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Tuning electrical and interfacial thermal properties of bilayer MoS₂ via electrochemical intercalation

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Abstract

Layered two-dimensional (2D) materials such as MoS₂ have attracted much attention for nano- and opto-electronics. Recently, intercalation (e.g. of ions, atoms, or molecules) has emerged as an effective technique to modulate material properties of such layered 2D films reversibly. We probe both the electrical and thermal properties of Li-intercalated bilayer MoS₂ nanosheets by combining electrical measurements and Raman spectroscopy. We demonstrate reversible modulation of carrier density over more than two orders of magnitude (from 0.8×10^{12} to 1.5×10^{14} cm⁻²), and we simultaneously obtain the thermal boundary conductance between the bilayer and its supporting SiO₂ substrate for an intercalated system for the first time. This thermal coupling can be reversibly modulated by nearly a factor of eight, from 14 ± 4.0 MW m⁻² K⁻¹ before intercalation to 1.8 ± 0.9 MW m⁻² K⁻¹ when the MoS₂ is fully lithiated. These results reveal electrochemical intercalation as a reversible tool to modulate and control both electrical and thermal properties of 2D layers.

Supplementary material for this article is available [online](#)

Keywords: two-dimensional, intercalation, tunable, Raman, thermal, electrical

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

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1. Introduction

Two-dimensional (2D) materials such as molybdenum disulfide (MoS₂) are widely considered to be promising candidates for next-generation nanoelectronics due to their unique material

properties (electrical, thermal, optical, mechanical) and their sub-nanometer thickness without dangling bonds [1, 2]. Potential applications for 2D materials include transistors [3, 4], interconnects [5], transparent electrodes [6], sensors [7], solar cells [8], thermoelectrics [9], and energy storage devices [10]. This wide range of applications has many requirements; thus, it is desirable to modulate the properties of 2D materials to optimize their performance for specific applications. Researchers have been actively developing ways to engineer electron and phonon transport in 2D materials via chemical doping, strain, and nanostructuring [11–13]. However, a controllable, reversible, and scalable method to engineer 2D material properties is still lacking. For instance, while some doping strategies effectively achieve high carrier concentrations [14, 15], it remains challenging to precisely control or modulate the doping level in 2D materials.

Intercalation has recently emerged as a promising technique to engineer 2D material properties for tunable electronic applications [16–20]. In layered 2D crystals, the van der Waals spacing between layers provides perfect sites to accommodate guest species such as ions and molecules (intercalants) through a process known as intercalation. These intercalants modify interlayer interactions in 2D thin films and affect material properties through charge transfer, band gap engineering, and phonon scattering [21–25]. Earlier efforts studying intercalation in 2D materials often employed a chemical intercalation approach [18, 26], where 2D crystals were immersed in a chemical solution containing the intended intercalant species (e.g. n-butyl lithium for chemical intercalation of lithium) for an extended time (up to 72 h). While chemical intercalation is relatively easy to perform and provides a convenient route to demonstrate its usefulness in doping and phase engineering 2D materials, this process is irreversible and lacks control over the intercalant concentration.

In contrast, in an electrochemical intercalation process, the number of ions (e.g. Li^+) intercalated between the 2D layers can be precisely and reversibly modulated by controlling the number of electrical charges (charging current \times time) transferred to the host materials [16, 17, 27, 28]. While electrochemical intercalation is extensively studied and forms the backbone of Li ion battery (LIB) industry, there has been limited work done leveraging this technique to engineer fundamental material properties in 2D materials. Electrically, electrochemical Li intercalation has demonstrated tunable electrical conductance over 2–3 orders of magnitude in graphitic thin films [17], few-layer MoS_2 [16], as well as 2D heterostructures [29]. Thermally, Li intercalation has been employed to achieve $\sim 8\text{--}10 \times$ modulation of cross-plane thermal conductance (combined volumetric contribution of MoS_2 , and interfacial contributions of Al/MoS_2 and $\text{MoS}_2/\text{SiO}_2$) in MoS_2 thin films [30] (~ 10 nm thick) and up to $5 \times$ change in cross-plane thermal conductivity in bulk MoS_2 samples [21] ($\sim 10\text{--}20$ μm thick). However, while these earlier studies provided valuable insights on how intercalation affects electrical and thermal transport in 2D materials, detailed studies on the charge transfer process in intercalated 2D films and the effect of intercalants on thermal boundary conductance (TBC) between 2D films and the substrate, a key parameter in determining energy dissipation in 2D electronics [31–33], are still lacking. The TBC

plays an important role in thermal transport across sub-100 nm thin films, even when quasi-ballistic effects are considered [34].

In this work, we investigate how the carrier concentration in MoS_2 and the TBC at $\text{MoS}_2/\text{SiO}_2$ interface vary as a function of Li concentration through electrical Hall measurements and Raman spectroscopy. In addition, prior intercalation studies often employ the well-characterized liquid electrolyte and Li metal as the reference electrode [16, 17], which are highly reactive and flammable and may not be ideal for electronics applications. We report a solid-state electrochemical intercalation platform using LiClO_4 in polyethylene oxide (PEO) as a solid electrolyte and the air-stable LiFePO_4 (LFP) as the reference electrode (Li reservoir). Our work addresses reversible doping and thermal dissipation that are two fundamental issues in 2D electronics, and provides a promising path towards tunable 2D electronics.

