Title
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Authors
Acikgoz, Ogulcan
Guerrero, Enrique
Yanilmaz, Alper
et al.

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Inverse Layer Dependence of Friction on Chemically Doped MoS_2

Ogulcan Acikgoz,[1*] Alper Yanilmaz,[2*] Omur E. Dagdeviren,[3,4] Cem Çelebi,[2†] and Mehmet Z. Baykara[1‡]

[1]Department of Mechanical Engineering, University of California Merced, Merced, California 95343, USA

[2]Department of Physics, Izmir Institute of Technology, Izmir 35430, Turkey

[3]Department of Physics, McGill University, Montréal, Québec H3A 2T8, Canada

[4]Department of Mechanical Engineering, École de Technologie Supérieure, University of Quebec, Quebec H3C 1K3, Canada

* These authors contributed equally to this work.

† Corresponding author. cemcelebi@iyte.edu.tr

‡ Corresponding author. mehmet.baykara@ucmerced.edu

We present the results of atomic-force-microscopy-based friction measurements on Re-doped molybdenum disulfide (MoS_2). In stark contrast to the seemingly universal observation of decreasing friction with increasing number of layers on two-dimensional (2D) materials, friction on Re-doped MoS_2 exhibits an anomalous, i.e. *inverse* dependency on the number of layers. Raman spectroscopy measurements reveal signatures of Re intercalation, leading to a decoupling between neighboring MoS_2 layers and enhanced electron-phonon interactions, thus resulting in increasing friction with increasing number of layers – a new paradigm in the mechanics of 2D materials.

Friction is among the most fascinating yet least understood subjects in classical mechanics. Despite its prevalence in mechanical systems, systematic studies aimed at uncovering the underlying physical mechanisms on fundamental length scales became only possible with the advent of modern experimental tools such as the atomic force microscope (AFM) [1,2]. Despite the outstanding resolution in space and force provided by such methods, a comprehensive physical picture of frictional processes remains yet to be formed, mainly because the phenomenon is a complex function of the multi-scale structural, mechanical and chemical properties of the involved surfaces, as well as environmental factors such as temperature and humidity [3].

The discovery of exotic electrical properties exhibited by graphene about fifteen years ago [4] and the ensuing boom in two-dimensional (2D) materials [5,6] led to new avenues in fundamental friction research. In particular, the atomically smooth and chemically inert surfaces exposed by the majority of 2D materials provide a simplified platform on which AFM-based friction experiments could be performed [7]. Such studies also exhibit practical relevance, as 2D materials could potentially be employed as solid lubricants in micro- and nano-scale mechanical systems where surface-based phenomena such as friction and wear bear increasing importance, and conventional, fluid-based lubrication schemes are not feasible [8-10].

A particularly crucial discovery in AFM-based 2D material friction research is that the friction decreases with increasing number of layers, as first reported in milestone experiments by Filleter *et al.* [11] and Lee *et al*. [12]. These observations were later confirmed by a number of independent studies performed on graphene, molybdenum disulfide (MoS_2), and other 2D materials [13-15], thus establishing decreasing friction with increasing number of layers as a seemingly universal characteristic of 2D materials. Among various theories proposed to explain the underlying physical mechanisms, the one that gained the most traction in the literature is the *puckering* effect [12]. In particular, it is proposed that the sharp AFM tip sliding on a 2D material leads to the formation of a *pucker* around itself, thus leading to an increase in contact area and enhanced friction. As the number of layers increases, the sample becomes stiffer in the vertical direction, resulting in the suppression of the pucker and thus decreasing friction. While this idea of puckering, which has been studied in detail via computational approaches [16], can explain the trend of decreasing friction with increasing number of layers, other theories have been proposed toward this goal, ranging from a suppression of electron-phonon coupling (and thus a reduction in energy dissipation) [11] as well as decreasing surface roughness [13] with increasing number of layers. On the other hand, no direct studies have been conducted to address the question of whether this apparently ubiquitous layer dependence trend of friction on 2D materials can be suppressed or even reversed through certain approaches, including but not limited to the application of strain [17], and the utilization of electrostatic fields [18], and chemical doping.

Motivated as above, we report here, by way of AFM-based friction measurements performed on Rhenium (Re) doped MoS_2, the observation of *inverse* layer dependence of friction, in stark contrast to the seemingly universal trend of decreasing friction with increasing number of layers of 2D materials. We employed Raman spectroscopy measurements to explore the underlying mechanisms and arrived at the conclusion that intercalation of Re between MoS_2 layers leads to a decoupling effect, resulting in enhanced electron-phonon interactions and thus increasing friction with increasing number of layers.

