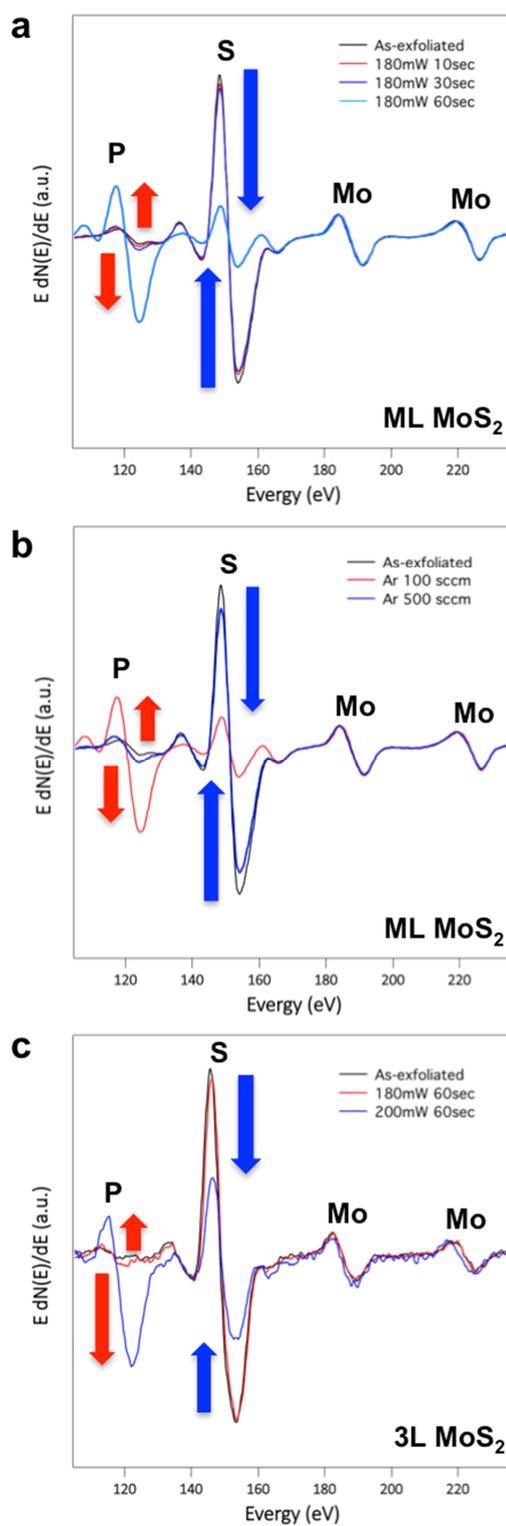


Figure S1. Auger electron spectroscopy spectra taken before and after the doping at a range of laser irradiation times (10, 30, and 60 sec at 180 mW on multi-layer MoS₂), dopant concentration by argon dilution (flow rate of 100 and 500 sccm with multi-layer MoS₂), and laser irradiation power (180 and 200 mW on tri-layer MoS₂).

2. Laser doping of WS₂

Another example of p-doping effect on p-type two-dimensional semiconducting ultrathin material is WS₂. The PL spectra of monolayer WS₂ before and after phosphorus doping by laser. The as-exfoliated monolayer WS₂ exhibits a direct band gap at 2.015 eV. With the phosphorus doping, the PL intensity is drastically reduced by 45 times. The phosphorus doped WS₂ shows the exact opposite behavior that is, incorporated excess hole carrier strongly suppress the exciton emission of monolayer WS₂. The spectral shape of peak becomes broader (22 % in FWHM) when after phosphorus doping by laser. The peak energy of the PL spectra in monolayer WS₂ were red-shifted approximately 49 meV, which are explained by the contributions of the exciton (X, e-h pair) and the positive trion (X⁺, e-h-h clusters) in the PL peak.

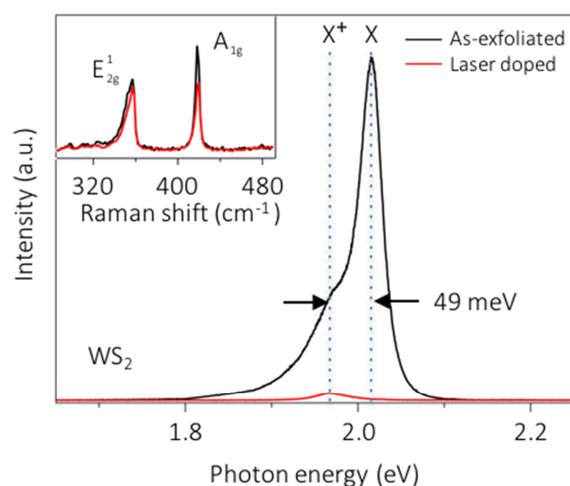


Figure S2. Photoluminescence of as-exfoliated and phosphorus-doped (250 mW for 60 sec) monolayer WS₂. Inset, Raman spectra of as-exfoliated and laser-doped WS₂.

3. Damage threshold of MoS₂

We investigate the surface morphology change of monolayer MoS₂ as a function of irradiation laser power by means of AFM and PL mapping technique to determine the damage threshold of monolayer MoS₂ at given conditions and fixed time of 60 sec. At the laser power of 150 mW (Figure S3 a,b,c) and 200 mW (Figure S3 d,e,f) cases, we could not observe any surface damage as 250 mW case of the body part even though the surface is not so clean due to the mechanically exfoliated by scotch tape method. And we observed the PL spectrum intensity incensement at the power of 200 mW (Figure S3 f). However, at the laser power of 300 mW, we can clearly see the surface deposition and damage of monolayer MoS₂ (Figure S3 j,k).

