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Tuning the optical and electrical properties of MoS_2 by selective Ag photo-reduction

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Two-dimensional transition metal dichalcogenides have demonstrated potential for advanced electrical and optoelectronic applications. For these applications, it is necessary to modify their electrical or optoelectronic properties. Doping is one of the most prevalent techniques to modify the band structure of semiconductor materials. Herein, we report the p-type doping effect on few-layer and multi-layer MoS_2 that are selectively decorated with Ag nanoparticles via laser-assisted direct photoexcitation of MoS_2 exposed in $AgNO_3$ solution. This method can control the doping level by varying the duration of the laser irradiation, which is confirmed by the observed gradual rise of MoS_2 device channel resistance and photoluminescence spectra enhancement. This study demonstrated a simple, controllable, and selective doping technique using laser-assisted photo-reduction. *Published by AIP Publishing.* https://doi.org/10.1063/1.5022705

Two-dimensional transition metal dichalcogenides (2D TMDs) have been investigated for next-generation semiconductor materials because of their unique and exceptional electrical and optoelectronic properties.[1–8] 2D TMDs have layered structures with weak van der Waals bonding so that they can be easily exfoliated from the bulk materials to yield two-dimensional structures.[2,6] They also have intrinsic energy bandgaps that vary with respect to their thickness. For instance, an n-type semiconductor, molybdenum disulfide (MoS_2), has an indirect bandgap of 1.2 eV for bulk compared to the direct bandgap of 1.8 eV for monolayer.[9] Similarly, a p-type semiconductor, tungsten diselenide (WSe_2), also has the indirect bandgap of 1.1 eV which changes to the direct bandgap of 1.7 eV as the number of layers is reduced.[10] The atomic layer TMDs' two-dimensional structure and electrical properties make them suitable for electronic and optoelectronic devices including field-effect transistors (FETs),[1,11] photodetectors,[12–16] photocatalysis,[17,18] and sensor applications.[1,4,5,7,8,19] For these applications, it is necessary to modify their electrical or optoelectronic properties. In order to realize these modifications, doping is the key process for local manipulation of its conductivity and charge density.[20,21] Several doping techniques have been developed for the modulation of the TMDs, such as surface charge transfer,[21–23] substitutional doping,[24,25] and electrostatics.[15,26] Specifically, chemical doping with noble metal nanoparticles such as Au and Ag exhibited a remarkable and stable p-type doping effect. However, controllability and spatial selectivity of this method have not been demonstrated yet.[27] Herein, we report the p-type doping effect on few-layer and multi-layer MoS_2 that are selectively decorated with Ag nanoparticles (Ag NPs) by laser-assisted photo-reduction. It is noted that MoS_2 is an n-type semiconductor. The Ag NP decorated MoS_2 FETs exhibit the p-type doping effect that is consistent with the photoluminescence (PL) spectra results.

Figure 1(a) shows a schematic diagram of the doping process using laser-assisted photo-reduction. In this study, the few-layer and multi-layer MoS_2 samples were prepared by mechanical exfoliation. Ag NPs were selectively formed on the surface of MoS_2 by laser-assisted photo-reduction in an $AgNO_3$ solution having the concentration of 0.1 M under 532 nm laser irradiation with the power density of 0.001 W/cm^2 for 10 s. This method utilizes the bandgap of MoS_2 which can absorb visible light and generate electron-hole pairs. Finally, Ag reduced on the surface of MoS_2 as a result of recombination between the generated free electrons and

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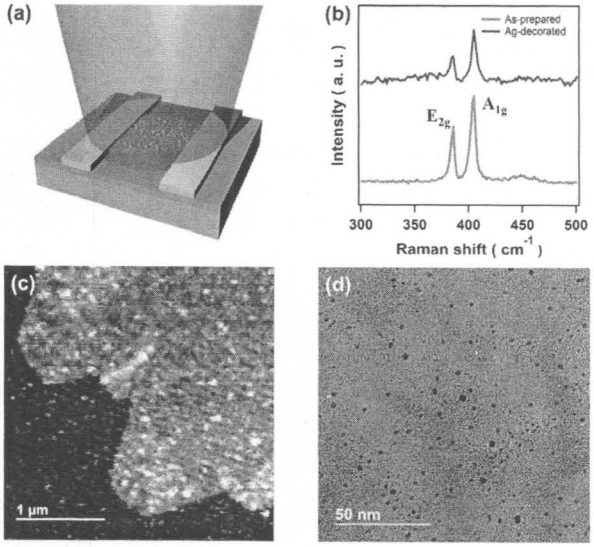