Both the undoped and Re-doped MoS_2 crystals studied here were synthesized over several weeks using the chemical vapor transport (CVT) technique in quartz ampoules at high temperatures, resulting in bulk crystals of 1 mm and above in size. Prior to the AFM and Raman spectroscopy experiments, flakes of Re-doped and undoped MoS_2 were deposited onto SiO_2 substrates via mechanical exfoliation. The AFM measurements were performed under ordinary laboratory conditions (Temperature: 22 – 23 ºC; Relative humidity: 20 – 40%) using a commercial AFM instrument (*Asylum Research, Cypher VRS*). Both Re-doped and undoped MoS_2 samples were characterized with the same AFM probe (*Nanosensors, CDT-CONTR*) with a normal spring constant value *k* of 0.84 N/m as determined by the Sader method [19]. The number of layers were determined from AFM topography maps. Friction force maps were recorded using established procedures [20]. Raman spectroscopy measurements were conducted using a commercial system (*Princeton Instruments, TriVista CRS*). Raman signals were recorded in a spectral range between 100 cm^{-1} and 600 cm^{-1} using an Ar^+ ion laser with a 514 nm excitation (600 grooves/mm grating) wavelength. For each sample, Raman measurements were repeated several times at different locations to ensure reproducibility. Each spectrum was normalized using *TriVista* software. The Si peak at 521 cm^{-1} was used as a calibration reference.

We started our investigation by studying the layer dependence of friction on undoped MoS_2. As demonstrated in Fig. 1(a,b) for a stair-like flake that progressively features one-to five-layer regions, the layer-dependence results obtained via friction force maps recorded on undoped MoS_2 are in harmony with previous experimental studies in the literature [12]. In particular, the friction force is monotonically decreasing with increasing number of layers, pointing toward an enhanced solid lubrication effect with increasing thickness.

As opposed to undoped MoS_2, AFM-based friction measurements on Re-doped MoS_2 surprisingly reveal that Re-doped flakes exhibit a completely unexpected, i.e. inverse layer dependence of friction. In particular, results reported in Fig. 1(c,d) for a Re-doped MoS_2 flake with one-, two-, and three-layer regions show a striking contrast to those in Fig. 1(a,b). Specifically, while solid lubrication is still achieved with Re-doped MoS_2 (i.e. the friction force recorded on Re-doped MoS_2 is always lower than the underlying SiO_2 substrate), single-layer Re-doped MoS_2 exhibits the lowest friction force and the friction force increases with the number of layers, in violation of the seemingly universal rule of decreasing friction with increasing number of layers.

In order to confirm the anomalous results obtained on Re-doped MoS_2 and ensure that the findings are not specific to one particular flake, measurements were repeated on a different Re-doped MoS_2 flake with two-, eleven-, thirteen-, fourteen- and fifteen-layer regions. The results (Fig. 2) demonstrate a similar overall trend: increasing friction with number of layers, with the trend reaching an apparent limit after fourteen layers.

It should be mentioned that an increasing friction trend with increasing number of layers was shown once before, on undoped MoS_2 samples [15], and attributed to an exceptionally large AFM probe apex. However, the "regular" results obtained on undoped MoS_2 using the same AFM probe in our experiments (Fig. 1(a,b)) exclude a possible link between probe characteristics and the unusual findings on Re-doped MoS_2. It also needs to be emphasized that the measurements were repeated multiple times on different days, with the same trends observed on undoped and Re-doped samples. The sharpness of the step edges in the friction maps provide further proof for the absence of an exceptionally blunt apex. Based on these observations, we are thus confident that the observed anomalous trend is intrinsic to Re-doped MoS_2 and not probe-dependent.

In order to explore the physical reasons behind the observation of an inverse layer-dependence of friction on Re-doped MoS_2, we first checked the potential presence of unexpected trends in adhesion and roughness with increasing number of layers. The results of these investigations, presented in the Supplemental Material [21], do not yield any significant trends in the layer-dependent behavior of adhesion and roughness that would explain the anomalous trend in friction we observe for the Re-doped samples. Subsequently, we performed Raman spectroscopy measurements on single-layer, few-layer (i.e. with less than 10 layers) and bulk flakes of undoped and Re-doped MoS_2, the results of which are summarized in Fig.

