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Patterning of Periodic Ripples in Monolayer MoS_2 by Using Laser Irradiation

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We have investigated the effect of laser irradiation on monolayer MoS_2 and observed the swelling-up of the monolayer from the SiO_2 substrate upon laser illumination. The mismatch in the thermal expansion between the substrate and MoS_2 can result in the structural deformation. Employing this method, one can induce structural deformation in a desired pattern, and one can demonstrate the patterning of periodic ripples in monolayer MoS_2 by using laser irradiation. The controlled fabrication of the ripple structure may be instrumental in understanding the effect of ripples on the interesting physical properties of monolayer MoS_2.

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I. INTRODUCTION

Two-dimensional (2D) transition-metal dichalcogenide materials such as MoS_2 have recently attracted much research interest for future electronics and optoelectronics due to their unique properties [1–6]. Structural defects such as ripples always modulate the physical properties of 2D materials, and ripples have been explored in monolayer (1L) MoS_2 [7–11]. Controlled fabrication of a periodic ripple structure will be instrumental in understanding the effect of ripples on the interesting physical properties of monolayer MoS_2. On the other hand, laser irradiation has been utilized to thin multilayer graphene or MoS_2 into a monolayer [12, 13]. In this letter, we report that by using laser irradiation, one can locally induce structural deformation and draw desired patterns of deformation down to a feature size of ∼250 nm in an atomic layer of MoS_2. We demonstrate a periodic ripple structure patterned in a MoS_2 monolayer by using simple laser irradiation.

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II. EXPERIMENTS AND DISCUSSION

Our experiments were performed on both exfoliated MoS_2 and MoS_2 monolayers directly grown on SiO_2 substrates by using a chemical vapor deposition (CVD) method. The thickness of MoS_2 was monitored by using optical contrast microscopy and was confirmed by using atomic force microscopy (AFM) and Raman spectroscopy.

Figure 1(a) shows a schematic diagram of our experimental method to locally modify the structure of a MoS_2 monolayer by irradiating it with a laser. A confocal Raman measurement system (Witec alpha 300R) was adapted. The wavelength of the laser was 532 nm, and the spot size was ∼1 μm. In Fig. 1(b), the laser was illuminated onto three different spots of an exfoliated MoS_2 monolayer prepared on a SiO_2 substrate. The power of the laser was 5 mW, and the illumination lasted 60 s on each spot. As shown in the optical microscopy image (Fig. 1(b)), the colors of the spots exposed to the laser were clearly changed. To further study the change in the structure, we used AFM to investigate the area within the black dashed rectangle. The AFM image is displayed in Fig. 1(c). Interestingly, we find that the spot exposed to the laser (∼1 μm^2) swells out from the substrate. The AFM height profile along the spot (Fig. 1(d)) reveals that it swells up by ∼1 nm. Notice that the ratio of the height to the width is about 1 to 1000. As an ori-

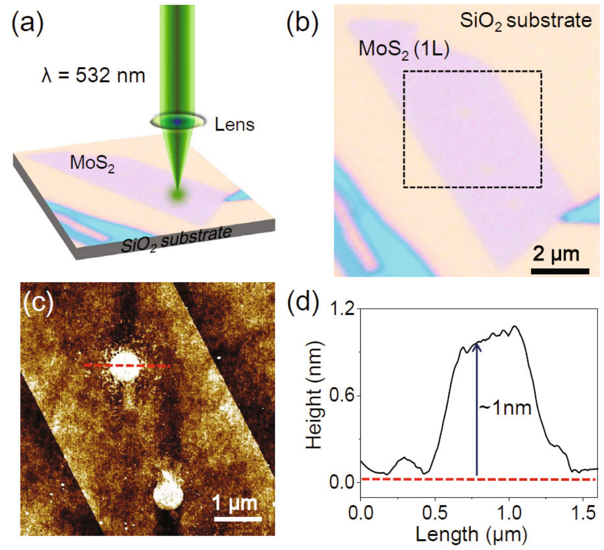

Fig. 1. (Color online) (a) Schematic diagram of a MoS_2 monolayer locally deformed by using laser illumination. (b) Optical microscopy image of a MoS_2 monolayer after laser irradiation (5 mW, 60 s) onto 3 different spots in the monolayer. (c) Atomic force microscopy image, zoomed in on the dashed rectangular area shown in (b). Spots exposed to the laser swell out from the substrate. (d) AFM height profile along the dashed red line indicated in (c).

