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Thermal effects on the characteristic Raman spectrum of molybdenum disulfide (MoS₂) of varying thicknesses

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In this letter, thermal effects on the Raman spectra of molybdenum disulfide with thicknesses ranging from bulk to monolayer were evaluated. We quantitatively determined the laser-induced heating effects on the peak position and the line-width of the Raman spectrum. We found considerable thickness-dependent red-shifts as well as line-width changes for both E_{2g}^1 and A_{1g} vibrating modes as laser power was increased. Our results enrich the knowledge of phononic behaviors of this material and demonstrate the important effects of the anharmonic terms in the lattice potential energy. © 2012 American Institute of Physics. [doi:10.1063/1.3673907]

Highly crystalline molybdenum disulfide (MoS₂) films are composed of atomic layers of tightly bonded atoms brought together by weak van der Waals interlayer forces. These materials are structurally similar to graphene and hexagonal boron nitride (h-BN). Recent reports demonstrate strong photoluminescence emergence and anomalous lattice vibrations in single- and few-layered MoS₂ films.^{1,2} This exemplifies the evolution of the physical and structural properties in MoS₂, due to the transition from a three- to two-dimensional configuration. The thickness-dependency of the peaks can be explained by a combination of a classical model for the coupled harmonic oscillators³ and the anomalous changes in the dielectric screening properties of MoS₂.⁴ Thickness-dependent changes are also reflected in the electronic properties of these materials. The indirect band gap of bulk MoS₂ films with a magnitude of ~ 1.2 eV transforms gradually to a direct band gap of ~ 1.8 eV in single-layer samples.^{5,6} This is in contrast to pristine graphene with a band gap of ~ 0 eV and few-layered h-BN with a band gap of ~ 5.5 eV.^{7,8} The existence of an intrinsic band gap in these layered materials implies possible applications in electronics, optics, and semiconductor technologies as promising complements to graphene and h-BN.^{5–8}

To realize such technological possibilities, thermal characterization of these materials is vital. Raman spectroscopy has been widely applied to characterize the structural and physical properties of atomic layered materials, such as graphene and h-BN.^{9,10} However, characteristic Raman spectra of materials are known to be influenced by a number of extrinsic interactions, including effects caused by localized laser-induced heating, substrate interactions, strain, and charge transfer.^{11–17} Understanding these changes may provide important information regarding the underlying physical properties of the interactions and the materials themselves. Therefore, a thorough analysis considering thermal effects is necessary before utilizing Raman spectroscopy as a reliable characterization tool.

In this letter, we monitor the changes in the Raman spectrum of MoS₂ caused by varied local heating, induced by the use of different laser powers. We demonstrate that the laser-induced heating generates a red-shift in both E_{2g}^1 and A_{1g}

vibrating modes of MoS₂ samples. Similarly, the changes in the line-width of the Raman peaks are examined. Such changes are representative of the anharmonic terms in the lattice potential energy of this material.¹⁷ This anharmonicity results in a shift in the peak position and widening of the line-width corresponding to the damping of the vibration.¹⁸ Both quantities are dependent on the heating effect by means of the thermal population factors of the interacting phonons.¹⁹

High-quality MoS₂ thin-film samples were prepared using both mechanical²⁰ and liquid exfoliation methods.²¹ Single- and few-layered MoS₂ films were obtained by both methods, and the samples can be viewed using an optical microscope. Single-, few-, and multi-layered MoS₂ films are seen in light purple (similar to the color of SiO₂ substrate), dark purple, and blue, respectively. Figures 1(a) and 1(b) show thin MoS₂ flakes, with thicknesses ranging from a single layer to more than twenty layers. A SEM image of a liquid-exfoliated, few-layer MoS₂ sample is illustrated in Figure 1(c). These samples' thicknesses were further determined by atomic force microscopy (AFM, Agilent PicoScan 5500), as shown in Figures 1(d) and 1(e). The inset in Figure 1(d) depicts cross-sections of sample regions of thicknesses ~ 0.7 nm and 1.5 nm, corresponding to single- and bi-layered MoS₂. The inset in Figure 1(e) shows thicknesses of ~ 3.5 nm and 6.5 nm MoS₂ films, referred to as few- and multi-layered MoS₂. The thickness of a liquid-exfoliated MoS₂ flake can be determined by high-resolution transmission electron microscope (HRTEM, JEOL-2100). Figure 1(f) demonstrates a three-layer MoS₂ sample, with layer spacing ~ 0.7 nm, and a Mo-Mo distance of about 0.31 nm, noted by the red dots. An atomic resolution HRTEM image of MoS₂—clearly showing the hexagonal lattice structure—is shown in Figure 1(g). Figure 1(h) is the HRTEM image of MoS₂ flakes on carbon film and the reduced-fast Fourier transform (R-FFT) of these samples, demonstrating the diffraction pattern of a single-layered MoS₂ sample.