2. Experiments

2.1. Device fabrication

MoS_2 flakes were mechanically exfoliated onto a highly doped (p-type) Si substrate with 90 nm thick thermally grown SiO_2 . The bilayer MoS_2 flakes were pre-sorted with an optical microscope and later confirmed with Raman spectroscopy and atomic force microscopy (AFM). The MoS_2 flakes were patterned into Hall structures with e-beam lithography and XeF_2 etching. Electrode contacts (Ti/Au, 1/50 nm) were deposited with e-beam evaporation.

2.2. Intercalation

Our 2D electrochemical device is similar to a planar nanobattery with MoS_2 and lithium iron phosphate LiFePO_4 serving as the working and reference/counter electrodes, respectively. The solid electrolyte was prepared by dissolving LiClO_4 (Sigma Aldrich) into PEO (Sigma Aldrich) matrix. PEO and LiClO_4 powders (500 and 150 mg, respectively) were mixed with 7.5 ml of anhydrous methanol and stirred for 12 h at 50 °C. An electrochemical workstation (Biologic SP-150) was used to perform the Li intercalation and de-intercalation and measure MoS_2 electrochemical potential.

2.3. Characterization and measurements

Raman spectroscopy was performed with a Horiba LabRam instrument with a 532 nm green laser and 1800 mm^{-1} grating. A $100\times$ long working distance objective (N.A. = 0.6) was used to accommodate the MoS_2 electrochemical devices with PEO electrolyte. For Raman thermometry measurements, the temperature calibrations were carried out with a Linkam THMS600 stage. Part of the electrical transport measurements was carried out using a semiconductor parameter analyzer (Keithley 4200 SCS). The temperature-dependent Hall measurement was conducted in a Quantum Design PPMS-7 system with digital lock-in amplifiers (Stanford Research Systems SR830).

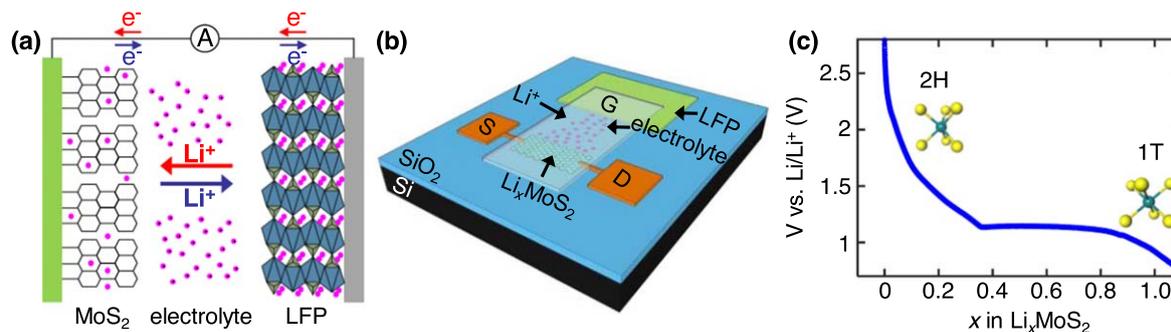


Figure 1. Electrochemical intercalation. (a) Schematics of electrochemical intercalation process with MoS₂ sheets as the working electrode and LiFePO₄ (LFP) as the reference electrode. The solid electrolyte is LiClO₄ in PEO. The red and blue arrows represent the direction of Li ions (in electrolyte) and electrons (in external circuit) movements during intercalation and de-intercalation, respectively. (b) Schematics of electrochemical intercalation device. (c) Galvanostatic discharge curve of MoS₂ with respect to LFP. The electrochemical potential (y-axis) is normalized to Li/Li⁺ potential by adding 3.5 V, the potential of LFP with respect to Li/Li⁺. The 2H to 1T phase transition plateau for MoS₂ occurs at 1.1 V with respect to Li, similar to previous reports [16, 35, 36]. This indicates that LFP works well as an air-stable reference electrode to replace the highly reactive Li metal.

3. Results and discussion

3.1. Electrochemical intercalation

Figure 1 shows the schematics of the electrochemical intercalation process, where Li ions move in and out of the interlayer spacing in 2D materials, depending on the external electrical current flow. Our intercalation platform consists of the 2D material (the working electrode), a Li reservoir (the reference electrode), and the electrolyte to allow ionic movement (no electron transport). The main advantage of electrochemical intercalation over the chemical intercalation process is that we can achieve reversible control over the intercalant concentration [16]. Governed by charge neutrality, for every negatively charged electron that flows from the reference electrode to the working electrode during intercalation, a positively charged Li⁺ ion moves from the reference electrode to the working electrode, i.e. a Li⁺ ion is intercalated in the 2D material. Thus, we can precisely modulate the Li concentration in the host 2D material by controlling the total amount of charge transferred from the reference electrode to the 2D material (current × time). To increase the Li content in 2D materials, i.e. intercalation, we will flow electrons from the reference electrode to the 2D material via an external circuit (indicated by the direction of red arrows in figure 1(a)); to decrease the Li content, i.e. de-intercalation, we will need to reverse the current flow (blue arrows in figure 1(a)). This allows us to engineer the electrical and thermal properties of our device by controlling the Li concentration in 2D materials.

