



Cite this: *RSC Adv.*, 2018, 8, 12900

Homogeneity and tolerance to heat of monolayer MoS₂ on SiO₂ and h-BN†

Ho-Jong Kim,^{ad} Daehee Kim,^a Suyong Jung,^a Myung-Ho Bae,^a Sam Nyung Yi,^b Kenji Watanabe,^c Takashi Taniguchi,^c Soo Kyung Chang^d and Dong Han Ha^{id,*,a}

We investigated the homogeneity and tolerance to heat of monolayer MoS₂ using photoluminescence (PL) spectroscopy. For MoS₂ on SiO₂, the PL spectra of the basal plane differ from those of the edge, but MoS₂ on hexagonal boron nitride (h-BN) was electron-depleted with a homogeneous PL spectra over the entire area. Annealing at 450 °C rendered MoS₂ on SiO₂ homogeneously electron-depleted over the entire area by creating numerous defects; moreover, annealing at 550 °C and subsequent laser irradiation on the MoS₂ monolayer caused a loss of its inherent crystal structure. On the other hand, monolayer MoS₂ on h-BN was preserved up to 550 °C with its PL spectra not much changed compared with MoS₂ on SiO₂. We performed an experiment to qualitatively compare the binding energies between various layers, and discuss the tolerance of monolayer MoS₂ to heat on the basis of interlayer/interfacial binding energy.

Received 2nd March 2018
Accepted 26th March 2018

DOI: 10.1039/c8ra01849a

rsc.li/rsc-advances

Introduction

Transition metal dichalcogenides (TMDCs), such as molybdenum disulfide (MoS₂), molybdenum diselenide (MoSe₂), tungsten disulfide (WS₂), and tungsten diselenide (WSe₂), are two-dimensional (2D) semiconducting materials with strong photoluminescence (PL) emission in the visible or near-infrared spectral regions, which makes them attractive in the development of electronic and optoelectronic devices.^{1–3} TMDC monolayers exfoliated on various substrates are doped with electrons, or holes, induced by the charged impurities trapped at the TMDC-substrate interfaces. As the electrons/holes are depleted, PL emissions from TMDC monolayers are greatly enhanced in intensity and shift toward higher energies by the transformation of trions (charged excitons) into excitons.^{4–6} Thus, PL emission has been used to analyze the local charge density, defects, and strain on TMDC monolayers in combination with the results of Raman spectroscopy.^{7–13}

Properties of 2D materials depend on the number of layers, defects, substrate, and so on. Monolayer MoS₂ is a direct bandgap semiconductor with strong PL emission at 1.8–1.9 eV, while bulk MoS₂ has an indirect bandgap at an energy approximately 0.6 eV lower than the monolayer.^{14,15} Photoluminescence maps of monolayer MoS₂ on SiO₂ have shown

that the PL peak energy of the edges might differ from that of the crystalline basal plane (interior),¹⁶ and moreover, thermal annealing at 450 °C or higher creates defects on its basal plane with a large enhancement of PL emission.^{1,7} It has been reported that the PL/Raman properties as well as carrier mobility of MoS₂ are affected by the substrate because of the changes in the doping level, extrinsic charge trap density, and optical interference within the substrate.^{17–20} In the present work, we went further to investigate the homogeneity of doping and tolerance to heat of monolayer MoS₂ on substrates SiO₂ and hexagonal boron nitride (h-BN) using PL spectroscopy. We found that monolayer MoS₂ on SiO₂ decomposed and lost its inherent crystal structure during thermal annealing up to 550 °C and subsequent optical mapping processes, while monolayer MoS₂ on h-BN, having a homogenous PL spectra over the entire area including both basal plane and edge, was well preserved. Our results are expected to be useful in the development of nano-devices that require homogeneous 2D materials and reliable functionality under harsh environmental conditions, such as high temperatures.

Experimental

MoS₂ and h-BN flakes were prepared on Si substrates capped with 300 nm-thick SiO₂ by mechanically exfoliating MoS₂ (SPI Supplies) and h-BN crystals (National Institute for Materials Science) onto the substrates. MoS₂ flakes were also prepared on SiO₂/Si substrates coated with water-soluble polystyrenesulfonic (PSS) and poly(methyl methacrylate) (PMMA). MoS₂ monolayers were identified by optical microscopy and confirmed by Raman spectroscopy. For the fabrication of MoS₂ and h-BN vertical heterostructures, MoS₂ monolayers on the

^aQuantum Technology Institute, Korea Research Institute of Standards and Science, Daejeon 34113, Republic of Korea. E-mail: dhha@kriss.re.kr

^bDepartment of Electronic Material Engineering, Korea Maritime and Ocean University, Busan 49112, Republic of Korea

^cNational Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan

^dDepartment of Physics, Yonsei University, Seoul 03722, Republic of Korea

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ra01849a



PMMA layer, obtained by removing the PSS layer, were brought into contact with thick h-BN flakes previously prepared on SiO₂ using a micro-manipulator, followed by removal of the PMMA layer with acetone.²¹ The detailed fabrication process of the heterostructures is described in the ESI.† Samples were heat treated in a quartz tube (diameter = 90 mm) in a mixed atmosphere of Ar (1000 sccm) and H₂ (100 sccm). Annealing was staged and accumulated: 1 hour at 250 °C, followed by 1 hour at 450 °C, and finally 1 hour at 550 °C. After each stage, the furnace was cooled down to room temperature.

