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The Amorphization of Monolayer MoS_2 Induced by Strong Oxygen Plasma treatment

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By strong oxygen plasma treatment with 100 W on monolayer MoS_2, we observe the disappearance of the Raman modes of MoS_2. The phenomena of no MoO_3 formation shown by Raman spectra and the appearance of the Mo^{6+} peak and decreased O concentration shown by X-ray photoelectron spectroscopy are attributed to that the state of MoS_2 translates from crystal to amorphous after strong oxygen plasma treatment. The amorphization of monolayer MoS_2 is further confirmed by the quenching of photoluminescence (PL) and the disappearance of two absorption peaks related to A, B exciton which demonstrates the disordered bandgap. Finally, we found that the amorphous MoS_2 can improve the absorption fraction at the visible light (500 ~ 750 nm) which is potential for future visible light photocatalysis.
Keywords: MoS_2, amorphization, oxygen plasma treatment.

1. INTRODUCTION

Recently, there is a great research interests in the two-dimensional (2D) material due to its adjustable properties. Molybdenum disulfide (MoS_2), among the two-dimensional semiconductors, offers a layer-dependent energy gap: an indirect gap of 1.2 eV for the bulk MoS_2 and a direct gap of 1.9 eV for the monolayer MoS_2, which has huge potential for optoelectronic applications [1, 2]. Tailoring the properties of MoS_2 can fulfill the requirements of novel applications. Strain engineering can be used to modulate electrical properties of MoS_2, which is a common method of modulating the material optical and electrical properties [3, 4, 5, 6]. For example, MoS_2 experienced a direct-to-indirect bandgap and semiconductor-to-metal transition by mechanical strains [7]. Defects engineering, especially ion bombardment, which is a controllable method of introducing defects can also be used to modulate the electrical and optical properties of MoS_2. The photoluminescence (PL) intensities can be enhanced by oxygen plasma irradiation on the MoS_2, which is due to the enhancement on the radiative recombination exciton caused by p doing on MoS_2 through oxygen adsorbed on the defects. [8-9] However, quenching of the PL also is observed by oxygen plasma treatment on monolayer MoS_2 [10]. This phenomenon is explained by the reduction of the radiative recombination efficiency due to the MoO_3 formation which causes the direct bandgap evolves to the indirect bandgap. The electrical properties of MoS_2 can also be tuned from semiconductor to insulator by the oxygen plasma treatment due to the MoO_3 regions formation in the same way [11]. The mechanism of the different phenomenon is caused by the reaction between oxygen and monolayer MoS_2 under different oxygen plasma power (which means that the oxygen plasma is generated at different radio frequency (RF) power), the enhancing of PL is supposed to the mild plasma treatment which means the plasma power is about no more than 20 W while the quenching of PL is supposed to the strong plasma treatment which means the plasma power is no less than 100 W.

In this work, we present the strong oxygen plasma treatment with plasma power 100 W on monolayer MoS_2. The crystalline structure of MoS_2 involves to amorphization after stronger oxygen plasma treatment which is demonstrated by that the Raman spectrum shows no evidence of MoO_3 while the X-ray photoelectron spectroscopy (XPS) shows the evidence of Mo^{6+} and the decreased oxygen concentration. The quenching of PL spectrum and the corresponding absorption spectrum also demonstrated that the bandgap lowered due to the amorphization. Also, we find that the amorphized MoS_2 can improve the absorption fraction in the visible light (500 nm – 750 nm). Theoretical calculation and experimental work all found that the pristine MoS_2 is good candidate as photocatalytic due to its bandgap (~ 1.9 eV) which is within the visible light range [12, 13]. For example, the MoS_2 nanosheet-coated TiO_2 exhibits high hydrogen production [14]. Hence, our finding can be applied to the visible light photocatalysis.

2. EXPERIMENTAL DETAILS

2.1. Sample preparation

The pristine monolayer MoS_2 was grown on c-face sapphire via chemical vapor deposition (CVD) method, which has been reported elsewhere [15]. The oxygen

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plasma was carried out using Plasma lab 80Plus. The oxygen plasma was operated with 100 sccm oxygen, 100 W power, 25 mtorr pressure and 3 s plasma exposure.

2.2. Characterization

The Raman spectra were measured by micro-confocal laser Raman spectrometer (Renishaw-invia) (λ = 532 nm, power = ~ 2 mW, beam spot size = ~ 1 μm) with a 532 nm laser in ambient environment at room temperature. The XPS spectra were recorded out using a AIXS supra photoelectron spectrometer (Kratos analytical Ltd, AlKαX-ray) operated at 15 kV and 10 mA and the beam spot size is = ~ 15 μm. PL measurements were carried out by fluorescence spectrometer (Horiba) with 50× objective. The absorption spectra were measured by UV-Visible-Near Infrared Spectrophotometer (Carry 5000).