We adopt the air-stable LiFePO₄ (LFP) (instead of the highly reactive Li metal) as the reference electrode (figure 1(b)) in our device. LFP has a very stable electrochemical plateau (~3.4 V versus Li/Li⁺) when its lithiation content is between 10% and 90% [37, 38]. LFP also has a long lifetime and a high power density; therefore, it has been used as a cathode material in rechargeable LIB [37, 38]. We also utilize a solid electrolyte, LiClO₄, in PEO for this work, instead of the liquid electrolyte (LiPF₆ in EC/DEC solution) that is prevalent in LIBs. Even though a liquid electrolyte

typically has better ionic mobility than the polymer electrolyte, it is prone to low-charge retention, leakage issues, and thermal instability at low and high operating temperatures [39]. This would severely limit the application of intercalation in tunable electronics. In contrast, the PEO electrolyte has better chemical and thermal stability, comparable ionic mobility, and higher energy density [40].

In principle, we could calculate the exact Li content in our 2D films, knowing the current flow and exact amount of charge flowing into the 2D nanosheet, as well as the exact molecular mass of the host 2D material. However, it is impractical to measure the weight of our MoS₂ nanosheet accurately. Thus, we first performed a galvanostatic discharge measurement (figure 1(c)) on bulk MoS₂ powder as a calibration, where we can measure the weight of the bulk MoS₂ accurately. Since the galvanostatic discharge measurement only depends on the chemical composition of the material, we expect the calibration result of the bulk powder to be transferable to MoS₂ thin films. From our calibration, we established a correlation between the electrochemical potential with respect to Li/Li⁺ and Li concentration in intercalated Li_xMoS₂ (figure 1(c)). The plateau at 1.1 V represents the 2H to 1T phase transition in MoS₂, consistent with previously reported values [16, 35, 36]. With the calibration result, we can modulate the Li content in MoS₂ conveniently by varying the electrochemical potential of MoS₂ with respect to Li/Li⁺ and read the Li concentration by comparing the potential in our calibrated sample. To prevent the irreversible conversion reaction that forms Li₂S [35], we avoid lithiating MoS₂ below 0.9 V with respect to Li/Li⁺ in this work.

3.2. Electrical transport

We fabricated Hall bar structures on bilayer MoS₂ samples to investigate how much carrier modulation we can achieve with electrochemical intercalation. The schematics and optical image of our electrochemical devices are shown in figure 2(a). Figure 2(a) inset shows the MoS₂ thickness (*t*_{MoS₂}) to be ~1.7 nm (bilayer) through AFM. More fabrication details can be found in the Methods and supporting information