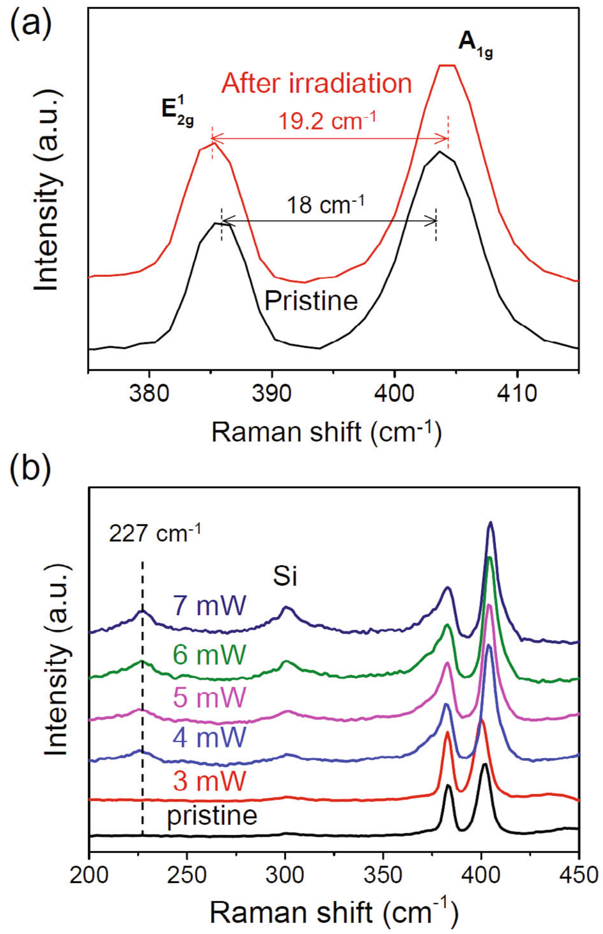

Fig. 2. (Color online) (a) Raman spectrum of the swollen-up MoS_2 monolayer (red) compared to that of pristine one (black). (b) Raman spectra of MoS_2 monolayer samples swollen up by using laser irradiation at various laser powers. The peak observed at $\sim$227 cm^{-1} is attributed to the structural disorder, produced by the swelling of MoS_2 surface.

gin of the formation of such a swollen-up structure, one can suggest the mismatch in the thermal expansion coefficients [10] between the SiO_2 substrate ($\sim 10^{-7}$ K^{-1}) and the MoS_2 ($\sim 10^{-5}$ K^{-1}). The spot exposed to the laser experiences a local increase in temperature. While heating or cooling, the local strain generated by the mismatch in the thermal expansion coefficient can be relieved by forming a swollen-up structure. In addition, the expansion of the gas trapped between the MoS_2 and the substrate may affect the formation of the swollen-up structure. The gap between the MoS_2 and the substrate change the diffraction of light, resulting in a change in the optical microscopy image.

Figure 2(a) presents the Raman spectrum of the swollen-up MoS_2 monolayer after 5-mW laser irradiation. We compare the Raman spectrum (red) to that of the pristine MoS_2 monolayer (black) measured before the irradiation. Raman spectra were obtained with the same confocal Raman measurement system, but with a laser power of 0.5 mW to avoid further structural deformation. For the pristine MoS_2 monolayer, two dominant Raman peaks are located each at $\sim$386 and $\sim$404 cm^{-1} corresponding to the E^1_{2g} and the A_{1g} modes, respectively. E^1_{2g} is the in-plane vibration mode between a Mo atom and two S atoms, and A_{1g} is the out-of-plane vibration mode between S atoms [14]. The frequency difference between the E^1_{2g} and the A_{1g} modes is generally used to determine the number of layers in MoS_2, and the observed value of $\sim$18 cm^{-1} confirms that our MoS_2 flake is a monolayer [14,15]. After the laser irradiation, the E^1_{2g} peak exhibits a red-shift by $\sim$0.6 cm^{-1} and the A_{1g} peak a blue-shift by $\sim$0.6 cm^{-1}, leading to a larger frequency difference, 19.2 cm^{-1}, between the two Raman modes. A red-shift of the E^1_{2g} peak has been reported for MoS_2 under a uniaxial strain [8,16–19] and for MoS_2 subjected to defects [20,21]. One can first consider the effect of the strain generated in the swollen-up structure. According to previous studies [8, 16–19], the observed red-shift of E^1_{2g} peak ($\sim$0.6 cm^{-1}) requires a strain of $\sim$1 %. However, this amount of strain is unlikely to exist in the swollen-up structure as the height-to-width ratio is $\sim$1/1000.