3. RESULTS AND DISCUSSION

Fig. 1 shows the effect of strong oxygen plasma exposure on the Raman spectra of as-grown monolayer MoS_2 on sapphire substrate. Except for the peaks of c-face sapphire substrate, two new peaks at 384 cm^{-1} with a full width at half maximum (FWHM) of 6.31 cm^{-1} and 403 cm^{-1} with a FWHM of 6.27 cm^{-1} are observed in the pristine MoS_2 sample which are shown in Fig. 1.

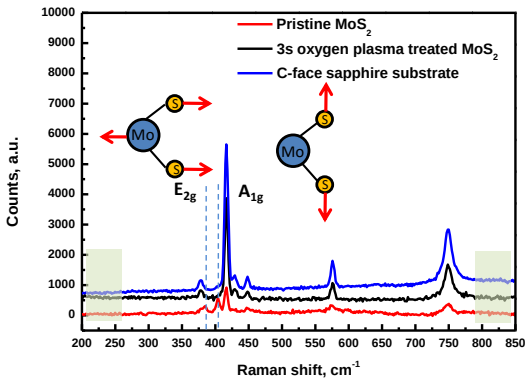

Fig. 1. Raman spectra of as-grown monolayer MoS_2 and MoS_2 treated by oxygen plasma with duration of 3s on sapphire substrate

The two prominent peaks correspond to the in-plane E_{2g} and out-of-plane A_{1g} vibrations of MoS_2 respectively. The narrow position difference (~ 19 cm^{-1}) further confirms the monolayer thickness of MoS_2 [16]. Once the sample is treated by strong oxygen plasma with duration of 3 s, here, we called it 3 s oxygen plasma for simplicity, both E_{2g} and A_{1g} vibration modes disappear obviously which is shown in Fig. 1. The disappearance of the modes indicates that the MoS_2 is damaged seriously.

The S atom is supposed to be removed by oxygen plasma firstly and then chemically bonded with O atoms. However, the MoS_2 is not completely oxidized into MoO_3 since the signature peaks (~ 225 cm^{-1} and ~ 820 cm^{-1}) of MoO_3 are not observed, marked by the grey area in Fig. 1. [11, 17]. To analyze the composition of the damaged MoS_2, XPS spectra of the pristine MoS_2 and 3 s oxygen plasma treated MoS_2 on sapphire substrate is shown in Fig. 2. Fig. 2 a shows the survey XPS spectra of pristine as-grown monolayer MoS_2 and 3 s oxygen plasma treated MoS_2 exhibiting typical signals of sapphire overlaid with Mo^{4+} and S^{2-} signals. As shown in Fig. 2 b, in pristine MoS_2 sample, a doublet Mo $3d_{3/2}$ and Mo $3d_{5/2}$ at ~ 233.0 eV and ~ 229.9 eV are observed, which has been reported elsewhere [18]. For the 3 s oxygen plasma treated MoS_2, the binding energy of doublet Mo $3d_{3/2}$ and Mo $3d_{5/2}$ shift little and an additional peak at energy 235.7 eV is observed, corresponding to the higher oxidation state Mo^{6+} [11, 19, 20, 21]. However, the decreased instead increased oxygen concentration after 3 s oxygen plasma treatment shown in Fig. 2 d exclude the formation of MoO_3. Since the signature peaks (~ 225 cm^{-1} and ~ 820 cm^{-1}) of MoO_3 are not observed, the data shows the possibility of the amorphization of monolayer MoS_2 under strong oxygen plasma treatment [22].

To analyze the energy band of the strong oxygen plasma treated MoS_2 and pristine MoS_2, we take photoluminescence (PL) measurements and the PL spectra are shown in Figure 3. The sharp peaks at ~611nm, ~692nm and ~694nm appeared in PL spectra of both samples originated form the sapphire substrate. The strong peak centered at 676.5nm (1.83eV) for pristine MoS_2 results from the direct excitonic transition of monolayer MoS_2 [23].

However, after 3s oxygen plasma treatment, the PL spectrum is quenched totally. The phenomenon has been observed and is attributed to the formation of MoO_3 [10]. MoO_3 is an indirect bandgap (3.2eV) semiconductor and the radiative recombination must be assisted by electron-phonon scattering, therefore, leading the PL quenching.

