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Controlled argon beam-induced desulfurization of monolayer molybdenum disulfide

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Abstract

Sputtering of MoS₂ films of single-layer thickness by low-energy argon ions selectively reduces the sulfur content of the material without significant depletion of molybdenum. X-ray photoelectron spectroscopy shows little modification of the Mo 3d states during this process, suggesting the absence of significant reorganization or damage to the overall structure of the MoS₂ film. Accompanying ab initio molecular dynamics simulations find clusters of sulfur vacancies in the top plane of single-layer MoS₂ to be structurally stable. Measurements of the photoluminescence at temperatures between 175 and 300 K show quenching of almost 80% for an ~10% decrease in sulfur content.

(Some figures may appear in colour only in the online journal)

Molybdenum disulfide, MoS₂, has attracted widespread attention as one of the interesting atomically thin materials beyond graphene [1–3]. Like graphene, it can be prepared in a stable form down to monolayer thickness. In contrast to graphene, however, MoS₂ has an intrinsic band gap: the indirect bandgap of bulk MoS₂ of ~1.4 eV crosses over to a direct optical bandgap of ~1.9 eV in the monolayer limit [4, 5]. In addition to this interesting electronic structure, MoS₂ has many established applications in catalysis, such as for hydrodesulfurization [6, 7], and it recently received attention as an electrode material for water splitting [8, 9].

Single-layer MoS₂ field effect transistors have been fabricated with mobilities on the order of 1 cm² V⁻¹ s⁻¹ and higher [10–13], as well as on–off ratios up to 10⁸ at room temperature. Bulk MoS₂, and most mono- or few-layer MoS₂ materials examined to date, exhibit n-doping [10–15], but p-doping has also been observed [16]. Ambipolar operation has been achieved by gating with an ionic liquid [17]. Another distinctive electronic property is the possibility of selective valley population of the monolayer, which has been achieved using excitation by circularly polarized light [18–22].

Although many of the studies to date have made use of mechanically exfoliated single-layer MoS₂ films [23], MoS₂ monolayers can also be prepared by means of chemical vapor deposition (CVD). A variety of substrates, including Cu [24], Au [16, 25–27], SiO₂ [16, 28], and various other insula-
MoS₂ films prepared by CVD [16, 37]. Once a sufficiently homogeneous area of the MoS₂ film exhibiting exclusively single-layer Raman and PL characteristics had been identified, the sample was attached to a temperature-controlled manipulator in an ultra-high vacuum system. For subsequent studies of sputtering, the system was evacuated and baked to reach a base pressure of $1 \times 10^{-9}$ Torr. A Varian sputter gun operated at 500 V acceleration potential, 20 mA emission current, and $5 \times 10^{-6} - 2 \times 10^{-5}$ Torr partial pressure of Ar was used for generating Ar⁺ ions. The sputter beam had a diameter of 0.5 cm. For reference, we measured the sputter current induced by this beam on a copper surface as 0.6–2.2 μA, respectively, for the Ar pressures given above. In the following, we will assume this value as an approximation of the beam current.

The XPS measurements were performed using excitation by Al Kα radiation with the emitted electrons detected by a Scienta R300 hemispheric analyzer equipped with a 2D detector. The PL experiments employed a Spectra Physics Millennia laser operating at a wavelength of 532 nm, a spectrometer with 1200 lines mm⁻¹ grating blazed at 750 nm, and a liquid-nitrogen cooled Princeton Instruments SPEC-10 CCD detector. For in situ measurements a 50 mm focal length lens inside our UHV system was used to focus $\sim 100$ mW of pump beam onto the sample surface with a spot of $\sim 100 \mu m$. This results in an intensity of approximately $10 \mu W \mu m^{-2}$, similar to that of typical microscope-based Raman measurements [4]. We collected the resultant PL signal in the back-scattered direction using a dichroic mirror to separate the excitation beam from PL signal.

Vacancy formation energy and thermal stability of the sputtered film was evaluated using the Vienna ab initio simulation package (VASP) [38, 39] to perform density functional theory (DFT) simulations. We employed projector-augmented wave (PAW) [40, 41] and plane-wave basis set methods. We used the Perdew–Burke–Ernzerhof functional (PBE) [42] to describe exchange correlation interactions and adopted a cut-off for plane-wave expansion at 500 eV. The conjugate-gradient algorithm [43] was employed to bond covalently to these materials, to render them attractive for many purposes, has proven a challenge for other needs. Intense processing is required, for example, to bond covalently to these materials, to render them soluble, and to alter their electronic properties, such as by hydrogenation or partial oxidation of graphene. For MoS₂, the inertness of the basal plane calls for interventions to facilitate chemical reactions. In this regard, theoretical studies indicate that sulfur vacancies are reactive [34, 35]. In this paper we show that sputtering with low-energy Ar⁺ ions can transform single-layer MoS₂ all the way to MoS₁.5, while in situ x-ray photoelectron spectroscopy (XPS) reveals substantially unchanged Mo 3d states. In situ monitoring of the photoluminescence (PL) allows us to gauge the impact of the sputter-induced defects/vacancies on the exciton dynamics; in the temperature regime between 175 and 300 K we find a decay of PL yield that decreases at $\sim 7.0 \pm 0.5$ times the rate of sulfur removal.