Raman and PL spectra were obtained under ambient conditions in backscattering geometry using a laser line of 532 nm as exciting light. Scattered light was analysed using a Horiba Jobin Yvon LabRAM HR spectrometer equipped with a cooled charge-coupled device. A grating of 600 grooves per mm was used for the PL experiment, while a grating of 1800 grooves per mm was used for the Raman experiment. The exciting light was focused on the samples with a diameter (full width at half maximum: FWHM) of approximately 0.65 μm using a 100× objective lens, and the total laser power on the samples was fixed below 300 μW to prevent local heating or the deterioration of sample MoS₂ by laser illumination.^{9,22,23} The Si Raman peak at 520.7 cm⁻¹ was used as an internal reference to calibrate the Raman peaks of MoS₂. In preliminary experiments, we monitored the PL and Raman spectra from an arbitrary point on monolayer MoS₂ for 2 hours under our experimental conditions, with no meaningful changes observed. That is, the intensities and positions of the PL and Raman peaks did not change even when the laser light continuously illuminated the same point for 2 hours, thus confirming the absence of laser heating effects on the PL and Raman spectra. Except for the acquisition time, all other experimental parameters for the PL and Raman measurements were fixed, such as confocal hole size and neutral density filter. The thickness of the h-BN flakes was measured by tapping-mode atomic force microscopy.

Results and discussion

Fig. 1(a) and (b) are optical microscopy images of MoS₂ flakes on SiO₂ and h-BN, respectively. The lower left of the MoS₂ flake on SiO₂ is monolayer, with the rest of the flake consisting of multilayer or bulk MoS₂. The MoS₂ flake on 97 nm thick h-BN is entirely monolayer except for the bottom end indicated by the arrow, with tiny yellow flakes of MoS₂ observed along the h-BN edge. Fig. 1(c) shows typical Raman spectra obtained from the basal plane of monolayer MoS₂, where two Raman peaks were observed: an E_{2g}¹ peak (in-plane vibration) and an A_{1g} peak (out-of-plane vibration).^{24–26} Compared with the MoS₂ on SiO₂, we notice that both Raman peaks are shifted for MoS₂ on h-BN. It has been reported that the E_{2g}¹ peak redshifts with increasing strain²⁵ and likewise, an increase of the interlayer van der Waals force also redshifts the E_{2g}¹ peak due to stacking-induced structural changes or long-range coulombic interlayer interactions.^{24,25,27} On the other hand, the position and FWHM of the A_{1g} peak were affected predominantly by local electron density: the peak blueshifted and sharpened with electron depletion due to reduced electron–phonon interactions,²⁸ although increased

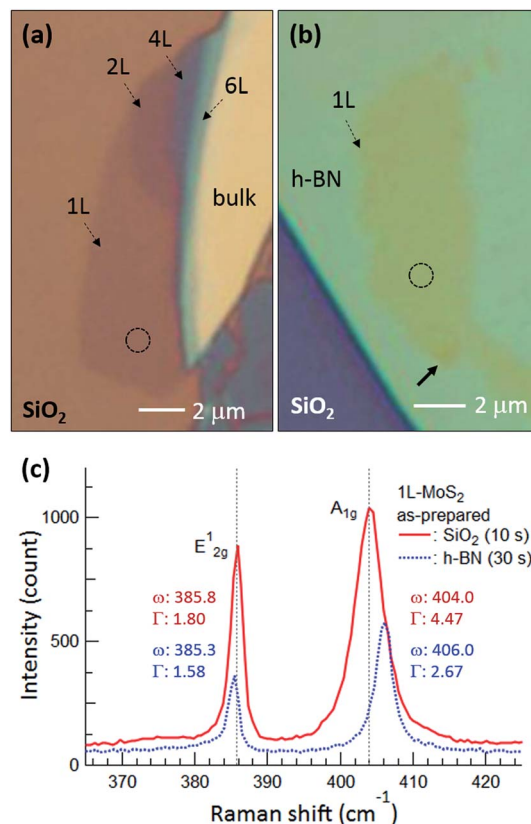


Fig. 1 Optical microscopy images of MoS₂ flakes on (a) SiO₂ and (b) h-BN, where 1L, 2L, 4L, and 6L indicate monolayer, bilayer, quadlayer, and hexalayer, respectively, estimated using the position difference between Raman E_{2g}¹ and A_{1g} peaks.²⁴ (c) Raman spectra of monolayer MoS₂ obtained from the dotted circles in (a) and (b). Red and blue curves and numbers represent MoS₂ on SiO₂ and h-BN, respectively, and the times in parentheses indicate the acquisition time. ω and Γ are position and FWHM of the Raman peaks. Gray dotted lines in (c) denote the positions of the E_{2g}¹ and A_{1g} peaks of monolayer MoS₂ on SiO₂.