FIG. 1. (a) Schematic diagram of the Ag NP decoration method on the MoS_2 surface by laser-assisted photo-reduction. (b) Raman spectra of MoS_2 before and after Ag NP decoration. (c) Atomic force microscopy (AFM) and (d) transmission electron microscopy (TEM) images of the Ag NP decorated MoS_2 surface. The Ag NPs appear as white and black in (c) and (d), respectively.

Ag ions, whereas no Ag NPs were deposited on the SiO_2 substrate due to the absence of photo-excited free electron generation.[28–30] In this manner, we can decorate Ag NPs selectively on the surface of MoS_2. Figure 1(b) shows Raman spectra of the few-layer MoS_2 before and after Ag NP decoration. After decoration of Ag NPs, Raman spectra display an A_{1g} peak upshift of $\sim 1\,cm^{-1}$, which indicates the p-type doping effect as a consequence of the presence of Ag NPs.[31,32] Furthermore, the structure of MoS_2 is not affected by Ag NP decoration since the Raman shift before and after Ag NP decoration is almost similar. Figure 1(c) shows an atomic force microscopy (AFM) image of the MoS_2 surface decorated with Ag NPs and the substrate with no Ag NPs. Figure 1(d) displays a transmission electron microscopy (TEM) image of the Ag NPs on the MoS_2 surface. The size of reduced Ag NPs is in the range of a few nanometers (3–10 nm) on the few-layer MoS_2. These results demonstrate that Ag NPs are selectively decorated on the MoS_2 surface by laser-assisted photo-reduction.

In order to confirm the doping effect induced by Ag NP decoration, the few-layer and multi-layer MoS_2 FETs were fabricated by the conventional device fabrication process and electrical characteristics were measured. Figure 2(a) shows the optical microscopy image of the few-layer MoS_2 FET. Figures 2(b) and 2(c) display electrical characteristic curves of the few-layer and multi-layer MoS_2 FETs measured in the ambient conditions, before and after Ag NP decoration, respectively. As summarized in Fig. 2, the FET devices based on the pristine MoS_2 channel exhibit n-type behavior clearly and Ag NP decoration leads to a decrease in channel conductance representing the reduction of charge carrier density. Also, the threshold voltages of the few-layer and multi-layer MoS_2 are shifted after Ag NP decoration as shown in the inset of Figs. 2(b) and 2(c); therefore, this result indicates the p-type doping effect. Interestingly, the multi-layer MoS_2 exhibits a higher doping effect than the few-layer MoS_2 at short irradiation time since more electron-hole pairs are generated.

The laser-assisted photo-reduction method can easily control the density and size of Ag NPs and therefore the p-type doping concentration. Figure 3(a) displays photoluminescence (PL) spectra of the few-layer MoS_2 with different irradiation times. In the case of 30 s irradiation time that yields the strongest PL enhancement, the peak is blue shifted by ~ 5 meV and it increased to ~ 22 meV at 120 s irradiation time. The result shows that Ag NPs enhance the excitonic emission of MoS_2, suggesting the p-type doping effect consistent with our device studies. Figure 3(b) indicates the energy band diagram of Ag-MoS_2 with a Schottky barrier height of ~ 0.35 eV.[33,34] By the Ag NP decoration, band bending between MoS_2 and Ag NPs occurs so that excited electrons on MoS_2 transfer to Ag NPs resulting in the suppression of recombination of two electrons and a hole, the so-called negatively charged trion.[35–38] By increasing the irradiation time, more Ag NPs are decorated so that additional free holes from Ag NPs suppress even more the negative trions of MoS_2.[39,40] The highest PL intensity is shown in after 30 s of irradiation time. However, the PL intensity decreases upon irradiation over 30 s time due to the light blockage by the overloaded Ag NPs on the MoS_2 surface. Figure 3(c) shows characteristic curves and I_{ds}-V_{ds} curves with different irradiation times of the few-layer MoS_2 FET, respectively. The result displays that the maximum I_{ds} is decreased and the threshold voltage is shifted as the irradiation time increases. It is also observed that the on/off ratio of the MoS_2 FET decreases as the irradiation time increases. The decrease of I_{ds} is almost saturated by the overloaded Ag NPs on the MoS_2 surface as the irradiation time exceeds 60 s.[22]