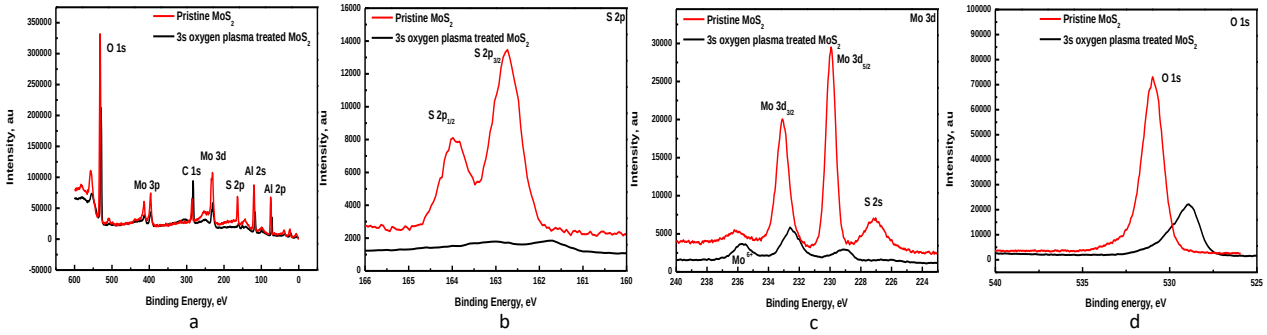

Fig. 2. a – the survey XPS of the as-grown monolayer MoS_2 and MoS_2 treated by oxygen plasma with duration of 3 s on sapphire substrate and XPS spectra: b – Mo 3d; c – S 2p; d – O 1s levels of the pristine MoS_2 and the 3s oxygen plasma treated MoS_2 on sapphire substrate

However, since the MoO_3 is not observed in our experiments, it is more likely attributed to the disordered band gap which is induced by the amorphization of crystalline structure.

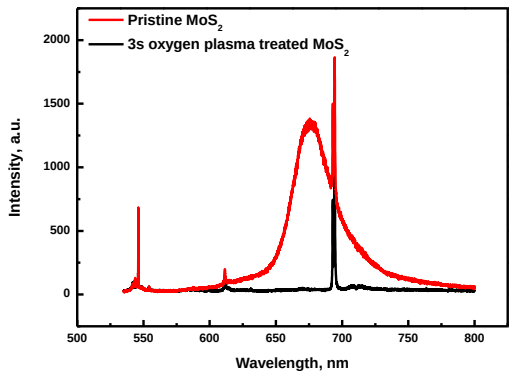

Fig. 3. Photoluminescence spectra of pristine MoS_2 and 3 s oxygen plasma treated MoS_2

We also take absorption spectrum measurements of pristine MoS_2 and strong oxygen plasma treated MoS_2 on sapphire substrate to further understand the energy band. In Fig. 4, two prominent peaks located at ~ 616 nm and ~ 667 nm, corresponding to ~ 2.0 eV and ~ 1.86 eV are observed in the pristine MoS_2. It is known to arise from direct-gap transitions between the maxima of split valence bands and the minimum of the conduction band [1]. The lower absorption (~ 1.86 eV) peak of pristine MoS_2 matches the PL peak (1.83 eV) with 0.3 eV difference within the measurements error which is related the A exciton. The higher absorption (~ 2.0 eV) peak of pristine MoS_2 is related to the B exciton though the PL peak is not observed due to the monolayer thickness [1]. However, the two peaks disappeared in strong oxygen plasma treated MoS_2 and it is attributed to the amorphization of crystalline structure which disordered the band gap. It is noted that the absorption of strong oxygen plasma treated MoS_2 on sapphire substrate is stronger than the pristine MoS_2 on substrate. It is also due to the disordered band gap which adsorbs the visible light (500 nm ~ 700 nm) more widely. Therefore, it is potential for the application of visible light photocatalysis.