interlayer interactions could also lead to a blueshift of the A_{1g} peak by increasing the restoring force.²⁶ The FWHM of the A_{1g} peak was 4.47 cm⁻¹ on SiO₂ but decreased to 2.67 cm⁻¹ on h-BN. The Raman spectra indicate that monolayer MoS₂ on h-BN was electron depleted compared with that on SiO₂ and/or that the monolayer MoS₂ attached more strongly to the h-BN than to the SiO₂, as discussed in detail later.

Annealing effects on the PL peak intensity (amplitude) maps of MoS₂ flakes are shown in Fig. 2. PL intensities significantly decreased with increasing thickness such that those of 6L and bulk MoS₂ appeared dark on the maps of Fig. 2(a)–(d). We noticed that the topography of the maps changed with each annealing, suggesting that the distribution of local charge density might be changed by annealing. A PL signal from MoS₂ was also observed along the edge of the thick h-BN where tiny flakes of MoS₂ were scattered.

The PL intensity of monolayer MoS₂ on SiO₂ was enhanced by approximately 20 times after annealing at 450 °C (see the scale bars next to the maps in Fig. 2). While the PL intensity of bilayer was slightly enhanced, those of multilayer and bulk were not changed on the whole, although they appear dark in

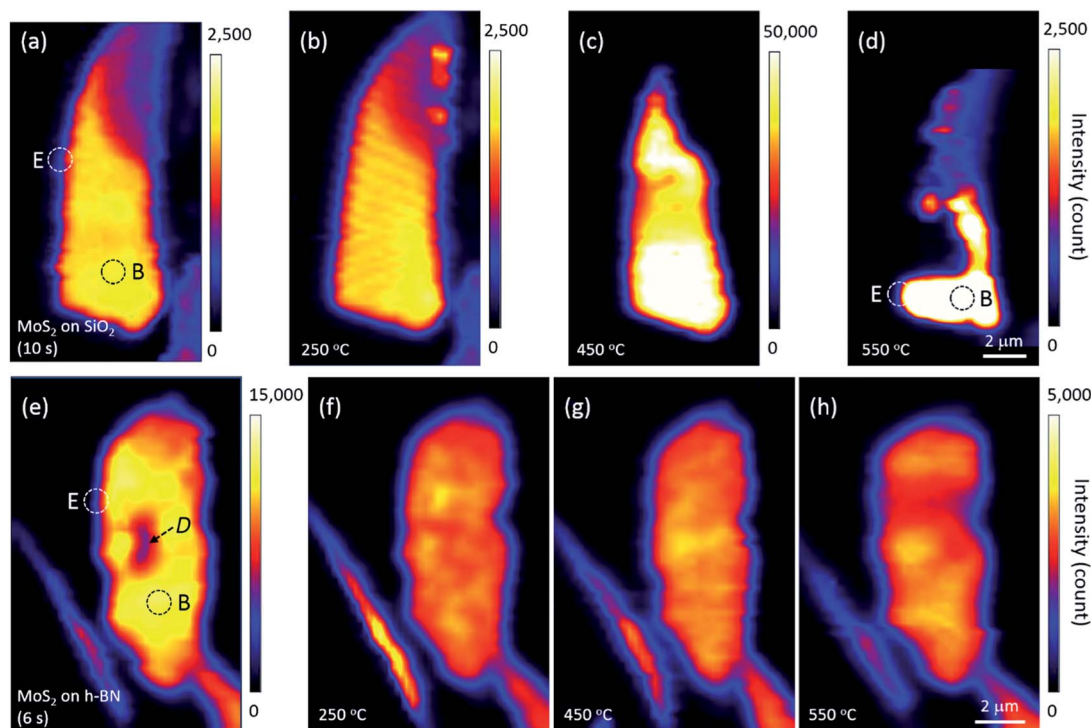


Fig. 2 Changes in the PL intensity maps of MoS₂ flakes on (a–d) SiO₂ and (e–h) h-BN upon annealing. Acquisition times for each measurement are denoted in parentheses. The mapping step was 0.25 μm. Dotted circles denote the typical edge (“E”) and basal plane (“B”) of monolayer MoS₂, and the dark area *D* in (e) is believed to be organic residue from the fabrication process that disappeared with annealing.