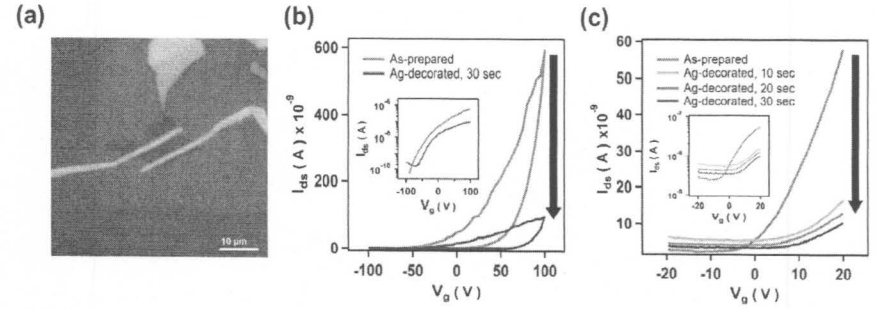

FIG. 2. (a) Optical image of the few-layer MoS_2 FET. Electrical characteristic curves (I_{ds}-V_g) of (b) few-layer MoS_2 and (c) multi-layer MoS_2 FETs before and after Ag NP decoration by laser-assisted photo-reduction. The insets are I_{ds}-V_g curves of few-layer MoS_2 and multi-layer MoS_2 FETs on the log-scale, respectively.

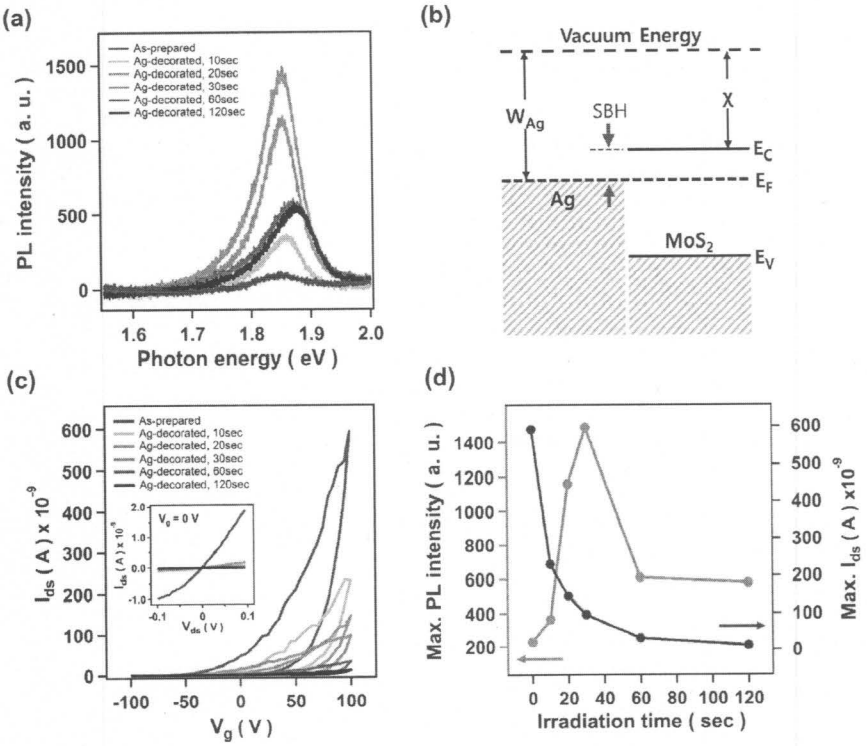

FIG. 3. (a) Photoluminescence (PL) spectra and (c) FET characteristic curves of the few-layer MoS_2 decorated with Ag NPs at varying irradiation times. (b) Energy band diagram of Ag-MoS_2. W_{Ag}: work function of Ag; χ: electron affinity of MoS_2; SBH: Schottky barrier height. (d) The maximum PL intensity (red) and I_{ds} (blue) versus irradiation time, respectively.

