**Effect of rapid thermal annealing in vacuum on the structural and optical properties of $MoS_2$ flakes in solution**

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## Abstract

Recently, top-down and bottom-up methods have been developed to fabricate single-layer (1L) $MoS_2$ nanosheets. The top-down method focuses on the mechanical [1-2] and solution-based exfoliation [3-4] of bulk $MoS_2$ crystals. Although the mechanical exfoliation of $MoS_2$ can produce the pristine 1L $MoS_2$ with high quality, its yield and reproducibility are low. The solution-based exfoliated $MoS_2$ is often accompanied by residual chemicals from the solution used, which in turn affects the properties of $MoS_2$ nanosheets [3]. In the previous studies, a thermal annealing method has been used in layer thinning and etching of mechanically exfoliated $MoS_2$ for achieving single-layer $MoS_2$ from multi-layer $MoS_2$ [1]. In this work, $MoS_2$ flakes of ~ 400 nm lateral size in ethanol solution were used to investigate the thermal annealing mechanism of $MoS_2$ flakes. For single-layer $MoS_2$ nanosheets, $MoS_2$ flakes solution was dropped on the whole surface of 100 nm $SiO_2$ substrate and subsequently, $MoS_2$ flakes were heated by rapid thermal annealing at various temperatures from 100 to 500 $^oC$ under vacuum for 10 min. The annealed samples were characterized by optical microscopy, Raman spectroscopy, and atomic force microscopy (AFM). Fig. 1 shows the optical images of $MoS_2$ nanosheets on 100 nm $SiO_2$ /Si, in which different color contrast represents different layer thickness of $MoS_2$. [5] Fig. 1 (a) shows the $MoS_2$ flakes before thermal annealing, which consists mainly of 6L nanosheets. Subsequently, thermal annealing was performed at 200 °C for 10 min. The formation of 2L $MoS_2$ nanosheet by thinning was observed after thermal annealing, as shown in Fig 1 (b). Raman spectra of the transferred layers exhibited two intense features, $E^1_{2g}$ and $A_{1g}$ peaks at ~ 384 and ~ 403 $cm^{-1}$, respectively, uniquely characteristic of $MoS_2$ film. The two Raman modes, $E^1_{2g}$ and $A_{1g}$, exhibited sensitive thickness dependences, with the frequency of the former decreasing and that of the latter increasing with thickness [6]. The annealing behaviors show several intriguing characteristics. Most strikingly, we find that the $E^1_{2g}$ vibration softens (blue shifts), while the $A_{1g}$ vibration stiffens (red shifts) with increasing annealing temperature, as shown in Fig 2. This Raman analysis reveals optimum annealing temperature of 200 $^oC$ for the synthesis of smallest-layer-number and best-quality $MoS_2$. The thickness of $MoS_2$ estimated by AFM was consistent with the Raman results. As a result of thermal annealing, the $MoS_2$ nanosheet is thinned, possibly due to its oxidation to form $MoO_3$. Possible mechanisms are proposed to explain the formation processes of $MoS_2$ nanosheets from $MoS_2$ flakes during the annealing.

## References

[1] H. Li, Z. Yin, Q. He, H. Li, X. Huang, G. Lu, D. W. H. Fam, A. I. Y. Tok, Q. Zhang, and H. Zhang,

Small, **1** (2012) 63-67

[2] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, Proc. Natl. Acad. Sci. USA, **30** (2005) 10451-10453

[3] Z. Zeng, Z. Yin, X. Huang, H. Li, Q. He, G. Lu, F. Boey, and H. Zhang, Angew. Chem. Int. Ed. **47** (2011) 11093-11097

[4] J. N. Coleman, M. Lotya, A. O'Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V. Shvets, S. K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Moriarty, A. Shmeliov, R. J. Nicholls, J. M. Perkins, E. M. Grieveson, K. Theuwissen, D. W. McComb, P. D. Nellist, and V. Nicolosi, Science, **6017** (2011) 568-571

[5] H. Li, G. Lu, Z. Yin, Q. He, H. Li, Q. Zhang, and H. Zhang, Small **5** (2012) 682-686

[6] Changgu Lee, Changgu Lee, Hugen Yan, Louis E. Brus, Tony F. Heinz, James Hone, and Sunmin Ryu, Acs Nano, **5** (2010) 2695-2700.

**Figures**

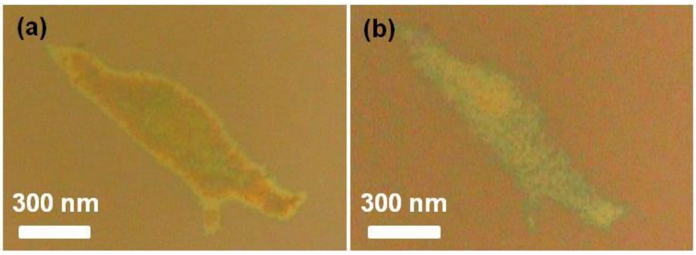


Fig. 1. Optical images of $MoS_2$ flacks before (a) and after (b) thermal annealing in vacuum for 10 min at 200 ° C

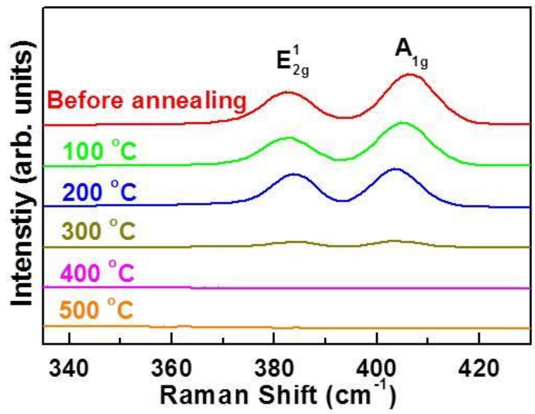


Fig. 2. Raman spectra of $MoS_2$ flakes for various annealing temperatures together with the spectrum before thermal annealing