As shown in Figure 2(a), two characteristic Raman active modes for mechanical- and liquid-exfoliated MoS₂— E_{2g}^1 383 cm⁻¹ and A_{1g} 409 cm⁻¹—are present in the spectrum. These vibrational modes have been theoretically and experimentally investigated in bulk MoS₂.^{22,23} The inset of Figure 2(a) demonstrates the Raman active planar vibrations E_{1g} and E_{2g}^1 , as well as A_{1g} , which associates with the vibration

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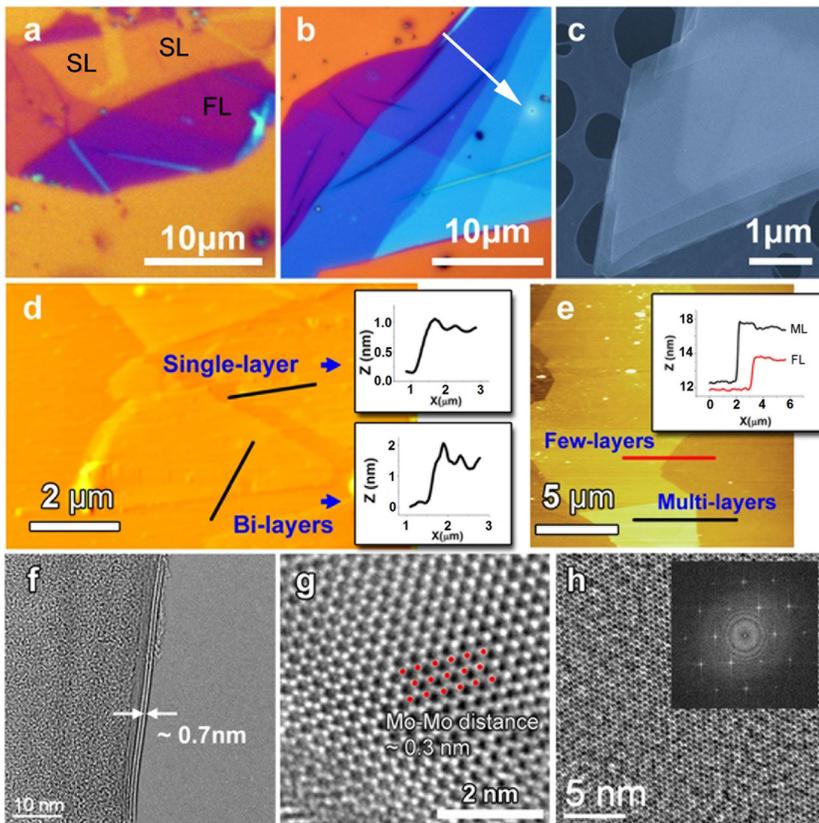


FIG. 1. (Color online) Optical images of mechanically exfoliated MoS₂ flakes on SiO₂ substrate. (a) The single- and few-layered samples, marked by SL and FL respectively, (b) Multi-layered MoS₂ regions, in which the number of layers increases in the direction indicated by the arrow. (c) SEM image of a chemically exfoliated, suspended, few-layer MoS₂ flake on a TEM grid. (d) and (e) AFM images of MoS₂ flakes on SiO₂ substrate. Insets show the MoS₂ with a thickness of ~0.7 nm, 1.5 nm in (d) and 3.5 nm, 6.5 nm in (e). (f) TEM image of a three-layer liquid exfoliated MoS₂ flake. The layer distance is ~0.7 nm. (g) Atomic HRTEM of a few-layer MoS₂ flake. The hexagonal lattice structure of the MoS₂ film is clearly observed. (h) HRTEM of a single-layer MoS₂ on thin-carbon film. Inset: corresponding reduced FFT image shows the typical diffraction patterns of single-layer MoS₂.

of sulfides in the out-of-plane direction. It is believed that E_{1g} peak is not visible because of the limited rejection of the Rayleigh scattered radiation by the SiO₂ substrate. A laser with an excitation wavelength of 514.5 nm (Renishaw inVia) was used to examine the thickness-dependence of the MoS₂ Raman spectrum. Similar to previously reported results, the thickness-dependent changes in the Raman spectra of MoS₂ samples on SiO₂ substrates were observed.² These results illustrate that the E_{2g}^1 and A_{1g} peaks move closer together as the thickness of pristine MoS₂ decreases, i.e., A_{1g} has a red-shift in the order of 5 cm⁻¹, while E_{2g}^1 has a blue-shift of approximately 2 cm⁻¹ from bulk- to single-layered MoS₂. A rate increase for these changes is observed from bi- to single-layered samples.