In conclusion, we have demonstrated the p-type doping effect on the few-layer and multi-layer MoS_2 FET devices selectively decorated with Ag NPs by laser-assisted photo-reduction. Both the few-layer and multi-layer MoS_2, an n-type semiconductor, exhibit a decrease in the source-drain current, and it is observed that the Ag NPs enhance the PL intensity of MoS_2 that attains a maximum at 30 s of irradiation time. Thus, laser-assisted photo-reduction can selectively decorate Ag NPs on MoS_2 and easily control the p-type doping effect by varying the irradiation time. We believe that this technique is potentially of wide range use for material selective doping to fabricate customized transition metal dichalcogenides and realize new electrical and optoelectronic device applications.

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[1]D. J. Late, Y. K. Huang, B. Liu, J. Acharya, S. N. Shirodkar, J. J. Luo, A. M. Yan, D. Charles, U. V. Waghmare, V. P. Dravid, and C. N. R. Rao, ACS Nano **7**(6), 4879 (2013).
[2]R. Ganatra and Q. Zhang, ACS Nano **8**(5), 4074 (2014).
[3]M. Pumera and A. H. Loo, TrAC, Trends Anal. Chem. **61**, 49 (2014).
[4]D. Sarkar, W. Liu, X. J. Xie, A. C. Anselmo, S. Mitragotri, and K. Banerjee, ACS Nano **8**(4), 3992 (2014).
[5]K. Kalantar-Zadeh and J. Z. Ou, ACS Sens. **1**(1), 5 (2016).
[6]Z. L. He and W. X. Que, Appl. Mater. Today **3**, 23 (2016).
[7]X. R. Gan, H. M. Zhao, and X. Quan, Biosens. Bioelectron. **89**, 56 (2017).
[8]J. Lee, P. Dak, Y. Lee, H. Park, W. Choi, M. A. Alam, and S. Kim, Sci. Rep. **4**, 7352 (2014).
[9]K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Phys. Rev. Lett. **105**(13), 136805 (2010).
[10]W. S. Yun, S. W. Han, S. C. Hong, I. G. Kim, and J. D. Lee, Phys. Rev. B **85**(3), 033305 (2012).
[11]B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, Nat. Nanotechnol. **6**(3), 147 (2011).
[12]Z. Y. Yin, H. Li, H. Li, L. Jiang, Y. M. Shi, Y. H. Sun, G. Lu, Q. Zhang, X. D. Chen, and H. Zhang, ACS Nano **6**(1), 74 (2012).
[13]J. Lin, H. Li, H. Zhang, and W. Chen, Appl. Phys. Lett. **102**(20), 203109 (2013).
[14]P. Agnihotri, P. Dhakras, and J. U. Lee, Nano Lett. **16**(7), 4355 (2016).
[15]B. W. H. Baugher, H. O. H. Churchill, Y. F. Yang, and P. Jarillo-Herrero, Nat. Nanotechnol. **9**(4), 262 (2014).
[16]J. S. Miao, W. D. Hu, Y. L. Jing, W. J. Luo, L. Liao, A. L. Pan, S. W. Wu, J. X. Cheng, X. S. Chen, and W. Lu, Small **11**(20), 2392 (2015).
[17]Y. Liu, Y. X. Yu, and W. D. Zhang, J. Phys. Chem. C **117**(25), 12949 (2013).
[18]E. Parzinger, B. Miller, B. Blaschke, J. A. Garrido, J. W. Ager, A. Holleitner, and U. Wurstbauer, ACS Nano **9**(11), 11302 (2015).
[19]S. Su, H. F. Sun, W. F. Cao, J. Chao, H. Z. Peng, X. L. Zuo, L. H. Yuwen, C. H. Fan, and L. H. Wang, ACS Appl. Mater. Interfaces **8**(11), 6826 (2016).
[20]V. P. Pham and G. Y. Yeom, Adv. Mater. **28**(41), 9024 (2016).
[21]D. H. Kang, J. Shim, S. K. Jang, J. Jeon, M. H. Jeon, G. Y. Yeom, W. S. Jung, Y. H. Jang, S. Lee, and J. H. Park, ACS Nano **9**(2), 1099 (2015).
[22]C. H. Chen, C. L. Wu, J. Pu, M. H. Chiu, P. Kumar, T. Takenobu, and L. J. Li, 2D Mater. **1**(3), 034001 (2014).
[23]D. H. Kang, S. R. Dugasani, H. Y. Park, J. Shim, B. Gnapareddy, J. Jeon, S. Lee, Y. Roh, S. H. Park, and J. H. Park, Sci. Rep. **6**, 20333 (2016).
[24]A. Nipane, D. Karmakar, N. Kaushik, S. Karande, and S. Lodha, ACS Nano **10**(2), 2128 (2016).
[25]E. Kim, C. Ko, K. Kim, Y. B. Chen, J. Suh, S. G. Ryu, K. D. Wu, X. Q. Meng, A. Suslu, S. Tongay, J. Q. Wu, and C. P. Grigoropoulos, Adv. Mater. **28**(2), 341 (2016).
[26]P. Dhakras, P. Agnihotri, and J. U. Lee, Nanotechnology **28**(26), 265203 (2017).
[27]Y. M. Shi, J. K. Huang, L. M. Jin, Y. T. Hsu, S. F. Yu, L. J. Li, and H. Y. Yang, Sci. Rep. **3**, 1839 (2013).
[28]L. C. Courrol, F. R. D. O. Silva, and L. Gomes, Colloids Surf., A **305**(1-3), 54 (2007).
[29]S. Tan, M. Erol, A. Attygalle, H. Du, and S. Sukhishvili, Langmuir **23**(19), 9836 (2007).
[30]T. Daeneke, B. J. Carey, A. F. Chrimes, J. Z. Ou, D. W. M. Lau, B. C. Gibson, M. Bhaskaran, and K. Kalantar-Zadeh, J. Mater. Chem. C **3**(18), 4771 (2015).