Fig. 2(c). However, the PL intensity of monolayer MoS₂ decreased significantly by annealing at 550 °C, with a large part disappearing from the PL map as shown in Fig. 2(d), indicating that monolayer MoS₂ on SiO₂ could no longer retain its intrinsic hexagonal crystal structure. Optical microscopy images showed that a part of the bilayer MoS₂ on SiO₂ was also decomposed, whereas thicker or multilayer MoS₂ was well preserved. Our results for MoS₂ on SiO₂ are consistent with the work of Liu and coworkers on oxygen etching activity with various numbers of graphene layers on SiO₂, which was discussed on the basis of substrate-induced deformations and preexisting defects;²⁹ they showed that oxidative etching proceeded faster in single layers than in multi-layers during annealing in an O₂/Ar gas flow, and moreover, etching did not occur on the defect-free basal plane of triple or thicker layer graphene at or below 600 °C.

Many experimental results have shown that defects can be created in monolayer MoS₂ on SiO₂ *via* thermal annealing, plasma treatment, electron/ion irradiation, or laser irradiation.^{1,2,7,8,30} Moreover, high-resolution transmission electron microscopy images have verified S-vacancies—the most common type of defect—in electron-irradiated monolayer MoS₂.³¹ Tongay, Nan, and their coworkers also reported that thermal annealing at 450 °C or higher creates S-vacancies by breaking the S–Mo–S bonds of MoS₂.^{1,7} Annealing at 550 °C removes even more S atoms, such that monolayer MoS₂ is considered to be fragmented into nano-domains that can be easily decomposed by laser light; this is in contrast to thicker or multilayer MoS₂ in which all atoms are bonded horizontally and

vertically. Here, Fig. 2 suggests that the interfacial interaction between MoS₂ and SiO₂ is weaker than the interlayer interaction between layers of MoS₂ because of impurities at the MoS₂–SiO₂ interface and SiO₂ surface roughness.^{19–21} Previous results on the comparison of binding energies between the interlayer/interface support our results. The interlayer binding energy between MoS₂ layers calculated using advanced density-functional theory was 330 mJ m^{−2}, and the energy required to peel off a single layer from the surface of a multilayer structure increased with the number of layers.³² On the other hand, the interfacial binding energy of MoS₂ on SiO₂ substrates measured by Deng and coworkers was 170 mJ m^{−2}.³³

We argue that the tolerance of monolayer MoS₂ to heat is influenced by the interlayer/interfacial binding energy as well as the interatomic bonding forces in the layer. In fact, monolayer MoS₂ on h-BN was well preserved even after annealing at 550 °C and subsequent PL mapping. Fig. 2 strongly indicates that due to the atomically flat, impurity-free surface of newly exfoliated h-BN,^{19,21} interfacial binding between MoS₂ and h-BN is stronger than that between MoS₂ and SiO₂, which is consistent with the results of the Raman experiments shown in Fig. 1(c). Our results are in good agreement with the dependence of MoS₂ interfacial binding energy on substrate roughness as measured by Deng and coworkers.³³ Strong interfacial binding is considered to enhance the tolerance of monolayer MoS₂ on h-BN to heat.

To support our argument, we performed an experiment to qualitatively compare the binding energies between the various