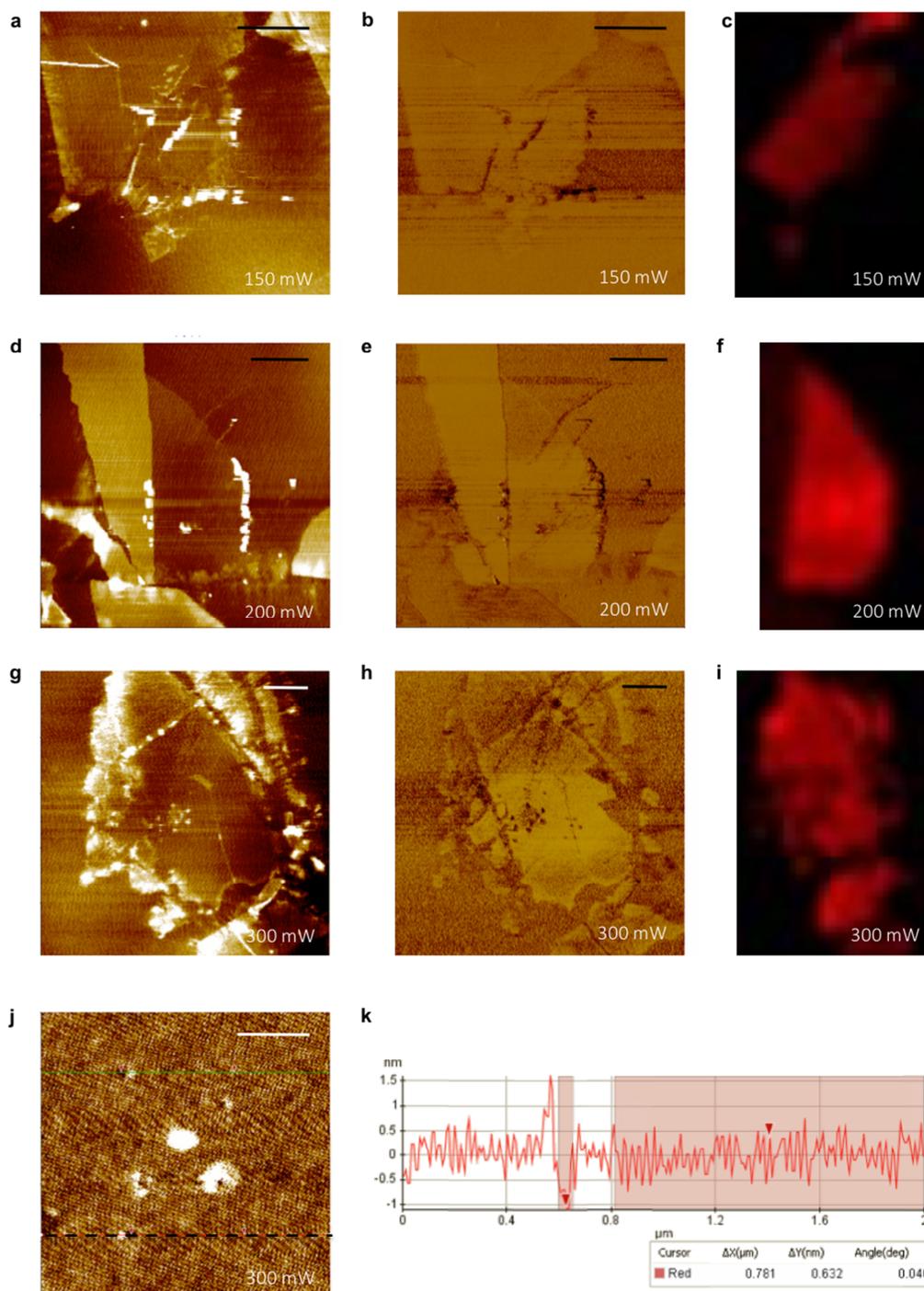


Figure S3. AFM topography (**a,d,g,j**), lateral force (**b,e,h**), and PL mapping images (**c,f,i**) of monolayer MoS₂ at various laser powers (150, 200, and 300 mW) at fixed irradiation time of 60 sec. The lateral force images help to see the deposited and damaged area more clearly with high image contrast. The line profile of damaged surface (**k**) from the dashed line in (**j**). The MoS₂ surface has some pits which have ~0.6 nm deep created by laser condition of 300 mW

at 60 sec. And it is similar to thickness of single layer of MoS₂. Scale bars of panels **(a)**, **(b)**, **(d)**, **(e)**, **(g)**, and **(h)** are all 2 μm and in **(j)** is 500 nm.

Laser-assisted phosphorus doping was demonstrated on ultra-thin TMDCs including n-type MoS₂ and p-type WSe₂. The temporal and spatial control of the doping is achieved by varying the laser irradiation power and time, demonstrating wide tunability and high site selectivity with the high stability. Laser-assisted doping method demonstrated here may enable a new avenue for functionalizing TMDCs for customized nano-device applications.

Keyword 2D materials, transition metal dichalcogenide, site selective doping, laser assisted doping, field-effect transistors

Eunpa Kim, Changhyun Ko, Kyunghoon Kim, Yabin Chen, Joonki Suh, Sang-gil Ryu, Kedi Wu, Xiuqing Meng, Aslihan Suslu, Sefaattin Tongay, Junqiao Wu and Costas P. Grigoropoulos**

Site selective doping of ultra-thin metal dichalcogenides by laser-assisted reaction