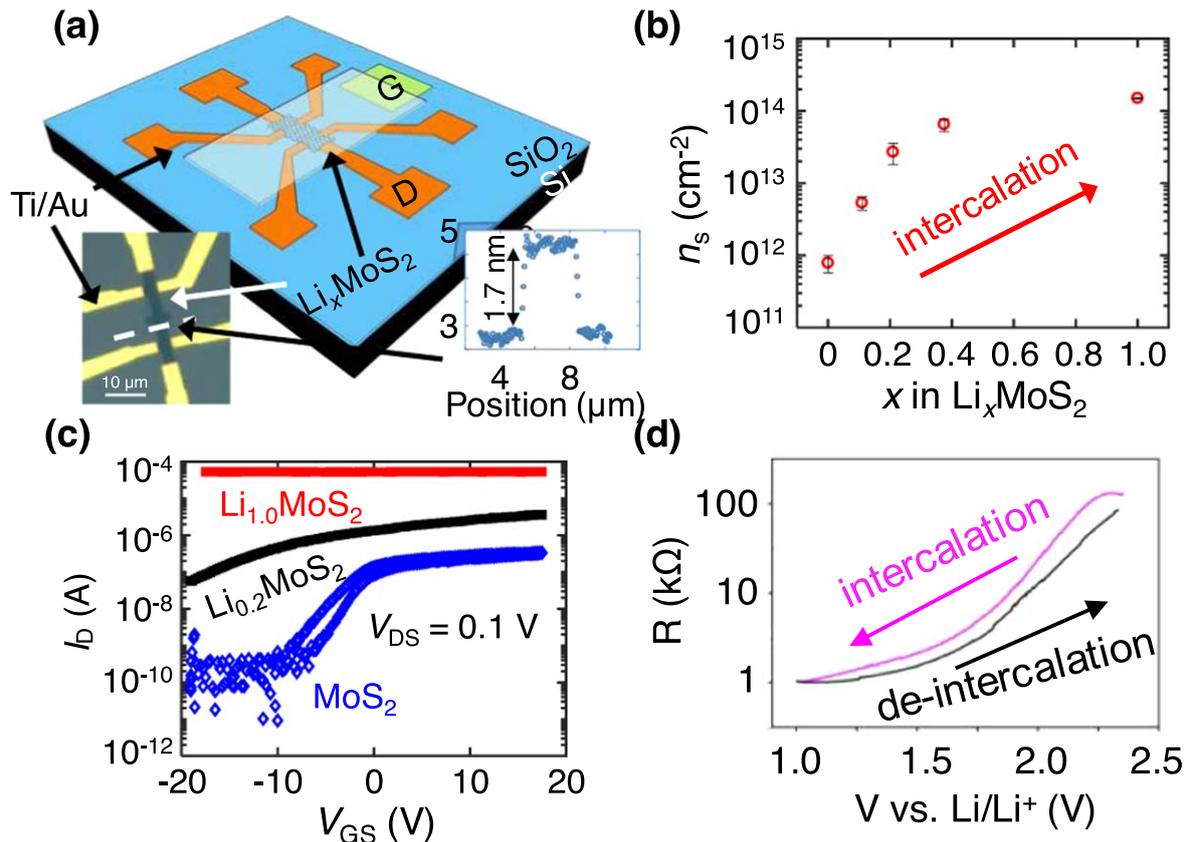


Figure 2. Tuning MoS₂ carrier concentration via intercalation. (a) Schematics of Hall bar structure with electrochemical intercalation platform. Inset is an optical image of fabricated MoS₂ device with Hall bar structure. The inset shows the AFM measurement of the MoS₂ device, confirming bilayer thickness (~ 1.7 nm). (b) Carrier concentration in MoS₂ as a function of Li concentration, controlled by the potential difference of MoS₂ with respect to the reference electrode. (c) Transfer characteristics of pristine MoS₂ (blue), Li_{0.2}MoS₂ (black), Li_{1.0}MoS₂ (red). The channel conductance increases as carrier concentration increases due to Li intercalation. Li_{1.0}MoS₂ shows metallic behavior (no V_{GS} dependence) because it is in the IT phase. (d) Reversible electrical properties as we lithiate and de-lithiate the MoS₂ thin film (a different bilayer sample than the one depicted in (a)–(c)) via changing its electrochemical potential.

sections (available online at stacks.iop.org/NANO/32/265202/mmedia).

Next, we applied the polymer electrolyte (LiClO₄ in PEO) to cover the entire MoS₂ channel and the reference electrode (LFP, see Methods for more details). This electrically-insulating solid polymer allows ionic exchange between LFP and the 2D material. Unlike an electric-double-layer transistor (EDLT), which does not have a reference electrode (only a metal contact) [41–44], we can controllably perform electrochemical intercalation in our device with a well-defined electrochemical reference potential (figure 1(a)). This provides additional control in electronics applications because the effect from electrochemical intercalation is long-term, while the ionic gating effect in EDLT is short-term (only persist with applied gate voltage). As we monitor the electrochemical potential of MoS₂ with respect to the reference electrode, we can precisely and reversibly tune the Li concentration in MoS₂ by adjusting the potential between MoS₂ and the reference electrode (figure 1(c)).

By controlling the electrochemical potential of MoS₂ with respect to our reference LFP electrode, we can intercalate/de-intercalate Li ions and therefore modulate the carrier concentrations in MoS₂, similar to a charging/discharging process

in a LIB. Initially, the pristine MoS₂ had an electrochemical potential of 2.5 V versus Li/Li⁺, i.e. -0.95 V with respect to LFP, since partially lithiated LFP has a stable potential plateau of 3.45 with respect to Li/Li⁺ (see Methods for more details) [37, 38]. The 2D carrier concentration n_s in this MoS₂ flake was 8×10^{11} cm⁻² before Li intercalation, as extracted from Hall measurement. As we intercalate more Li ions into MoS₂ by lowering the potential of MoS₂ with respect to the reference electrode (figure 1(c)), we observe a significant increase in carrier concentration (figure 2(b)), with n_s reaching 1.5×10^{14} cm⁻² when Li concentration approached the maximum intercalation capacity Li_{1.0}MoS₂, equivalent to one Li ion per unit cell. This large increase in carrier concentration is likely due to the combined results of charge transfer from the intercalated Li ions and the effect of ionic gating. We also measured the temperature dependence of the lithiated MoS₂ device's electrical resistance from room temperature down to 2 K (see figure S2 in the supporting information) but did not observe any superconductive behavior in our device.

The Hall bar structure also behaves as a 2D transistor with a Si back gate below the 90 nm thick SiO₂. Figure 2(c) shows the transfer curves of a typical device at room temperature with different Li concentrations under a source-drain