[31]H. Li, Q. Zhang, C. C. R. Yap, B. K. Tay, T. H. T. Edwin, A. Olivier, and D. Baillargeat, Adv. Funct. Mater. **22**(7), 1385 (2012).
[32]B. Chakraborty, A. Bera, D. V. S. Muthu, S. Bhowmick, U. V. Waghmare, and A. K. Sood, Phys. Rev. B **85**(16), 161403(R) (2012).
[33]M. Farmanbar and G. Brocks, Phys. Rev. B **91**(16), 161304(R) (2015).
[34]P. Zhou, X. F. Song, X. Yan, C. S. Liu, L. Chen, Q. Q. Sun, and D. W. Zhang, Nanotechnology **27**(34), 344002 (2016).
[35]S. Mouri, Y. Miyauchi, and K. Matsuda, Nano Lett. **13**(12), 5944 (2013).
[36]U. Bhanu, M. R. Islam, L. Tetard, and S. I. Khondaker, Sci. Rep. **4**, 5575 (2014).
[37]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, and D. H. Kim, Sci. Rep. **5**, 8052 (2015).
[38]S. S. Singha, D. Nandi, T. S. Bhattacharya, P. K. Mondal, and A. Singha, J. Alloys Compd. **723**, 722 (2017).
[39]K. F. Mak, K. L. He, C. Lee, G. H. Lee, J. Hone, T. F. Heinz, and J. Shan, Nat. Mater. **12**(3), 207 (2013).
[40]T. F. Yan, X. F. Qiao, X. N. Liu, P. H. Tan, and X. H. Zhang, Appl. Phys. Lett. **105**(10), 101901 (2014).