Turning to the effect of disorder, we have investigated in Fig. 2(b) the Raman spectra of MoS_2 monolayer samples, swollen up by laser irradiation at different laser powers. With increasing laser power, we observed in the Raman spectra increases in full widths at half maximum

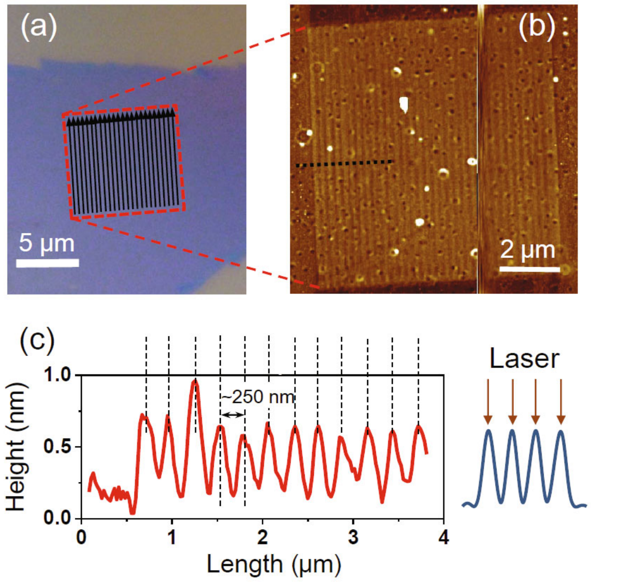

Fig. 3. (Color online) (a) Optical image of a CVD-grown MoS_2 monolayer. Black lines present periodic sweeping of a 5-mW laser at line intervals of 250 nm, imposing a periodic ripple structure inside a red dashed square. (b) Zoomed-in AFM image of the ripple-patterned MoS_2 monolayer. (c) AFM height profile along the black dotted line indicated in (b) shows in the monolayer a periodic modulation of the height due to the laser illumination. The lines irradiated by the laser swell up periodically from the substrate.

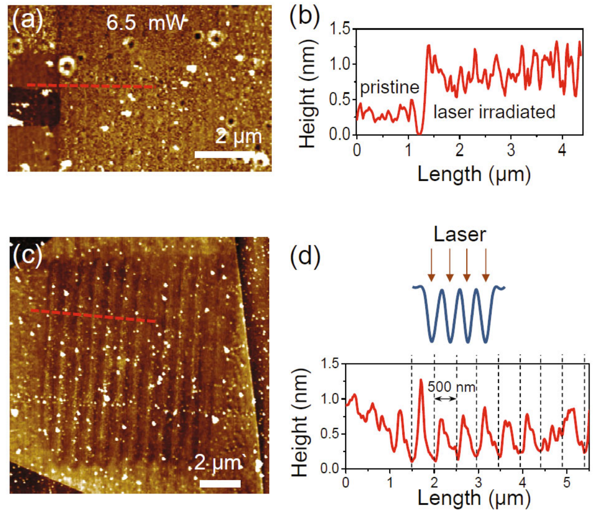

Fig. 4. (Color online) (a) AFM image of a part of the MoS_2 monolayer after sweeping a laser beam of 6.5 mW at periodic line-intervals of 250 nm for an area of 10 × 10 μm^2. (b) AFM height profile along the red dashed line indicated in (a). The area irradiated by laser swells up overall by ~1 nm, suggesting the importance of the proper choice of the laser power. (c) AFM image of ripple-patterned MoS_2 monolayer with a ripple width of 500 nm for an area of 10 × 10 μm^2. Here, the effective distance between the MoS_2 and the substrate was as large as ~1 nm because of a wet-transfer process. (d) AFM height profile along the red dashed line indicated in (c). The areas irradiated by the laser sink periodically to reach the substrate at the designed intervals of 500 nm.