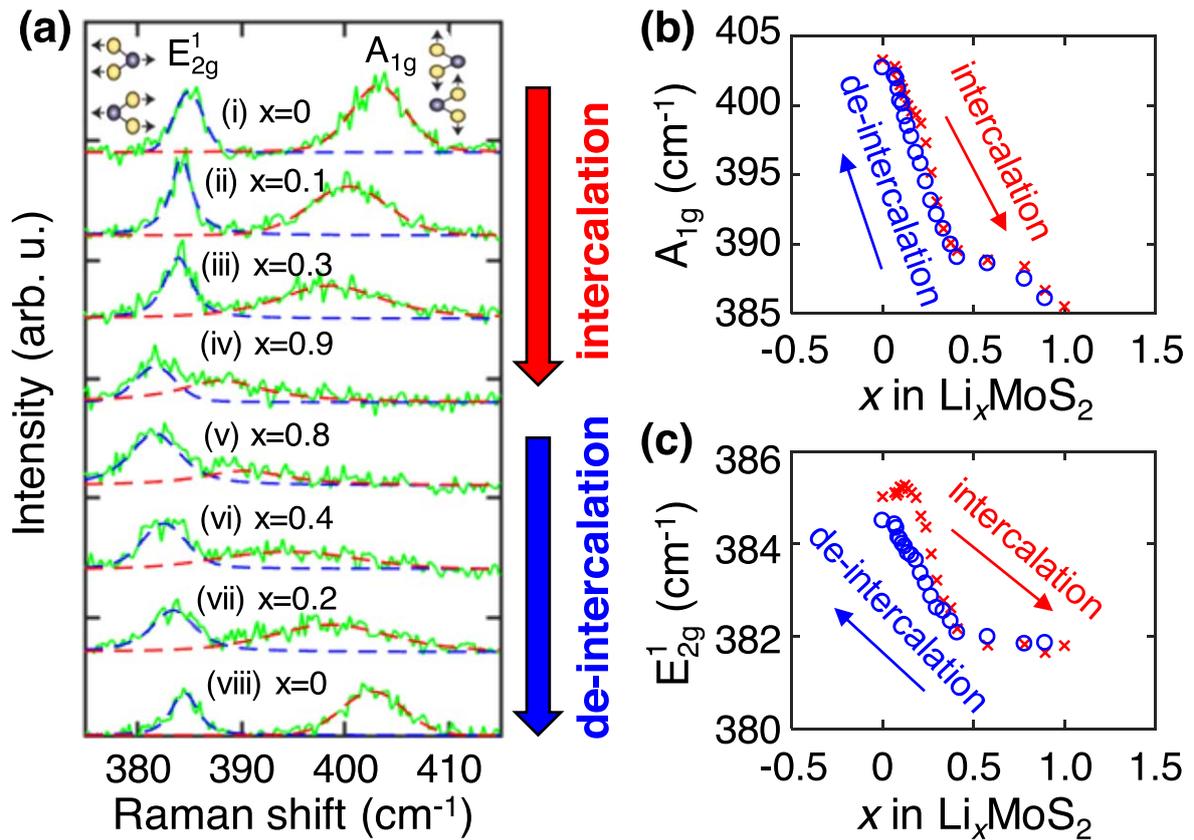


Figure 3. Raman spectroscopy of Li-intercalated MoS₂. (a) Raman spectroscopy of bilayer MoS₂ thin film during the intercalation (i)–(iv) and de-intercalation (v)–(viii) steps. Green curves are the raw data; blue and red curves are the fitted results for the Raman modes, E_{2g}^1 and A_{1g} , respectively. The insets show the corresponding vibrational modes. (b)–(c) The measured frequency shift of A_{1g} and E_{2g}^1 modes as a function of Li content in Li_xMoS_2 . Red crosses and blue circles represent the intercalation and the subsequent de-intercalation steps, respectively.

bias $V_{DS} = 0.1$ V. Before Li intercalation, the exfoliated MoS₂ (blue curve in figure 2(c)) was in a semiconducting 2H phase and showed an on/off ratio of $\sim 1000\times$ through back-gate control. Upon Li intercalation (black curve, $\text{Li}_{0.2}\text{MoS}_2$), we noticed an increase in channel conductance due to doping and decreased on/off ratio ($\sim 50\times$). When the MoS₂ flake was fully lithiated to $\text{Li}_{1.0}\text{MoS}_2$ (red curve), the channel became metallic as MoS₂ underwent a 2H (semiconducting) to 1T (metallic) phase transformation upon lithiation as previously reported [16, 18, 35, 36]. We observed $\sim 500\times$ improvement in drive current I_{on} upon Li intercalation ($\text{Li}_{1.0}\text{MoS}_2$) likely because of the higher carrier concentration [29] ($\sim 200\times$) upon intercalation as well as lower contact resistance due to the semiconducting-to-metallic phase transition [18, 45]. This 2H to 1T phase transition is likely triggered by the strain from the influx of Li ions [46]. Upon intercalation, Li atoms occupy octahedral sites between the 2H-MoS₂ layers, forming an unstable 2H- Li_xMoS_2 phase. As more Li atoms enter the MoS₂ structure [47], the strain causes the crystal structure to transform into the thermodynamically-stable 1T- Li_xMoS_2 phase with stacking sequence AA shown in the figure 1(c) inset. The associated ($\sim 2\%$ – 5%) increase in interlayer spacing allows it to accommodate more Li atoms in the unit cell, as similarly reported in previous *in situ* XRD measurements [23] and first-principle

calculations [46]. The change in electrical conductance is reversible as we lithiate and de-lithiate the MoS₂ device (figure 2(d)), opening up opportunities for applications in memory and synaptic devices[48–51].

3.3. Raman spectroscopy

We also studied how intercalation affected the doping and strain in these 2D layers via Raman microscopy. Figure 3 illustrates our Raman measurements on a bilayer MoS₂ flake as we intercalate and de-intercalate the device. Green curves are the original Raman spectra; blue and red curves represent the fitted E_{2g}^1 and A_{1g} modes, respectively. By intercalating Li^+ ions into a bilayer MoS₂ film (series (i)–(iv) in figure 3(a)), we noticed a significant peak shift and broadening of the A_{1g} mode (figure 3(b)), which is attributed to doping in MoS₂ [16, 52, 53]. Similarly, the E_{2g}^1 mode also decreased in frequency (figure 3(c)) and broadened upon intercalation, albeit to a much lesser extent. This likely indicates strain build-up in the lattice due to the influx of Li^+ ions [16, 54]. These changes in Raman spectra were fully reversible as we moved Li^+ ions out of MoS₂ during the de-intercalation process [series (v)–(viii) in figure 3(a)] and are consistent with our density functional theory calculations (see figure S7 in the supporting information). The A_{1g} mode shift