Our measurements were performed on films and isolated islands of single-layer MoS₂ grown on a SiO₂ substrate from MoO₃ and elemental sulfur, as described elsewhere [36]. Figure 1(a) shows an optical microscopy image of a representative area of a MoS₂ film used in this study. Figure 1(b) is a schematic representation of the structure of single-layer MoS₂, which consists of hexagonal top and bottom layers of sulfur surrounding a molybdenum layer. The samples were characterized in air prior to our experiments using Raman and PL spectroscopy. The right portion of the image in figure 1(a) shows a continuous film of monolayer thickness, while the left area consists of single-layer MoS₂ islands. Both regions exhibit the same PL peak at 1.87 eV, corresponding to the direct band gap. Raman spectra reveal the $E_{2g}^1$ and $A_{1g}$ modes, with a separation of 21 cm⁻¹, as typically seen in single-layer MoS₂ films prepared by CVD [16, 37].
In order to account for potential charging of the MoS$_2$ superposition below the individual spectra in figures 2(a) and 2(b), we scaled and shifted for the best overlay of the peak shape, as well as the corresponding spectra after exposure to air. The lower parts of (a) and (b) show spectra modified of the Mo XPS signal referenced to the substrate Si peak and normalized to unity, and the S:Mo XPS ratio normalized to 2. While the Mo content is seen to remain essentially constant, the amount of sulfur decreases significantly during sputtering.

For structural relaxation and to optimize lateral atomic coordinates by minimizing the in-plane components of the stress tensor; relaxation was allowed with periodic boundary conditions until all components of the force reached a value below 0.01 eV Å$^{-1}$. Given the large number of atoms in the computational supercell (up to 192), we found sampling of the Brillouin zone with one k-point to be adequate for evaluation of the total energy. *Ab initio* molecular dynamic (MD) simulations utilized the Nosé algorithm [44] for setting the system temperature and a 3 fs time step. To minimize the computational cost, the cut-off for plan-wave expansion was reduced to 300 eV and the simulations ran for a total time of 12 ps.

Our measurements involved cycles of sputtering at room temperature, *in situ* acquisition of XPS spectra of the Mo 3d, the S 2p, and the Si 2s levels, as well as *in situ* PL measurement at variable temperature. To avoid sample degradation, all experiments were conducted in immediate succession to one another, with the sample maintained in ultra-high vacuum. Figures 2(a)–(c) displays the evolution of the Brillouin zone with one k-point to be adequate for evaluation of the total energy. *Ab initio* molecular dynamic (MD) simulations utilized the Nosé algorithm [44] for setting the system temperature and a 3 fs time step. To minimize the computational cost, the cut-off for plan-wave expansion was reduced to 300 eV and the simulations ran for a total time of 12 ps.

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The sulfur signal (figure 2(b)), in contrast to the Mo 3d feature, exhibits a significant reduction in strength from sputtering, with little change of the overall peak shape. Figure 2(d) shows that the total sulfur content, normalized to 2 for the unsputtered film to account for the different XPS yields of the Mo and S states, decreases with sputter time. Within the duration of this experiment, we observe a reduction of the sulfur content of the film by 25%, or 50% of the top sulfur layer in the MoS$_2$ structure (figure 1(b)). This corresponds to an average sputter yield of 0.03 per Ar$^+$ ion. A first-order approximation of the sulfur signal decay (red line in figure 2(d)) corresponds to an exponential fit with a rate constant of 1.6 × 10⁻³ s⁻¹ or 1.4 × 10⁻⁴ cm² s⁻¹.

We ascribe the selectivity to sulfur removal to the close mass match between the Ar$^+$ ions and the sulfur atoms, as well as to the low Ar$^+$ energy; 3 keV Ar$^+$ ions are capable of removing Mo completely from our substrates. The silicon peak (figure 2(c)) serves as an internal reference and is not significantly affected by sputtering or exposure to air.

Apart from a shift to lower binding energy, likely arising from charging of the sputtered MoS$_2$ film with respect to the underlying SiO$_2$ layer, we observe little change of the peak shape of the Mo- and S-derived features (lower part of figures 2(a) and (b)). The latter suggests that despite sputtering, the MoS$_2$ film retains its homogeneity and its overall MoS$_2$ structure; we speculate that this is achieved by the presence of an unperturbed bottom sulfur layer that retains the structure of the Mo layer rigid, despite the absence of some of the top-layer sulfur atoms. We further support this argument in the following paragraphs.