3. The main conclusions from these measurements can be described as follows: (i) The two predominant Raman active modes of MoS_2 (the E_{2g} mode which arises from the opposite vibration of two S atoms against a Mo atom and the A_{1g} mode which corresponds to the out-of-plane vibrations of S atoms in opposite directions) [22] are observed in all samples, with no noticeable shifts in their positions upon Re doping; (ii) the spectra of Re-doped MoS_2 are devoid of peaks associated with the formation of ReS_2 (an E_{2g} peak at 163 cm^{-1} and an A_{1g}-like peak at 213 cm^{-1}), ruling out phase segregation as a result of Re doping [23]; (iii) the separation in inverse wavelength between the E_{2g} and A_{1g} modes (19 cm^{-1}, 23 cm^{-1}, and 25 cm^{-1} for single-layer, few-layer and bulk MoS_2 regions, respectively) decreases with decreasing thickness in accordance with the literature [24]; and perhaps most significantly, (iv) there is a significant decrease in the intensity of the E_{2g} and A_{1g} peaks for all Re-doped samples (with the intensity of the reference Si peak at 521 cm^{-1} remaining unchanged) when compared with the undoped ones.

The strong influence of Re doping on MoS_2 peak intensities in Raman spectra is a prominent feature that warrants further investigation. In particular, it has been recently shown for 2D materials (and heterostructures built from them), that the peak intensity of phonon modes observed in Raman spectroscopy can be utilized as a direct tool to qualitatively evaluate electron-phonon coupling (EPC) [25]. This is particularly important for friction measurements, as the suppression of EPC when switching from single-layer to bi-layer has been previously proposed to be the dominant mechanism for decreasing friction with increasing number of layers, based on the argument that the decreasing EPC consequently leads to fewer channels for energy dissipation, thus resulting in low friction [11]. On the other hand, the strong suppression of peak intensities in our Raman measurements suggests an *enhancement* of EPC upon Re doping, thus leading to an inverse trend for the layer dependence of friction: With each additional layer of material, and in the absence of EPC suppression, an increasing number of energy dissipation channels become available, resulting in higher friction.

It should be indicated that similar observations in Raman spectra have been reported before for MoS_2 doped with Co [26] and Li ions [27]. In both studies, while the signature peak positions of MoS_2 did not shift, peak intensities significantly decreased, suggesting an enhancement of EPC which occurs through a *decoupling* between the layers occurring through the intercalation of dopant ions between the MoS_2 layers. The close similarity between the results of our Raman analysis and the works in question (whereby ion intercalation was also confirmed for other 2D materials such as $MoSe_2$, WSe_2, WS_2, and graphene [26]), in addition to the fact that the ionic radius of the Re ion is smaller than those of Co, Li and Na ions (which have also been shown to intercalate MoS_2 [28]), thus strongly suggests that the majority of Re dopants in our MoS_2 samples are in intercalated states. Further support for this line of argumentation comes in the form of roughness measurements presented in the Supplemental Material [21]: While the roughness of bulk undoped MoS_2 regions are appreciably lower than single-, bi- and tri-layers (as expected from results presented previously on graphene [13]), no such decrease in roughness is observed for the Re-doped samples, potentially due to the presence of intercalated Re dopants remaining on the exfoliated surfaces exposed to the AFM probe.

We presented here the unique observation of an *inverse* layer dependence of friction on Re-doped MoS_2, in violation of the so-far unchallenged observation that friction on 2D materials decreases with increasing number of layers. While this new paradigm, explained by the intercalation of Re dopants between the MoS_2 layers and the resulting enhancement in EPC, is of fundamental physical interest, it also opens the way for selective tuning of friction in micro- and nano-scale mechanical systems, by the combined use of undoped 2D materials and those with intercalated dopants. More work will need to be conducted to determine if there is a limit to the friction increase with increasing number of layers (as suggested by the data presented in Fig. 2) and the associated physical mechanisms.