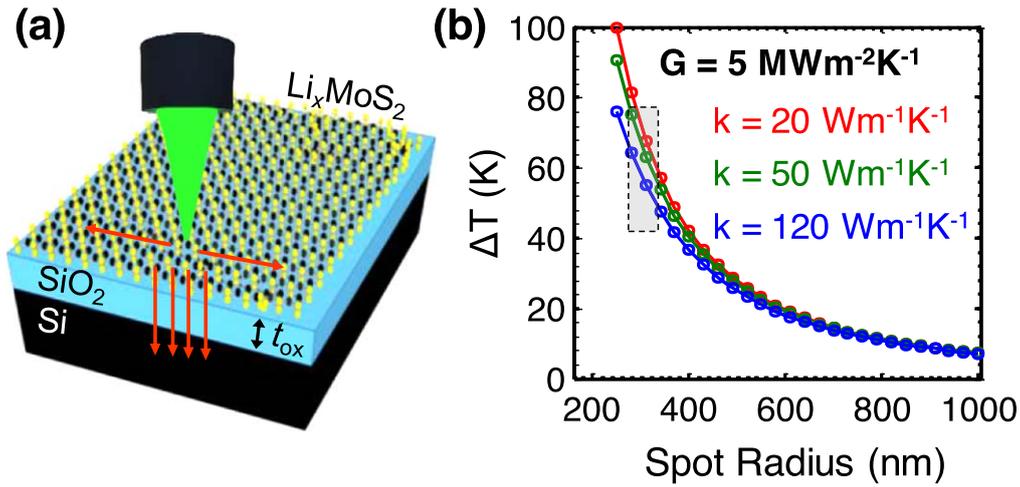


Figure 4. MoS₂/SiO₂ thermal boundary conductance (TBC) before and after intercalation. (a) Schematic of Raman thermometry platform of the bilayer MoS₂ on the SiO₂/Si substrate. (b) The simulated temperature rise of MoS₂ as a function of laser spot size at an absorbed power of 1.2 mW, when the MoS₂/SiO₂ TBC = 5 MW m⁻² K⁻¹, near the lower bound of the TBC after intercalation. Red, green and blue curves are for in-plane thermal conductivity of MoS₂ $k = 20, 50,$ and $120 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. This suggests that the temperature rise in MoS₂ is insensitive to its in-plane k , most of the heat flows through the SiO₂/Si substrate, and we can fit the TBC of MoS₂/SiO₂ by assuming a typical $k \approx 50 \text{ W m}^{-1} \text{ K}^{-1}$.

was as large as 18 cm^{-1} at Li_{1.0}MoS₂ (figure 3(b)), confirming a heavy doping concentration ($n_s = 1.5 \times 10^{14} \text{ cm}^{-2}$ from our Hall measurement in figure 2(c)) [25].

3.4. Raman thermometry

In addition to the use of Raman spectroscopy to probe the carrier concentration of intercalated Li_{*x*}MoS₂, we also employ a Raman thermometry technique (figure 4(a)) to characterize how the TBC between bilayer MoS₂ and its supporting substrate (SiO₂/Si) changes as we intercalate and de-intercalate Li ions into the van der Waals gap between MoS₂ layers and between the bottom MoS₂ layer and the SiO₂ substrate. As illustrated in figure 4(a), TBCs between 2D thin films and their supporting substrate play significant roles in limiting the heat and energy dissipation of 2D devices [31–33, 55, 56]. Drive currents in 2D transistors are limited by their local temperatures, which TBCs largely determine [57]. However, measuring the TBC in ultrathin 2D electronics has been challenging due to uncertainties in measuring the heat flow and the local temperature [58, 59].

Recently, we reported the TBC of pristine monolayer MoS₂ on SiO₂ via Raman thermometry [31, 33]. In a Raman thermometry measurement, we characterize the temperature rise of 2D thin films optically (through peak shift of the Raman mode) as a function of the input power (either optically from the Raman laser or electrically by Joule heating). We then fit the temperature rise and the input power into a thermal model [60] to calculate the TBC and the in-plane thermal conductivity of the 2D film by solving the heat diffusion equation in our model [33].

For bilayer MoS₂ thin films on SiO₂/Si substrates and with a spot size r_0 between 310 and 370 nm (without and with electrolyte through a 100× objective, see figure S3 in the supporting information for more details), we expect most of the heat in MoS₂ will be dissipated through the substrate and rendering the system to be insensitive to the in-plane thermal conductivity

of MoS₂, as shown in figure 4(b) (see figure S4 in the supporting information for more analysis). This allows us to only use a supported structure (figure 4(a)) to calculate our single fitting parameter, the TBC at the MoS₂/SiO₂ interface significantly simplifies our measurement and analysis.