for the E^1_{2g} and the A_{1g} peaks, together with a red-shift of the E^1_{2g} peak and a blue-shift of the A_{1g} peak. In addition, a new Raman peak at ~227 cm^{-1} became prominent. These observations are in accord with previous reports on the effect of disorder on Raman scattering of a MoS_2 monolayer [20, 21]. Similar to the D peak in graphene, the ~227-cm^{-1} peak in MoS_2 is attributed to disorder-induced Raman scattering [20]. This suggests the role of structural disorder, generated by the swelling of the MoS_2 surface, in our Raman spectra. Partial oxidation of MoS_2 by laser irradiation can also result in the ~227-cm^{-1} peak [22,23]. However, the most prominent peak of MoO_3 at ~820 cm^{-1} was not seen in our Raman spectra (data not shown), ruling out the role of oxidation.

To further exploit the swelling of the MoS_2 monolayer upon laser illumination, we employed this phenomenon to induce a structural deformation in a desired pattern. As shown in Fig. 3(a), we attempted a periodic line pattern. We swept a 5-mW laser beam in a line at a speed of 250 nm/s and then moved to the next lines at periodic intervals of 250 nm over the area of a red dashed square (10 × 10 μm^2) on a CVD-grown MoS_2 monolayer. After the laser irradiation, one can already notice a line pattern in the optical contrast microscopy image. Figure 3(b) displays an AFM image of the line-patterned MoS_2 monolayer. The AFM height profile, taken perpendicular to the sweeping lines of the laser beam, shows a periodic modulation of the height (~0.5 nm) in the monolayer (Fig. 3(c)). Note that the lines irradiated by using a laser swell up periodically from the substrate with the designed intervals of 250 nm. The resulting structure has a similarity to the periodic ripple structure of a MoS_2 monolayer, thus opening a new possibility to control the ripple structure for strain and bandgap engineering [9, 10]. Also, our experiments demonstrate that one can use laser irradiation to draw desired patterns of structural deformation down to ~250 nm in an atomic layer of MoS_2.

The patterning of the periodic ripple structure is sensitive to various parameters, such as the laser power and the effective distance between the MoS_2 monolayer and the substrate. For example, we attempted ripple patterning in the same way as presented in Fig. 3, but changed the laser power from 5 to 6.5 mW. As shown in Fig. 4(a), the line patterns blurred in the AFM image. The AFM height profile along the red dashed line, perpendicular to the sweeping lines of laser irradiation, shows that the area irradiated by using the laser swells up overall by ~1 nm (Fig. 4(b)). Strong laser irradiation causes more heat to transfer to areas surrounding the beam spots, blurring the designed patterns. Also, for laser powers less than 4 mW, the ripple patterns became indistinct as MoS_2 surface did not swell up enough. The proper choice of laser power is important for the patterning of a ripple structure in a MoS_2 monolayer.

On the other hand, the effective distance between the MoS_2 and the substrate plays a role in the patterning of a ripple structure. In Fig. 4(c), we show a MoS_2 monolayer that was transferred from the CVD-grown substrate to a new SiO_2 substrate by using a wet transfer technique [24]. After the wet-transfer, the effective distance between the MoS_2 and the substrate was as large as $\sim$1 nm because of the moisture and some chemicals residing between them. When we conducted a periodic sweeping of a 5-mW laser beam at line-intervals of 500 nm for an area of 10×10 μm^2, the ripple-patterns appeared in the AFM image with designed intervals of 500 nm, as displayed in the Fig. 4(c). However, the AFM height profile along the red dashed line shows that the patterning worked in the opposite manner (Fig. 4(d)). We note the areas irradiated by using a laser sink periodically to reach the substrate with the designed intervals of 500 nm. Heat generated by the laser irradiation possibly removed the moisture and the chemicals underlying it, so the MoS_2 surface sinked accordingly. Optimization for the laser patterning and a systematic study of the effect of ripples on the properties of a MoS_2 monolayer are now under progress.

III. CONCLUSIONS

In summary, we studied the effect of laser irradiation on monolayer MoS_2 and reported structural deformation upon laser illumination. We demonstrated the patterning of periodic ripples in monolayer MoS_2 by using laser irradiation. The controlled fabrication of the ripple structure may be instrumental in understanding the effect of ripples on the physical properties of monolayer MoS_2. Furthermore, structure engineering by using laser irradiation might provide a useful tool with enhancing the performance of electronic and optoelectronic devices based on 2D atomic layers.

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