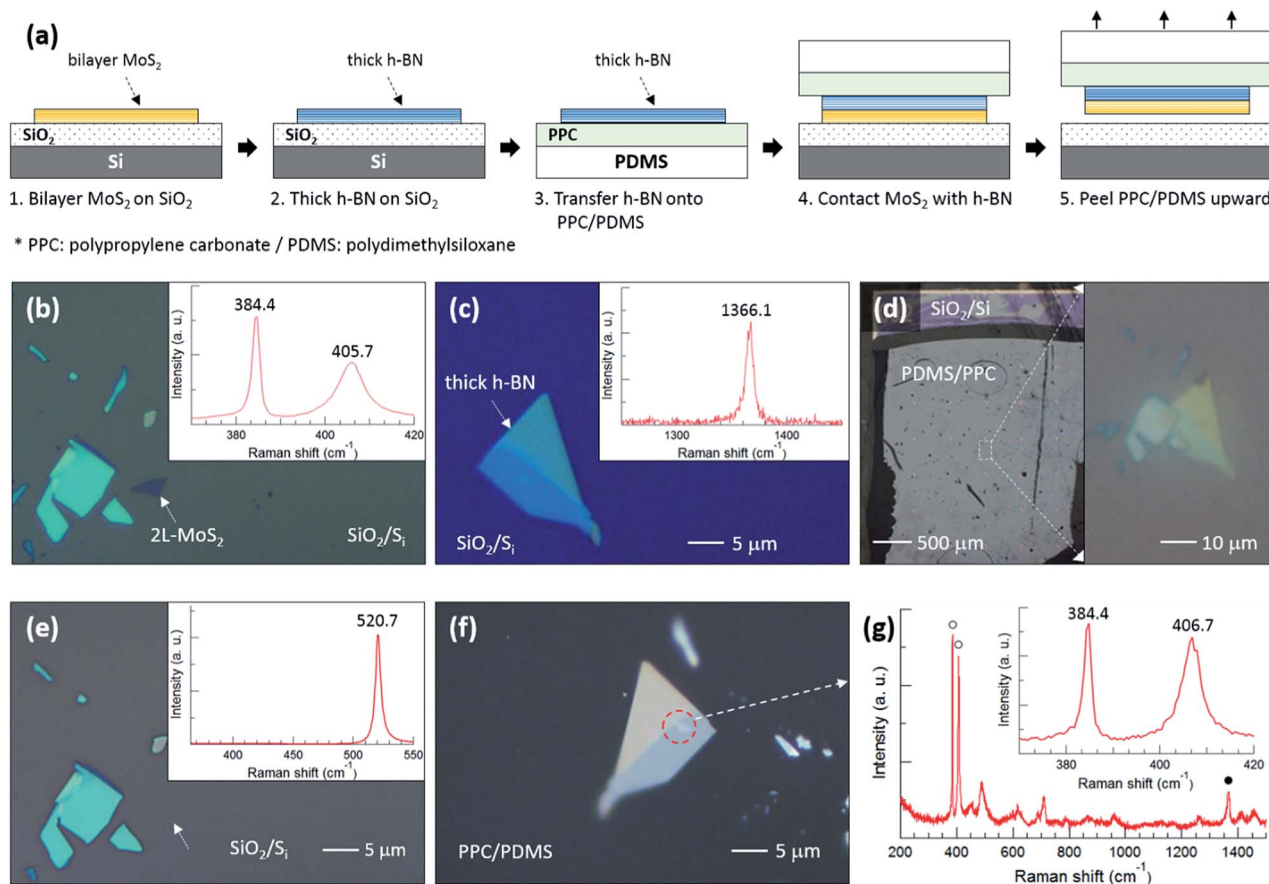


Fig. 3 (a) Schematic diagram of the experimental process to qualitatively compare the binding energies between various layers. (b and c) Optical microscopy images with corresponding Raman spectra for steps 1 and 2 in (a), respectively. (d) Optical microscopy image for steps 3 and 4 in (a). The right image is an enlargement of the white rectangular region on the left. (e and f) Optical microscopy images for the lower and upper sections of step 5 in (a), respectively, with corresponding Raman spectrum in (e). (g) Raman spectrum obtained from the red dotted circle in (f).

layers as summarized in Fig. 3. The flake designated by a white dotted arrow in Fig. 3(b) is bilayer MoS₂, the thickness of which was determined using the position difference between the E_{2g}¹ and A_{1g} peaks in the inset Raman spectrum. The h-BN flake in Fig. 3(c) was also confirmed using the Raman spectrum. Fig. 3(d) shows optical images of PDMS/PPC/h-BN placed on MoS₂/SiO₂/Si; the right image demonstrates that the thick h-BN is precisely positioned on the bilayer MoS₂. Fig. 3(e) shows that the bilayer MoS₂ was completely separated from SiO₂, as only a single Si Raman peak at 520.7 cm⁻¹ was observed from the position where bilayer MoS₂ was located. The bilayer MoS₂ flake was then transferred onto the thick h-BN, as can be observed in the red dashed circle in Fig. 3(f), after peeling PDMS/PPC upward. In the Raman spectrum of Fig. 3(g) obtained from the red dashed circle, open (closed) circles denote Raman peaks of bilayer MoS₂ (h-BN), while other peaks are from the PDMS/PPC. The inset in Fig. 3(g) shows the Raman spectrum of the MoS₂ flake in detail. The A_{1g} peak at higher frequency was blueshifted but the position of the E_{2g}¹ peak at lower frequency was unchanged compared with those of the MoS₂ flake on SiO₂, indicating a depletion of electrons from MoS₂ on h-BN compared with that on SiO₂. The position difference between the E_{2g}¹ and A_{1g} peaks verifies that it is bilayer—not

monolayer—MoS₂. That is, bilayer MoS₂ was not separated between the layers of MoS₂ nor at the interface between MoS₂ and SiO₂. Our results demonstrate that the MoS₂–SiO₂ interfacial binding energy is weaker than the MoS₂–MoS₂ interlayer binding energy as well as the MoS₂–h-BN interfacial binding energy.

Fig. 4 displays PL spectra obtained from the typical edge and basal plane of monolayer MoS₂ on SiO₂ and h-BN. Compared with the PL spectrum of the as-prepared MoS₂ on SiO₂, that of MoS₂ on h-BN greatly increased in intensity even though the acquisition time was reduced from 10 to 6 s; further, the PL peak due to valence band splitting disappeared.^{6,14} Moreover, the peak position shifted from 1.83 to 1.89 eV and the FWHM decreased from 0.11 to 0.04 eV on h-BN, verifying that MoS₂ on h-BN was electron depleted compared with that on SiO₂ due to the impurity-free surface of h-BN.^{1,4,19}

The basal plane of the as-prepared monolayer MoS₂ on SiO₂ had a PL maximum of negatively charged trions at approximately 1.83 eV, whereas the edge had a single PL peak of excitons at approximately 1.87 eV. This can be ascribed to local electron depletion by foreign molecules adsorbed on the dangling bonds along the edge. The edge was defined as the