A key parameter in Raman thermometry is the power absorbed (P_{abs}) by bilayer MoS₂. A significant portion of the uncertainty in optically-heated Raman thermometry measurements stems from P_{abs} estimations because it is challenging to directly measure the absorbed power of a 2D thin film supported on a substrate where multiple optical reflections interfere. We employed the following approach to minimize those uncertainties. The power absorbed by such a 2D film is calculated as follows: $P_{\text{abs}} = P_{\text{in}} \alpha_f E$, where P_{in} is the incident laser power, α_f is the absorption coefficient of free-standing MoS₂. E is a wavelength-dependent enhancement factor, the intensity of the electric field (of the electromagnetic wave of the laser) at the top surface of SiO₂/Si substrate relative to the intensity of the incident electric field, accounting for the multiple reflections within the SiO₂/Si substrate. We characterized the incident laser power and the spot radius r_0 during our calibration measurements (see figure S3 in the supporting information for more details).

We measured the absorption coefficient of free-standing monolayer MoS₂ over a range of temperatures (see figure S6 in the supporting information). This temperature-dependence of α_f is important as we observed a 30% increase in absorption (at a laser wavelength of 532 nm) at 250 °C compared to that at room temperature. Neglecting this temperature dependence (and therefore underestimating P_{abs}) will underestimate the TBC in the Raman thermometry analysis. We expect the optical dielectric functions of monolayer and bilayer MoS₂ to be very similar away from the peak energies of those transitions, such as at a wavelength of 532 nm. Thus we assume that the absorption of free-standing

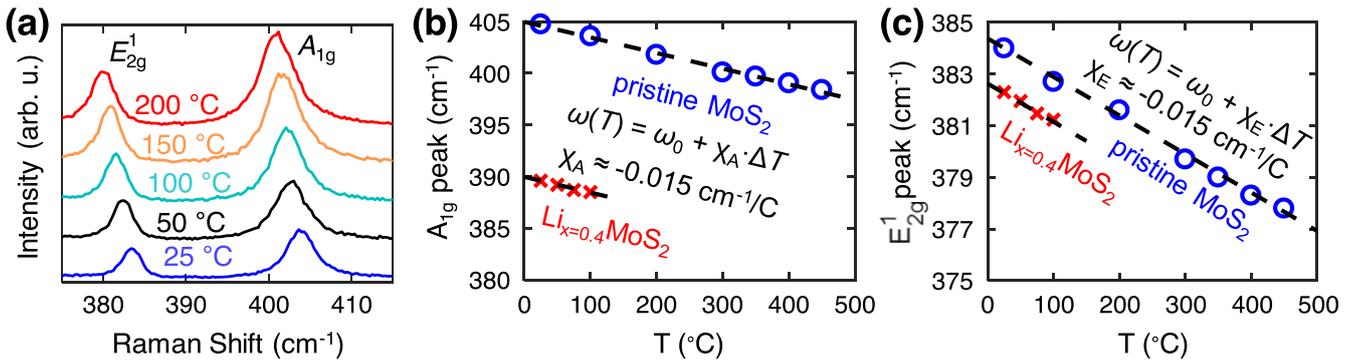


Figure 5. Temperature dependence of Raman peaks. (a) Raman spectra of pristine bilayer MoS₂ as a function of temperature. (b)–(c) Temperature calibration by substrate heating for A_{1g} and E_{2g}¹ modes, respectively. Blue and red circles represent calibration for pristine MoS₂ and intercalated Li_{0.4}MoS₂, respectively. The slopes of the linear fits are the temperature coefficients χ_A and χ_E for A_{1g} and E_{2g}¹ modes, respectively.

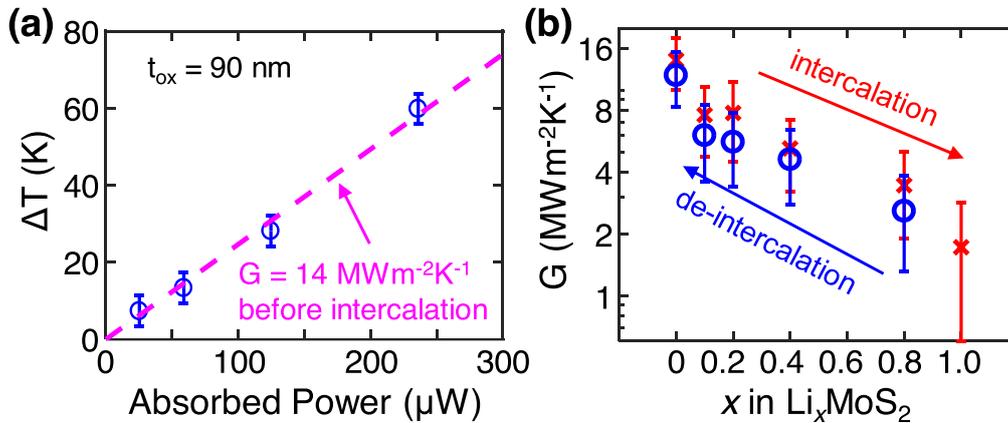


Figure 6. Thermal boundary conductance (TBC) between MoS₂ and SiO₂. (a) The measured temperature rise of a pristine bilayer MoS₂ device (no intercalation) versus absorbed laser power. The dashed line represents a thermal resistance with TBC = 14 ± 4 MW m⁻² K⁻¹. (b) TBC as a function of Li concentration in MoS₂. As we intercalate (red crosses) more Li ions into MoS₂, the TBC decreases to ~ 1.8 MW m⁻² K⁻¹ at Li_{1.0}MoS₂. As we de-intercalate (blue circles) Li ions out of the system, the TBC almost recovers to its original value (~ 11.8 MW m⁻² K⁻¹).

