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Tuning electrical and interfacial thermal properties of bilayer MoS$_2$ via electrochemical intercalation

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Abstract

Layered two-dimensional (2D) materials such as MoS$_2$ 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 MoS$_2$ nanosheets by combining electrical measurements and Raman spectroscopy. We demonstrate reversible modulation of carrier density over more than two orders of magnitude ($0.8 \times 10^{12}$ to $1.5 \times 10^{14}$ cm$^{-2}$), and we simultaneously obtain the thermal boundary conductance between the bilayer and its supporting SiO$_2$ substrate for the first time. This thermal coupling can be reversibly modulated by nearly a factor of eight, from $14 \pm 4.0$ MW m$^{-2}$ K$^{-1}$ before intercalation to $1.8 \pm 0.9$ MW m$^{-2}$ K$^{-1}$ when the MoS$_2$ 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)

1. Introduction

Two-dimensional (2D) materials such as molybdenum disulfide (MoS$_2$) 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], inter-
connects [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 lack-
ning. For instance, while some doping strategies effectively
achieve high carrier concentrations [14, 15], it remains challen-
ging 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 appli-
cations [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 che-
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 lever-
aging 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 \(\sim8–10 \times\) modulation of cross-plane
thermal conductance (combined volumetric contribution of MoS\(_2\),
and interfacial contributions of Al/MoS\(_2\) and MoS\(_2\)/SiO\(_2\)) in
MoS\(_2\) thin films [30] (\(\sim10 \text{ nm}\) thick) and up to \(5 \times\) change in
cross-plane thermal conductivity in bulk MoS\(_2\) samples [21]
(\(\sim10–20 \mu\text{m}\) thick). However, while these earlier studies pro-
vided 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 inter-
calants 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 MoS\(_2\)/SiO\(_2\) interface vary as a
function of Li concentration through electrical Hall measure-
ments and Raman spectroscopy. In addition, prior inter-
calation 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 electro-
chemical 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 pat-
tered 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 nano-
battery with MoS\(_2\) and lithium iron phosphate LiFePO\(_4\) serv-
ing as the working and reference/counter electrodes, respec-
tively. 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-inter-
calation 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× 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 temp-
perature 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 con-
ducted in a Quantum Design PPMS-7 system with digital lock-
in amplifiers (Stanford Research Systems SR830).
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, a 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 LiₓMoS₂ (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.
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 $8 \times 10^{11}$ 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 $1.5 \times 10^{14}$ cm$^{-2}$ when Li concentration approached the maximum intercalation capacity $Li_{1.0}MoS_2$, 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 2](image-url)

**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), $Li_{0.2}MoS_2$ (black), $Li_{1.0}MoS_2$ (red). The channel conductance increases as carrier concentration increases due to Li intercalation. $Li_{1.0}MoS_2$ shows metallic behavior (no $V_{GS}$ dependence) because it is in the 1T 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.
bias $V_{DS} = 0.1$ V. Before Li intercalation, the exfoliated MoS$_2$ (blue curve in figure 2(c)) was in a semiconducting 2H phase and showed an on/off ratio of $\sim 1000 \times$ through backgate control. Upon Li intercalation (black curve, Li$_{0.2}$MoS$_2$), we noticed an increase in channel conductance due to doping and decreased on/off ratio ($\sim 50 \times$). When the MoS$_2$ flake was fully lithiated to Li$_{1.0}$MoS$_2$ (red curve), the channel became metallic as MoS$_2$ 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 (Li$_{1.0}$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-MoS$_2$ layers, forming an unstable 2H-Li$_x$MoS$_2$ phase. As more Li atoms enter the MoS$_2$ structure [47], the strain causes the crystal structure to transform into the thermodynamically-stable 1T-Li$_x$MoS$_2$ 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 MoS$_2$ 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 MoS$_2$ 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 MoS$_2$ 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 MoS$_2$ [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 MoS$_2$ 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
was as large as 18 cm$^{-1}$ at Li$_{1.0}$MoS$_2$ (figure 3(b)), confirming a heavy doping concentration ($n_i = 1.5 \times 10^{14}$ 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$_x$MoS$_2$, we also employ a Raman thermometry technique (figure 4(a)) to characterize how the TBC between bilayer MoS$_2$ and its supporting substrate (SiO$_2$/Si) changes as we intercalate and de-intercalate Li ions into the van der Waals gap between MoS$_2$ layers and between the bottom MoS$_2$ layer and the SiO$_2$ 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 ultra-thin 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 MoS$_2$ on SiO$_2$ 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 MoS$_2$ thin films on SiO$_2$/Si substrates and with a spot size $r_s$ between 310 and 370 nm (without and with electrolyte through a $100\times$ objective, see figure S3 in the supporting information for more details), we expect most of the heat in MoS$_2$ will be dissipated through the substrate and rendering the system to be insensitive to the in-plane thermal conductivity of MoS$_2$, 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 MoS$_2$/SiO$_2$ interface significantly simplifies our measurement and analysis.