Thermal effects on the Raman spectrum of the MoS₂ samples on SiO₂ substrate were evaluated. It is known that laser power can be used to effectively control the heat-generating interactions between light and mater.²⁴ To illustrate the thermal effects in the Raman spectra of MoS₂, samples of different thicknesses ranging from bulk to single atomic layer at high (20 mW), intermediate (8 mW), and low (2 mW) laser power levels were examined. The resulting difference in the peak position, obtained for the varied laser powers, clearly signifies a considerable thickness-dependent change in the laser-induced thermal effects. These differences are represented by an expected softening of bonds (Fig. 2(b)). In thick samples (number of layers $N > 6$ to bulk), negligible changes in both peak positions is seen (Fig. 2(c)). In thinner samples ($N < 6$), we observed a red-shift for both A_{1g} and E_{2g}^1 modes. The rate of this shift for both modes of vibration is roughly equal in many- and few-layered samples. An increasing discrepancy between the magnitudes of

the red-shifts for the two modes of vibration is observed as the number of layers is decreased. This is believed to be a reflection of the thickness-dependency of the Raman spectrum due to the thermal effects. A decrease in material thickness results in the stiffening of the E_{2g}^1 mode, which contributes to the gradual mitigation of the thermal softening rate.^{2,4} In contrast, the A_{1g} mode softens with a decrease in thickness, resulting in enhanced thermal softening. In single-layered samples, the maximum difference between the responses of the two peaks is measured, and the change in the peak position of A_{1g} mode is about 1 cm⁻¹ larger than E_{2g}^1 . This can be explained by the observed increased stiffening of E_{2g}^1 and increased softening of A_{1g} modes from bi- to single-layered MoS₂.

It has been shown that the evolution of line-width, resulting from changes in the thermal effects, can provide important information about phonon-phonon coupling, as well as the decay process and population number of phonons in the material.²⁵ Here, we have measured the full width at half maximum (FWHM) of the peaks and have observed their change as laser power is increased (Figs. 3(a) and 3(b)). Results obtained from a low-power laser are in accordance with a previous study of the thickness-dependence of the line-width.² We observed that enhanced thermal effects result in an amplified phonon coupling of both peaks, represented by an increased line-width as the laser power is increased. The reduced sensitivity to thickness of the E_{2g}^1 mode has been explained by the less-efficient inter-layer coupling of the in-plane phonons.² However, this is subjected to change as the laser power is increased; thicker samples are more susceptible to such couplings (Fig. 3(a)). For the A_{1g} mode at low laser powers, the maximum line-width