bilayer MoS₂ at 532 nm to be twice that of the monolayer MoS₂ at 14% at 300 K, with similar temperature dependence as monolayer MoS₂ (see more discussion in supporting information section S6) [33]. We measured the absorption coefficient of lithiated MoS₂ in an earlier study [16], where we observed a 60% decrease in absorption (8.4% for bilayer Li_{1.0}MoS₂) at 532 nm due to the 2H to 1T phase transformation and the associated elimination of a band gap (see figure S6 in the supporting information). We also calculated the enhancement factor (~ 1.46 at 532 nm) based on the thickness, interface, and refractive index of the materials in our stack (PEO/MoS₂/SiO₂/Si). More details on the estimation of the absorbed power can be found in the supporting information section S6 and our prior analysis [33].

Another important parameter in Raman thermometry is the temperature rise $\Delta T = T - T_0$, where T and $T_0 = 300$ K are the sample and background temperature, respectively. As shown in figure 5(a), we first performed the temperature calibrations using a Linkam heating stage to measure the Raman peak position (A_{1g} and E_{2g}¹ modes for MoS₂) as a function of the sample temperature (through stage heating). This allows us to fit a linear relationship between the Raman peak position ω and the sample temperature T : $\omega(T) = \omega_0 + \chi(T - T_0)$, where ω_0 is the

peak position at room temperature T_0 and χ is the temperature dependence coefficient for the particular Raman mode. For E_{2g}¹ and A_{1g} modes in pristine bilayer MoS₂, χ_E and χ_A were fitted to be -0.015 ± 0.002 cm⁻¹ °C⁻¹ and -0.015 ± 0.002 cm⁻¹ °C⁻¹, as shown in the blue dashed lines in figures 5(b) and (c).

For intercalated Li_xMoS₂, the initial peak position and temperature dependence coefficient can differ from that of pristine MoS₂, as illustrated in figure 3. Thus, we performed a series of temperature calibrations at different Li concentrations, $x = 0, 0.2, 0.4, 0.8$, and 1.0 , for our Li_xMoS₂ samples. The calibration and fitted results for Li_{0.4}MoS₂ are shown in figures 5(b) and (c), where the temperature dependence coefficients are found to be similar for Li_xMoS₂ samples (more details on the calibrations can be found in figure S5 in the supporting information). We kept the laser power low (and therefore Li_xMoS₂ temperature < 100 °C) during our calibration and actual thermometry measurements to avoid unintentional phase transformation and minimize ionic diffusion (and therefore a change in carrier concentration) that has been observed in high-temperature annealing (> 300 °C) of chemically lithiated MoS₂ thin films [18, 61].

As shown in figure 6(a), the TBC at the bilayer MoS₂/SiO₂ interface before intercalation is $G = 14 \pm 4.0$ MW m⁻² K⁻¹,

consistent with previous reports ($\sim 15 \text{ MW m}^{-2} \text{ K}^{-1}$) for monolayer MoS_2 with electrical [31] and optical [33] heating. Upon Li intercalation (figure 6(b)), we observe a significant decrease in TBC at the $\text{MoS}_2/\text{SiO}_2$ interface, to $G = 1.8 \pm 0.9 \text{ MW m}^{-2} \text{ K}^{-1}$ for $\text{Li}_{1.0}\text{MoS}_2$. This large decrease in TBC is likely due to a combination of effects, including an increase in the van der Waals spacing at the $\text{MoS}_2/\text{SiO}_2$ interface and changes in $\text{MoS}_2/\text{SiO}_2$ bonding. Upon de-intercalation, the TBC can be mostly recovered to its pre-lithiation value when we removed Li ions from the system ($G = 11.8 \pm 3.5 \text{ MW m}^{-2} \text{ K}^{-1}$). This large and reversible TBC modulation opens interesting opportunities to engineer the heat dissipation for 2D applications such as nanoscale thermal transistors [30] and thermoelectric devices.

4. Conclusion

In summary, we developed a solid-state Li intercalation platform for 2D materials and achieved reversible control of their electrical and thermal properties via electrochemical intercalation. Through Hall measurements, we demonstrated $\sim 200\times$ tuning of carrier concentration in Li-intercalated bilayer MoS_2 , ranging from 0.8×10^{12} to $1.5 \times 10^{14} \text{ cm}^{-2}$. Combining with an improved contact resistance, almost three orders of magnitude increase ($500\times$) in the drive current of such bilayer MoS_2 transistors. Raman spectroscopy confirmed the reversible doping effect, recording peak shifts as large as 18 cm^{-1} and 3 cm^{-1} for A_{1g} and E_{2g}^1 modes of MoS_2 , respectively. Using Raman thermometry, we extracted the TBC between MoS_2 and SiO_2 to be $14 \pm 4.0 \text{ MW m}^{-2} \text{ K}^{-1}$ before intercalation, and as low as $1.8 \pm 0.9 \text{ MW m}^{-2} \text{ K}^{-1}$ after intercalation, due to weakened bonding and phonon scattering. Thus our study suggests that electrochemical intercalation is a powerful technique to engineer and reversibly tune 2D material electrical and thermal properties. Our findings also provide a convenient method to measure the carrier concentration and TBC of 2D materials using Raman spectroscopy, crucial for 2D electronic applications.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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