A key parameter in Raman thermometry is the power absorbed ($P_{\text{abs}}$) by bilayer MoS$_2$. A significant portion of the uncertainty in optically-heated Raman thermometry measurements stems from $P_{\text{abs}}$ 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: $P_{\text{abs}} = P_{\text{in}}\alpha_l E$, where $P_{\text{in}}$ is the incident laser power, $\alpha_l$ is the absorption coefficient of free-standing MoS$_2$, $E$ is a wavelength-dependent enhancement factor, the intensity of the electric field (of the electromagnetic wave of the laser) at the top surface of SiO$_2$/Si substrate relative to the intensity of the incident electric field, accounting for the multiple reflections within the SiO$_2$/Si substrate. We characterized the incident laser power and the spot radius $r_s$ during our calibration measurements (see figure S3 in the supporting information for more details).

We measured the absorption coefficient of free-standing monolayer MoS$_2$ over a range of temperatures (see figure S6 in the supporting information). This temperature-dependence of $\alpha_l$ 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 $P_{\text{abs}}$) will underestimate the TBC in the Raman thermometry analysis. We expect the optical dielectric functions of monolayer and bilayer MoS$_2$ 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
intercalation

**Figure 5.** Temperature dependence of Raman peaks. (a) Raman spectra of pristine bilayer MoS\(_2\) 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 MoS\(_2\) and intercalated Li\(_{x}\)MoS\(_2\), respectively. The slopes of the linear fits are the temperature coefficients \(\chi_A\) and \(\chi_E\) for \(A_{1g}\) and \(E_{2g}^{1}\) modes, respectively.

**Figure 6.** Thermal boundary conductance (TBC) between MoS\(_2\) and SiO\(_2\). (a) The measured temperature rise of a pristine bilayer MoS\(_2\) 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 MoS\(_2\). As we intercalate (red crosses) more Li ions into MoS\(_2\), the TBC decreases to ~1.8 MW m\(^{-2}\) K\(^{-1}\) at Li\(_{1.0}\)MoS\(_2\). 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 MoS\(_2\) at 532 nm to be twice that of the monolayer MoS\(_2\) at 14% at 300 K, with similar temperature dependence as monolayer MoS\(_2\) (see more discussion in supporting information section S6) [33]. We measured the absorption coefficient of lithiated MoS\(_2\) in an earlier study [16], where we observed a 60% decrease in absorption (8.4% for bilayer Li\(_{1.0}\)MoS\(_2\)) 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/MoS\(_2\)/SiO\(_2\)/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 MoS\(_2\) as a function of the sample temperature (through stage heating). This allows us to fit a linear relationship between the Raman peak position \(\omega\) and the sample temperature \(T\): \(\omega(T) = \omega_0 + \chi(T - T_0)\), where \(\omega_0\) is the peak position at room temperature \(T_0\) and \(\chi\) is the temperature dependence coefficient for the particular Raman mode. For \(E_{2g}^{1}\) and \(A_{1g}\) modes in pristine bilayer MoS\(_2\), \(\chi_E\) and \(\chi_A\) were fitted to be \(-0.015 \pm 0.002\) cm\(^{-1}\) K\(^{-1}\) and \(-0.015 \pm 0.002\) cm\(^{-1}\) K\(^{-1}\), as shown in the blue dashed lines in figures 5(b) and (c).

For intercalated Li\(_{x}\)MoS\(_2\), the initial peak position and temperature dependence coefficient can differ from that of pristine MoS\(_2\), 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\(_{x}\)MoS\(_2\) samples. The calibration and fitted results for Li\(_{0.0}\)MoS\(_2\) are shown in figures 5(b) and (c), where the temperature dependence coefficients are found to be similar for Li\(_{x}\)MoS\(_2\) 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\(_{x}\)MoS\(_2\) 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 MoS\(_2\) thin films [18, 61].

As shown in figure 6(a), the TBC at the bilayer MoS\(_2\)/SiO\(_2\) interface before intercalation is \(G = 14 \pm 4.0\) MW m\(^{-2}\) K\(^{-1}\).
consistent with previous reports (∼15 MW m⁻² K⁻¹) for monolayer MoS₂ with electrical [31] and optical [33] heating. Upon Li intercalation (figure 6(b)), we observe a significant decrease in TBC at the MoS₂/SiO₂ interface, to \( G = 1.8 \pm 0.9 \) MW m⁻² K⁻¹ for LiₓMoS₂. This large decrease in TBC is likely due to a combination of effects, including an increase in the van der Waals spacing at the MoS₂/SiO₂ interface and changes in MoS₂/SiO₂ bonding. Upon de-intercalation, the TBC can be mostly recovered to its pre-lithiation value when we removed Li ions from the system (\( G = 11.8 \pm 3.5 \) MW m⁻² 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 MoS₂, ranging from \( 0.8 \times 10^{12} \) to \( 1.5 \times 10^{14} \) cm⁻². Combining with an improved contact resistance, almost three orders of magnitude increase (\( 500 \times \)) in the drive current of such bilayer MoS₂ 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 \( E_{1g}^1 \) modes of MoS₂, respectively. Using Raman thermometry, we extracted the TBC between MoS₂ and SiO₂ to be \( 14 \pm 4.0 \) MW m⁻² K⁻¹ before intercalation, and as low as \( 1.8 \pm 0.9 \) MW m⁻² 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 corresponding author.

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