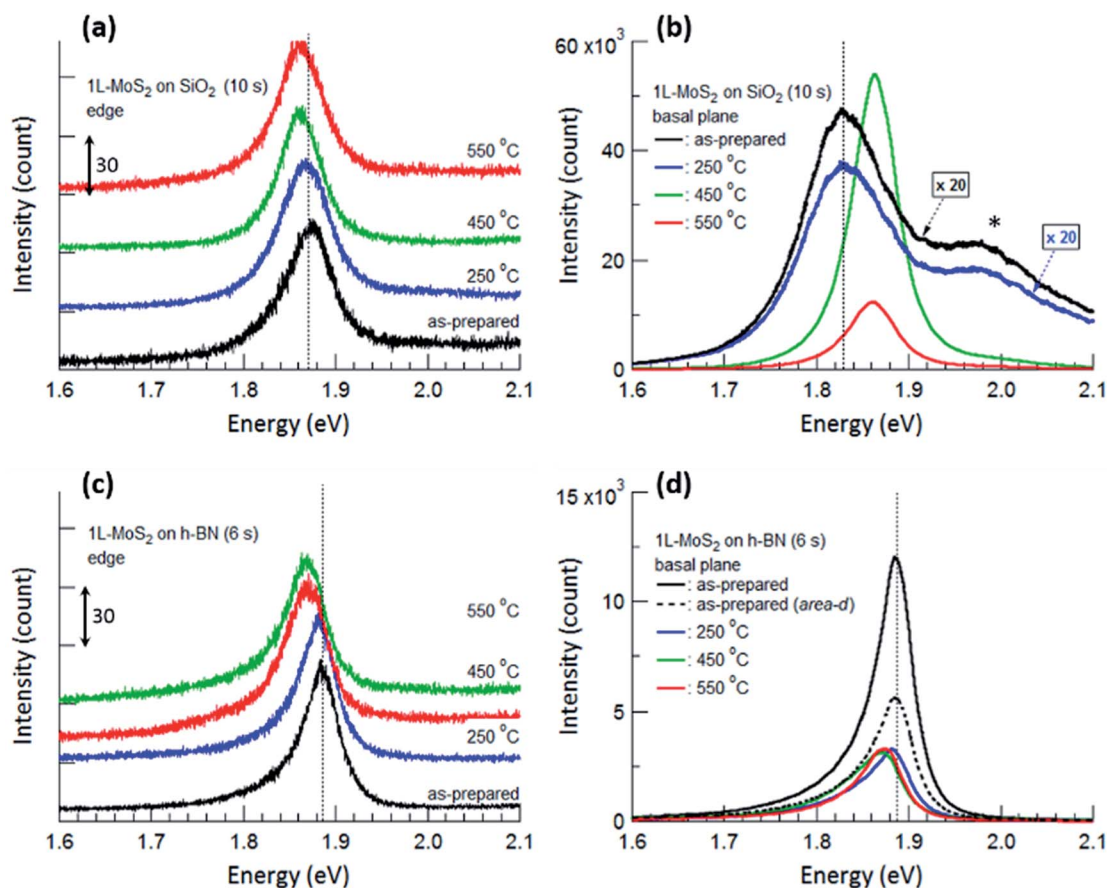


Fig. 4 PL spectra obtained from the edge (a and c) and basal plane (b and d) of monolayer MoS₂ shown in Fig. 2. The PL spectra of as-prepared MoS₂ and MoS₂ annealed at 250 °C are multiplied by 20 in (b). The shoulder peak at 1.98 eV marked by an asterisk in (b) is due to the splitting of the monolayer MoS₂ valence band. PL spectra obtained from the edges are shifted vertically for ease of viewing, and the unit value of the Y-axis in (a) and (c) is 30 count. The times in parentheses denote the acquisition time for each measurement. Vertical dotted lines denote the PL peak positions of the as-prepared MoS₂ monolayers.

points corresponding to the initial upturns of the PL intensity profiles across the edge of MoS₂ (to be precise, the PL signal of the edge is the sum of the signals from the true edge and the basal plane near the edge since the laser light has a finite size). The difference in PL spectra between the basal plane and the edge of MoS₂ on SiO₂ was evident even after annealing at 250 °C. However, annealing at 450 °C resulted in remarkable changes in the PL spectrum of the basal plane *via* the chemisorption of foreign molecules, such as O₂ and H₂, at newly created defects; such changes include a shift of the peak position to approximately 1.86 eV, an increase in the peak intensity by more than 20 times, and the disappearance of the shoulder peak at 1.98 eV. On the other hand, the PL peak of the edge only slightly shifted toward a lower energy, such that both PL spectra of the basal plane and edge of MoS₂ on SiO₂ had a single peak at the same position of approximately 1.86 eV.