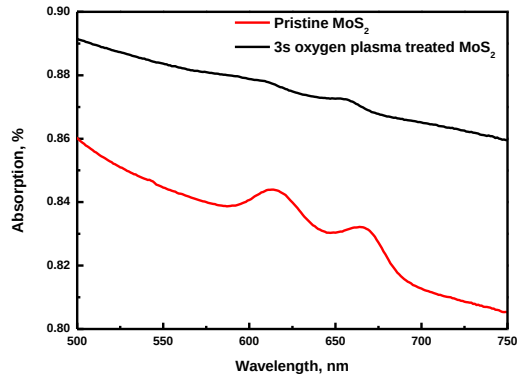

Fig. 4. Absorption spectra of pristine MoS_2 and 3 s oxygen plasma treated MoS_2

4. CONCLUSIONS

In conclusion, the missing of in-plane E_{2g} and out-of-plane A_{1g} vibrations of MoS_2 after strong oxygen plasma treatment with 100 W was observed. The Raman spectra of oxygen plasma treated MoS_2 with no MoO_3 peaks observed and XPS spectra with Mo^{6+} peak observed are attributed to that the state of MoS_2 translates from crystal to amorphous after strong oxygen plasma treatment. The quenching of the PL and the disappearance of two prominent absorption peaks also demonstrate the amorphization of crystalline MoS_2 which causes the bandgap disordered. Also, our findings that the absorption fraction of strong oxygen plasma treated MoS_2 is higher than pristine MoS_2 provide a promising material candidate for future photocatalysis application.

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REFERENCES

1. **Mark, K.F., Lee, C., Hone, J., Shan, J., Heinz, T.** Atomically Thin MoS_2: A New Direct-Gap Semiconductor *Physical Review Letters* 105 (13) 2010: pp. 1368051 – 1368054. https://doi.org/10.1103/PhysRevLett.105.136805
2. **Yin, Z.Y., Li, H., Li, H., Jiang, L., Shi, Y.M., Sun, Y.H., Lu, G., Zhang, Q., Chen, X.D., Zhang, H.** Single-Layer MoS_2 Phototransistors *ACS Nano* 6 (1) 2012: pp. 74 – 80. https://doi.org/10.1021/nn2024557
3. **He, K., Poole, C., Mak, K.F., Shan, J.** Experimental Demonstration of Continuous Electronic Structure Tuning via Strain in Atomically Thin MoS_2 *Nano Letters* 13 (6) 2013: pp. 2931 – 2936. https://doi.org/10.1021/nl4013166
4. **Castellanos-Gomez, A., Roldan, R., Cappelluti, E., Buscema, M., Guinea, F., van der Zant, H.S.J., Steele, G.A.** Local Strain Engineering in Atomically Thin MoS_2 *Nano Letters* 13 (11) 2013: pp. 5361 – 5366. https://doi.org/10.1021/nl4013166
5. **Scalise, E., Houssa, M., Pourtois, G., Afanas'ev, V.V., Stesmans, A.** Strain Induced Semiconductor to Metal Transition in the Two-Dimensional Honeycomb Structure of MoS_2 *Nano Research* 5 (1) 2012: pp. 43 – 48. https://doi.org/10.1007/s12274-011-0183-0
6. **Ben, X., Park, H.S.** Strain Engineering Enhancement of Surface Plasmon Polariton Propagation Lengths for Gold Nanowires *Applied Physics Letters* 102 (4) 2013: pp. 041909. https://doi.org/10.1063/1.4790293
7. **Conley, H.J., Wang, B., Ziegler, J.I., Haglund, R.F., Pantelides, S.T., Bolotin, K.I.** Bandgap Engineering of Strained Monolayer and Bilayer MoS_2 *Nano Lett*ers 13 (8) 2013: pp. 3626 – 3630. https://doi.org/10.1021/nl4014748
8. **Nan, H.Y., Wang, Z.L., Wang, W.H., Liang, Z., Lu, Y., Chen, Q., He, D.W., Tan, P.H., Miao, F., Wang, X.R.** Strong Photoluminescence Enhancement of MoS_2 through

Defect Engineering and Oxygen Bonding *ACS Nano* 8 (6) 2014: pp. 5738 – 5745. https://doi.org/10.1021/nn500532f

