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 °C 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, $E_{2g}^1$ and $A_{1g}$ peaks at ~ 384 and ~ 403 cm$^{-1}$, respectively, uniquely characteristic of MoS$_2$ film. The two Raman modes, $E_{2g}^1$ 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 $E_{2g}^1$ 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 °C 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

Small, 1 (2012) 63-67


Figures

Fig. 1. Optical images of MoS$_2$ flakes 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