For monolayer MoS₂ on h-BN, both PL peaks of the basal plane and edge of MoS₂ unexpectedly had maxima at the same energy, as shown in Fig. 4(c) and (d), even though foreign molecules were considered to be chemisorbed on the edge. This tendency was not changed by thermal annealing up to 550 °C. Fig. 4 indicates that the PL properties and doping of electron-

depleted MoS₂ on h-BN is insensitive to the adsorption of electron-accepting molecules, which is contrary to the case of monolayer MoS₂ on SiO₂. In other words, electron transfer from the electron-depleted MoS₂ to the adsorbed molecules is considered to be insignificant compared with that from MoS₂ on SiO₂, on which the electron transfer from an S-vacancy of MoS₂ to a chemisorbed O₂ molecule reaches 0.997 *e*.⁷ Our results show that with or without annealing, local electron density was nearly homogeneous over the entire monolayer MoS₂ on h-BN, including both basal plane and edge.

Thermal annealing decreased the PL intensity of monolayer MoS₂ on h-BN; in addition, the PL peaks of both the basal plane and edge of MoS₂ shifted toward a lower energy. First-principle calculations showed that both O₂ and H₂ molecules physisorbed on monolayer MoS₂ act as electron acceptors with charge transfer values of 0.04 *e* and 0.004 *e* for O₂ and H₂, respectively. In addition, the adsorption energies for O₂ and H₂ on ideal MoS₂ were calculated to be -116 and -82 meV.³⁴ Replacing some O₂ molecules physisorbed on the basal plane of MoS₂ with H₂ molecules during annealing in a H₂/Ar gas flow could increase the local electron density on the basal plane, resulting in the changes in the intensity and position of PL

spectrum. Our results show that the electron-depleted MoS₂ on h-BN responds to the substitution of O₂ with H₂ which results in the electron-doping, although it was insensitive to the adsorption of electron-accepting molecules. Nevertheless, we consider that few of the O₂ molecules chemisorbed on the edge or other defects could be removed during thermal annealing since the binding energy of an O₂ molecule on an S-vacancy of MoS₂ calculated by first-principle method is -2.395 eV.⁷

Conclusions

The PL spectra of the edge for the as-prepared MoS₂ on SiO₂ differed in peak position and shape from those of the basal plane, but annealing at 450 °C rendered the PL spectra homogeneous by creating many defects on the basal plane. On the other hand, MoS₂ on h-BN demonstrated a homogenous PL spectra over the entire area regardless of annealing, although foreign molecules were expected to chemisorb to the dangling bonds along the edge. Electron-depleted MoS₂ on h-BN responded to the adsorption of foreign molecules which results in the electron-doping, while it was insensitive to the adsorption of electron-accepting molecules. Monolayer MoS₂ on SiO₂ was further decomposed and almost lost its inherent crystal structure during thermal annealing at 550 °C and subsequent optical mapping process, while monolayer MoS₂ was well preserved on h-BN. We contend that the tolerance of monolayer MoS₂ to heat is influenced by interlayer/interfacial binding energy as well as the interatomic bonding forces in the layer, strongly supported by experimental results on the comparison of binding energies between various layers.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by the National Research Foundation of Korea (NRF) (Grant No. 2015R1A2A1A10056103) funded by the Ministry of Education, and also supported by the Korea-Hungary joint laboratory program for Nanosciences through the National Research Council of Science and Technology.