9. **Shen, C., Zhang, J., Shi, D.X., Zhang, G.Y.** Photoluminescence Enhancement in Monolayer Molybdenum Disulfide by Annealing in Air *Acta Chimica Sinica* 73 (9) 2015: pp. 954 – 958. https://doi.org/10.6023/A15030220
10. **Kang, N.R., Paudel, H.P., Leuenberger, M.N., Tetard, L., Khondaker, S.I.** Photoluminescence Quenching in Single-Layer MoS_2 via Oxygen Plasma Treatment *The Journal of Physical Chemistry C* 118 (36) 2014: pp. 21258 – 21263. https://doi.org/10.1021/jp506964m
11. **Islam, M.R., Kang, N., Bhanu, U., Paudel, H.P., Erementchouk, M., Tetard, L., Leuenberger, M.N., Khondaker, S.I.** Tuning the Electrical Property Via Defect Engineering of Single Layer MoS_2 by Oxygen Plasma *Nanoscale* 6 (17) 2014: pp. 10033 – 10039. https://doi.org/10.1039/C4NR02142H
12. **Li, Y.G., Li, Y.L., Araujo, C.M., Luo, W., Ahuja, R.** Single-Layer MoS_2 as an Efficient Photocatalyst *Catalysis Science& Technology* 3 (9) 2013: pp. 2214. https://doi.org/10.1039/C3CY00207A
13. **Zhuang, H.L., Hennig, R.G.** Computational Search for Single-Layer Transition-Metal Dichalcogenide Photocatalysts *Journal of Materials Chemistry C* 117 (40) 2014: pp. 20440 – 20445. https://doi.org/10.1021/jp405808a
14. **Zhou, W.J., Yin, Z.Y., Du, Y.P., Huang, X., Zeng, Z.Y., Fan, Z.X., Liu, H., Wang, J.Y., Zhang, H.** Synthesis of Few-layer MoS_2 Nanosheet-coated TiO_2 Nanobelt Heterostructures for Enhanced Photocatalytic Activities *Small* 9 (1) 2013: pp. 140 – 147. https://doi.org/10.1002/smll.201201161
15. **Yu, H., Liao, M.Z., Zhao, W.J., Liu, G.D., Zhao, X.J., Wei, Z., Xu, X.Z., Liu, K.H., Hu, Z.H., Deng, K., Zhou, S.Y., Shi, J.A., Gu, L., Shen, C., Zhang, T.T., Du, L.J., Xie, L., Zhu, J.Q., Chen, W., Yang, R., Shi, D.X., Zhang, G.Y.** Wafer-Scale Growth and Transfer of Highly-Oriented Monolayer MoS_2 Continuous Films *ACS Nano* 11 (12) 2017: pp. 12001 – 12007. https://doi.org/10.1021/acsnano.7b03819
16. **Li, H., Zhang, Q., Yap, C.C.R., Tay, B.K., Edwin, T.H.T., Olivier, A., Baillargeat, D.** From Bulk to Monolayer MoS_2: Evolution of Raman Scattering *Advanced Functional Materials* 22 (7) 2012: pp. 1385 – 1390. https://doi.org/10.1002/adfm.201102111
17. **Chow, W.L., Luo, X., Quek, S.Q., Tay, B.K.** Evolution of Raman Scattering and Electronic Structure of Ultrathin Molybdenum Disulfide by Oxygen Chemisorption *Advanced Electronic Materials* 1 (1 – 2) 2015: pp. 1400037. https://doi.org/10.1002/aelm.201400037
18. **Chen, W., Zhao, J., Zhang, J., Gu, L., Yang, Z.Z., Li, X.M., Yu, H., Zhu, X.T., Yang, R., Shi, D.X., Lin, X.C., Guo, J.D., Bai, X.D., Zhang, G.Y.** Oxygen-Assisted Chemical Vapor Deposition Growth of Large Single-Crystal and High-Quality Monolayer MoS_2 *Journal of the Americann Chemical Society* 137 (50) 2015: pp. 15632 – 15635. https://doi.org/10.1021/jacs.5b10519
19. **Khondaker, S.I., Islam, M.R.** Bandgap Engineering of MoS2 Flakes via Oxygen Plasma: A Layer Dependent Study *Journal of Materials Chemistry C* 120 (25) 2016: pp. 13801 – 13806. https://doi.org/10.1021/acs.jpcc.6b03247
20. **Verma, P., Jain, K.P., Abbi, S.C.** Raman Scattering Probe of Ion-implanted and Pulse Laser Annealed GaAs *Journal of Applied Physics* 79 (8) 1996: pp. 3921 – 3926. https://doi.org/10.1063/1.361818
21. **Yang, J., Kim, S., Choi, W., Park, S.H., Jung, Y., Cho, M.H., Kim, H.** Improved Growth Behavior of Atomic-Layer-Deposited High-k Dielectrics on Multilayer MoS_2 by Oxygen Plasma Pretreatment *ACS Applied Materials & Interfaces* 5 (11) 2013: pp. 4739 – 4744. https://doi.org/10.1021/am303261c
22. **Brown, N.M.D., Cui, N.Y., McKinley, A.** An XPS Study of the Surface Modification of Natural MoS_2 Following Treatment in an RF-oxygen Plasma *Applied Surface Science* 134 (1 – 4) 1988: pp. 11 – 21. https://doi.org/10.1016/S0169-4332(98)00252-9
23. **Splendiani, A., Sun, L., Zhang, Y.B., Li, T.S., Kim, J., Chim, C.Y., Galli, G., Wang, F.** Emerging Photoluminescence in Monolayer MoS_2 *Nano Letters* 10 (4) 2010: pp. 1271 – 1275. https://doi.org/10.1021/nl903868w