Prior to processing, the sulfur and the molybdenum coverage of the samples correlate with one another. There is neither a significant quantity of sulfur in the absence of molybdenum nor is there appreciable incorporation of sulfur into the substrate surface during preparation. We reach these conclusions by aligning the sample so that the spatially resolved axis of our 2D detector lies along the horizontal of figure 1(a), i.e., by detecting the XPS yield from sample areas covered by a thick MoS$_2$ film on one side (where we find strong signal both for S and Mo), across an area with MoS$_2$ islands (where we find reduced signals for both S and Mo), and ending at a sample area devoid of MoS$_2$ features on the other side (where we find neither significant Mo nor S signal). This observation indicates that the S/Mo ratio that we track in the XPS-sputter cycles can indeed be related to modification of the MoS$_2$ monolayer and is not significantly
affected by any other possible sulfur source in the surface region. The fact that the MoS$_2$ film is the material being modified is further buttressed by the film’s dramatic change in stability after processing. XPS measurement on a sputtered film after exposure to air exhibit significantly broadening Mo 3d 3/2 and 5/2 peaks, as well as S 2p peaks (bottom of figures 2(a) and (b)). We attribute this to extensive oxidation. After sputtering and air exposure, atomic force microscopy reveals degradation in film smoothness, and the film’s Raman response is significantly reduced. On the other hand, the original, unprocessed films are found to be stable in air.

To confirm that a MoS$_2$ film with a significant fraction of its top sulfur atoms removed is structurally stable in vacuum for the temperature range of our measurements (≤350 K), we performed DFT calculations on (6 × 6) and (8 × 8) MoS$_2$ units supercells from which we removed a hexagon of 7 adjacent top-layer sulfur atoms (figure 1(d)). Such an arrangement allows us to examine the effect of creation of a relatively large vacancy cluster on the stability of the single-layer MoS$_2$. Structural relaxation maintains the overall shape of the film and changes the original Mo–Mo bond length inside the S-depleted region ≤5%. Allowing the film to evolve at 350 K over a 12 ps interval within ab initio MD leads to no structural change of the film, further supporting the stability of such a sulfur-depleted structure. We note that our calculations do not account for the support of the film structure through an underlying substrate and assume a comparatively large region of depletion of the surface sulfur. Both of these effects generate higher strain than is likely present in the films under experimental conditions.

To explore the impact of sputtering on the optical response of our films, we performed in situ PL measurements. Figures 3(a) and (b) show PL spectra acquired at temperatures of 175 and 300 K. In both cases, we observe a clear PL signal prior to sputtering, which decays with sputter exposure. The inset of figures 3(a) and (b) shows the Mo 3d XPS spectra acquired at 300 K at each of the sputter times, which are virtually unchanged throughout the experiment. By comparison of their intensity to the sulfur XPS intensity (not shown), we obtain the amount of sulfur removed. In addition, we observe a well-known reduction of PL yield with increasing temperature [45].

We fitted each PL peak with a Gaussian curve and a constant background. Figure 3(c) shows the evolution of the Gaussian amplitude with sputter time. For purposes of comparison, we plot the relative evolution of the PL yield for each temperature as a function of the reduction in sulfur content of the film (figure 3(c)).

The PL yield decreases as sulfur is removed. For 10% of sulfur depletion, the PL yield is reduced by almost 80%, i.e., an average decrease of (∼7.0 ± 0.5) × the rate of decrease of the sulfur concentration. Note that in figure 3 and in our discussion the fraction of sulfur is referred to the overall sulfur content of the MoS$_2$ monolayer structure. As sputtering is far more likely to remove sulfur in the top layer than in the bottom sulfur layer, the percentage values are twice as high if referred only to the top sulfur layer. As seen in figure 3(c), the quenching behavior of the PL is largely unchanged over the temperature regime addressed in this study.

The exciton dynamics underlying the quenching of the PL by sputtering is likely complicated. A rigorous treatment has to account for changes to the MoS$_2$ band structure, absorbance, and charging, which is beyond the scope of this study. However, we note that good agreement with the data can be achieved if one assumes (a) that the MoS$_2$ single-layer absorbance is not significantly changed by sputtering, (b) that quenching occurs whenever a photon is absorbed in a MoS$_2$ unit cell that is perturbed, i.e., missing its top sulfur atom or missing lateral coordination due to a sulfur atom being removed from a directly adjacent unit cell, and (c) that in all other cases the PL yield is identical to the that of the unperturbed system. To obtain values for the PL quenching from these assumptions we have performed a simple simulation (dotted line in figure 3(c)). Using a MoS$_2$ film of 200 × 200 unit cells, we randomly remove a varying fraction of the top-layer sulfur atoms and evaluate for 1000 arbitrarily chosen locations whether or not the unit cell is perturbed (as defined above). While this model provides agreement with the experiment, we note that a combination of less than unity quenching efficiency of defects and longer exciton diffusion lengths would yield similar overall behavior [37].

In summary, we have shown that sputtering with a beam of low-energy argon ions provides a method for selective
desulfurization of monolayer MoS$_2$. The spectroscopic studies and DFT modeling suggest that the basic physical structure of the MoS$_2$ remains largely intact as the sulfur is removed. Our findings suggest that low-energy argon sputtering may have significant potential for the activation, functionalization, and modification of MoS$_2$ layers. Although not studied systematically, the sharp increase in reactivity of the processed MoS$_2$ monolayer is apparent from its rapid oxidation in air.

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Acknowledgments

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