References

- 1 S. Tongay, J. Zhou, C. Ataca, J. Liu, J. S. Kang, T. S. Matthews, L. You, J. Li, J. C. Grossman and J. Wu, *Nano Lett.*, 2013, **13**, 2831–2836.
- 2 S. Tongay, J. Suh, C. Ataca, W. Fan, A. Luce, J. S. Kang, J. Liu, C. Ko, R. Raghunathanan, J. Zhou, F. Ogletree, J. Li, J. C. Grossman and J. Wu, *Sci. Rep.*, 2013, **3**, 2657.
- 3 F. Xia, H. Wang, D. Xiao, M. Dubey and A. Ramasubramaniam, *Nat. Photonics*, 2014, **8**, 899–907.
- 4 S. Mouri, Y. Miyauchi and K. Matsuda, *Nano Lett.*, 2013, **13**, 5944–5948.
- 5 N. Scheuschner, O. Ochedowski, A.-M. Kaulitz, R. Gillen, M. Schleberger and J. Maultzsch, *Phys. Rev. B*, 2014, **89**, 125406.
- 6 J. S. Ross, S. Wu, H. Yu, N. J. Ghimire, A. M. Jones, G. Aivazian, J. Yan, D. G. Mandrus, D. Xiao, W. Yao and X. Xu, *Nat. Commun.*, 2013, **4**, 1474.
- 7 H. Nan, Z. Wang, W. Wang, Z. Liang, Y. Lu, Q. Chen, D. He, P. Tan, F. Miao, X. Wang, J. Wang and Z. Ni, *ACS Nano*, 2014, **8**, 5738–5745.
- 8 H. M. Oh, G. H. Han, H. Kim, J. J. Bae, M. S. Jeong and Y. H. Lee, *ACS Nano*, 2016, **10**, 5230–5236.
- 9 E. Kim, C. Ko, K. Kim, Y. Chen, J. Suh, S.-G. Ryu, K. Wu, X. Meng, A. Suslu, S. Tangay, J. Wu and C. P. Grigoropoulos, *Adv. Mater.*, 2016, **28**, 341–346.
- 10 H. R. Gutiérrez, N. Perea-López, A. L. Elías, A. Berkdemir, B. Wang, R. Lv, F. López-Urías, V. H. Crespi, H. Terrones and M. Terrones, *Nano Lett.*, 2013, **13**, 3447–3454.
- 11 W. Shi, M.-L. Lin, Q.-H. Tan, X.-F. Qiao, J. Zhang and P.-H. Tan, *2D Mater.*, 2016, **3**, 025016.
- 12 A. Michail, N. Delikoukos, J. Parthenios, C. Galiotis and K. Papagelis, *Appl. Phys. Lett.*, 2016, **108**, 173102.
- 13 W. Su, H. Dou, J. Li, D. Huo, N. Dai and L. Yang, *RSC Adv.*, 2015, **5**, 82924–82929.
- 14 A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli and F. Wang, *Nano Lett.*, 2010, **10**, 1271–1275.
- 15 K. F. Mak, C. Lee, J. Hone, J. Shan and T. F. Heinz, *Phys. Rev. Lett.*, 2010, **105**, 136805.
- 16 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.*, 2013, **12**, 554–561.
- 17 Y. Li, Z. Qi, M. Liu, Y. Wang, X. Cheng, G. Zhang and L. Sheng, *Nanoscale*, 2014, **6**, 15248–15254.
- 18 M. Buscema, G. A. Steele, H. S. J. van der Zant and A. Castellanos-Gomez, *Nano Res.*, 2014, **7**, 561–571.
- 19 M. Y. Chan, K. Komatsu, S.-L. Li, Y. Xu, P. Darmawan, H. Kuramochi, S. Nakaharai, A. Aparecido-Ferreira, K. Watanabe, T. Taniguchi and K. Tsukagoshi, *Nanoscale*, 2013, **5**, 9572–9576.
- 20 Y. Guo, X. Wei, J. Shu, B. Liu, J. Yin, C. Guan, Y. Han, S. Gao and Q. Chen, *Appl. Phys. Lett.*, 2015, **106**, 103109.
- 21 C. R. Dean, A. F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard and J. Hone, *Nat. Nanotechnol.*, 2010, **5**, 722–726.
- 22 S. Sahoo, A. P. S. Gaur, M. Ahmadi, M. J.-F. Guinel and R. S. Katiyar, *J. Phys. Chem. C*, 2013, **117**, 9042–9047.
- 23 N. Lundt, E. Cherotchenko, O. Iff, X. Fan, Y. Shen, P. Bigenwald, A. V. Kavokin, S. Höfling and C. Schneider, *Appl. Phys. Lett.*, 2018, **112**, 031107.
- 24 C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone and S. Ryu, *ACS Nano*, 2010, **4**, 2695–2700.
- 25 C. Rice, R. J. Young, R. Zan, U. Bangert, D. Wolverson, T. Georgiou, R. Jalil and K. S. Novoselov, *Phys. Rev. B*, 2013, **87**, 081307(R).
- 26 A. G. Bagnall, W. Y. Liang, E. A. Marseglia and B. Welber, *Physica B+C*, 1980, **99**, 343–346.

- 27 B. Chakraborty, H. S. S. Ramakrishna Matte, A. K. Sood and C. N. R. Rao, *J. Raman Spectrosc.*, 2013, **44**, 92–96.
- 28 B. Chakraborty, A. Bera, D. V. S. Muthu, S. Bhowmick, U. V. Waghmare and A. K. Sood, *Phys. Rev. B*, 2012, **85**, 161403(R).
- 29 L. Liu, S. Ryu, M. R. Tomasik, E. Stolyarova, N. Jung, M. S. Hybertsen, M. L. Steigerwald, L. E. Brus and G. W. Flynn, *Nano Lett.*, 2008, **8**, 1965–1970.
- 30 S. Mignuzzi, A. J. Pollard, N. Bonini, B. Brennan, I. S. Gilmore, M. A. Pimenta, D. Richards and D. Roy, *Phys. Rev. B*, 2015, **91**, 195411.
- 31 H.-P. Komsa, J. Kotakoski, S. Kurasch, O. Lehtinen, U. Kaiser and A. V. Krasheninnikov, *Phys. Rev. Lett.*, 2012, **109**, 035503.
- 32 T. Björkman, A. Gulans, A. V. Krasheninnikov and R. M. Nieminen, *Phys. Rev. Lett.*, 2012, **108**, 235502.
- 33 S. Deng, E. Gao, Z. Xu and V. Berry, *ACS Appl. Mater. Inter.*, 2017, **9**, 7812–7818.
- 34 Q. Yue, Z. Shao, S. Chang and J. Li, *Nanoscale Res. Lett.*, 2013, **8**, 425.