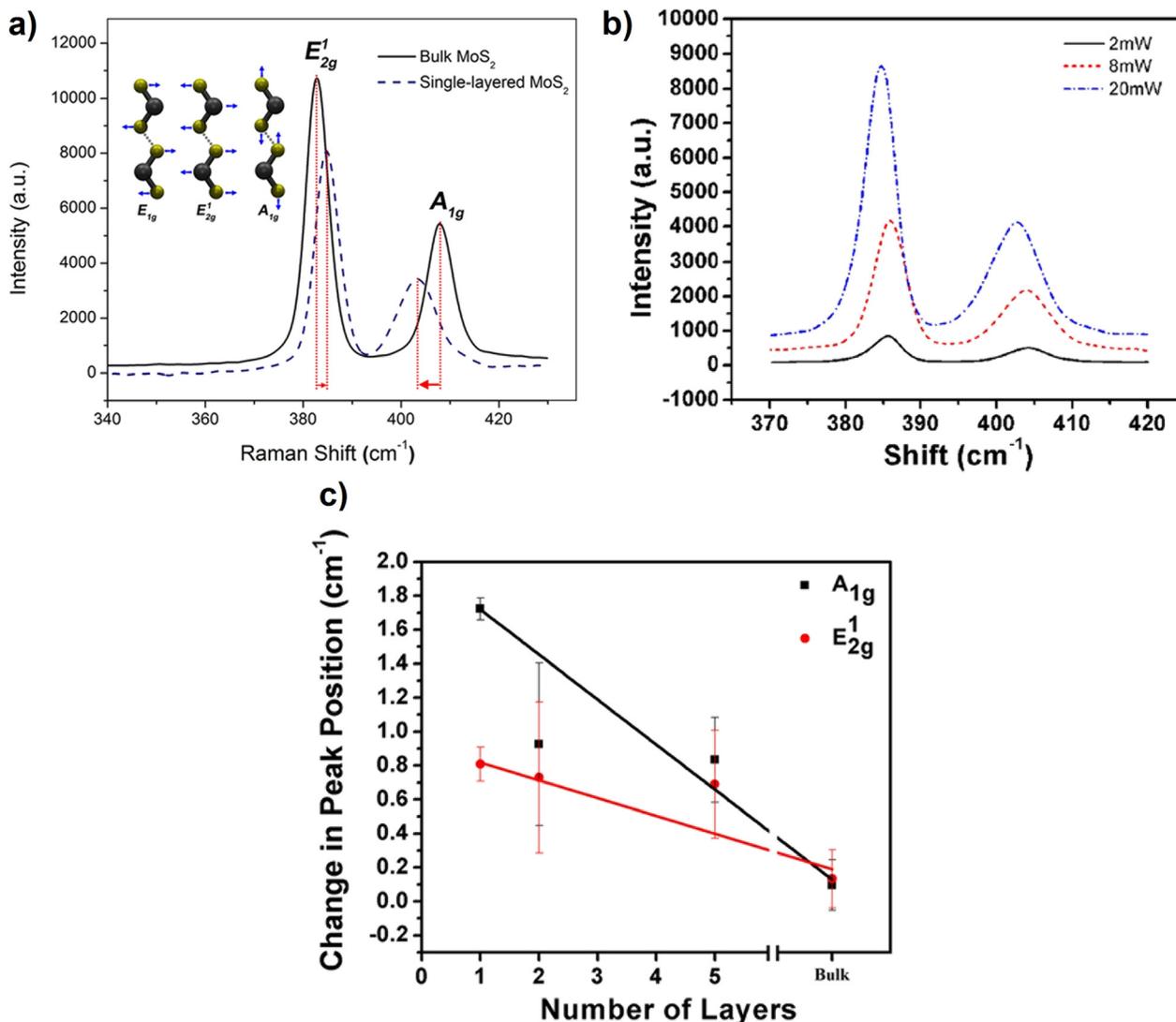


FIG. 2. (Color online) (a) Raman spectra of bulk MoS₂ and a single-layer MoS₂ flake on SiO₂ substrate. Inset: illustration of the three Raman Active modes: E_{1g} , E_{2g}^1 , and A_{1g} . Molybdenum atoms are in black and yellow represents sulfurs. The blue arrays indicate the orientation of the vibrations. (b) Illustrating the characteristic red shift observed in the Raman spectra of single-layered MoS₂ at varying laser powers. (c) The change in peak positions of MoS₂ samples of different thicknesses represented by the difference in the peak position for A_{1g} and E_{2g}^1 modes as the laser power is increased from 2mW to 20 mW.

is observed for the bi-layered samples, and a gradual decrease in the line-width is observed as thickness increases. The rapid line-width, decreases from bi- to single-layered samples, has been explained by an intrinsic difference in their symmetry.² The thermally induced rate of change in the line-width of the A_{1g} mode is highest in single-layered samples. As a result, single-layered samples obtain the maximum line-width value at high laser powers (Fig.

3(b)). Thus, due to heating, A_{1g} phonon coupling is most rapidly increased in single-layered samples.

In conclusion, our results suggest that the Raman spectrum of MoS₂ shows significant temperature dependency. We reveal that both characteristic peaks, A_{1g} and E_{2g}^1 , are sensitive to temperature changes, which are reflected in the peak position and line-width of the Raman spectra. This behavior is thickness-dependent, and a dramatic difference is

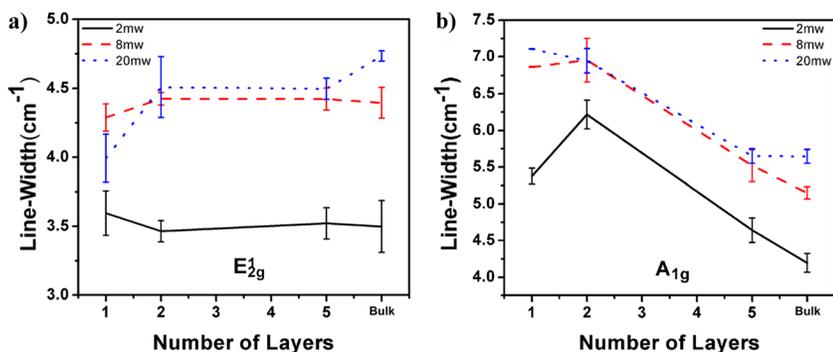


FIG. 3. (Color online) The change in Raman peak line-width as a result of change in laser power and its thickness dependency (a) for E_{2g}^1 and (b) A_{1g} modes.

observed for single-layered, relative to bi-layered, samples. The findings from this work reveal the importance of considering thermal effects on characterization of these materials and enrich our knowledge of the phononic behavior of MoS₂ materials with varying thicknesses.

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