Acknowledgements

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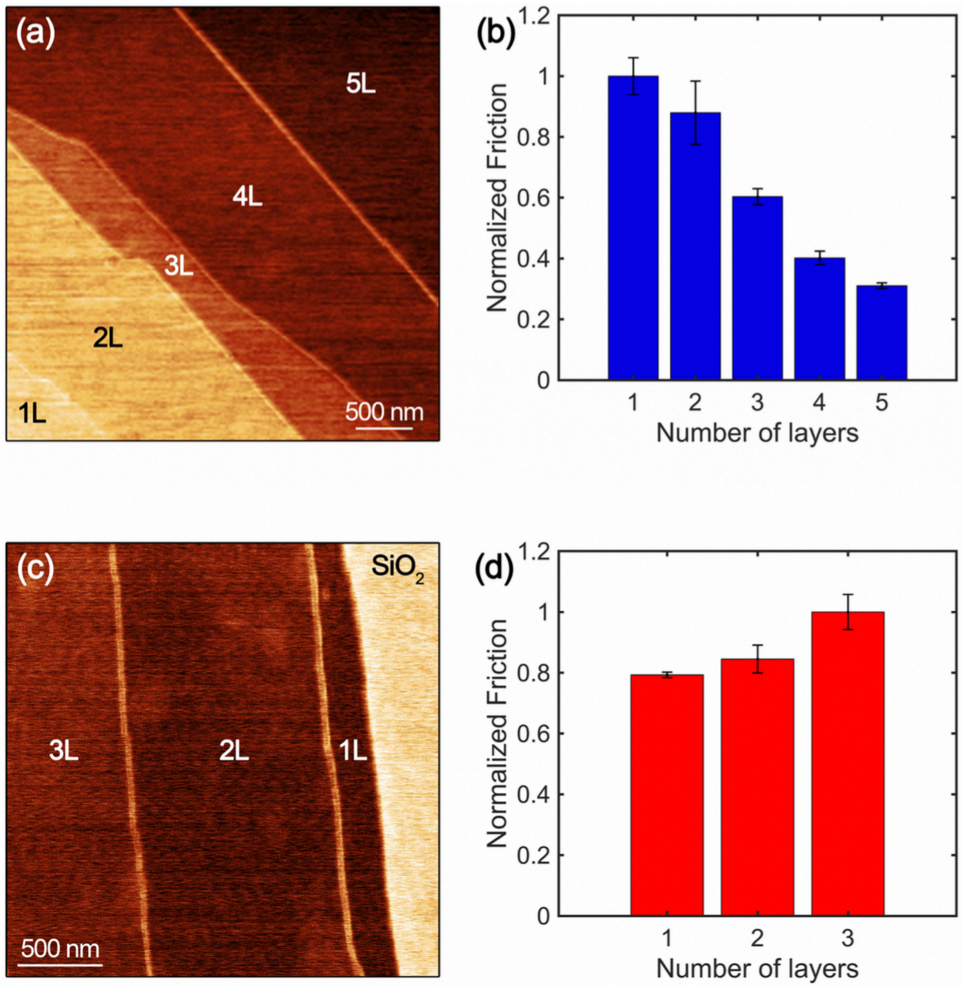

FIG. 1. (a) Friction force map obtained on an undoped MoS_2 flake with 1, 2, 3, 4, and 5 layers (1L, 2L, 3L, 4L, and 5L, respectively). situated on a SiO_2 substrate. (b) Friction on undoped MoS_2 areas with different number of layers. Friction is normalized to the value obtained on the 1L area. (c) Friction force map obtained on a Re-doped MoS_2 flake with 1, 2, and 3 layers (1L, 2L, and 3L, respectively), situated on a SiO_2 substrate. (d) Friction on Re-doped MoS_2 areas with different number of layers. Friction is normalized to the value obtained on the 3L area.

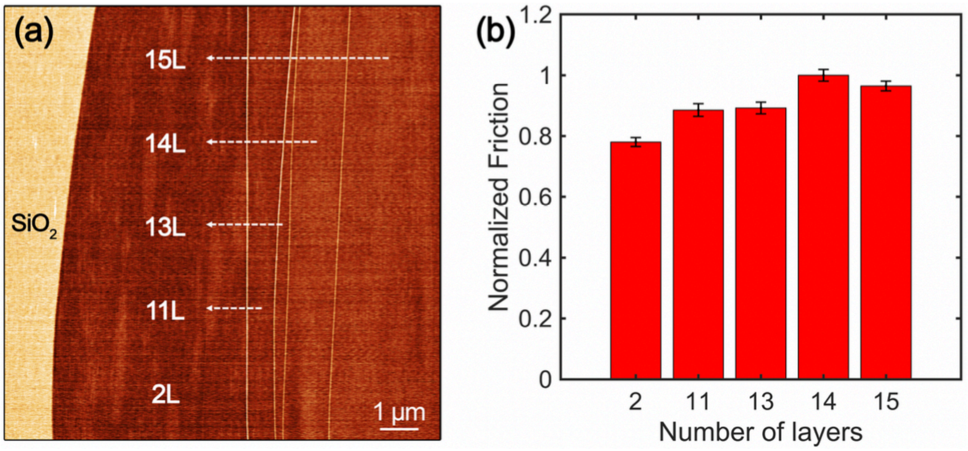

FIG. 2. (a) Friction force map obtained on a Re-doped MoS_2 flake with 2, 11, 13, 14, and 15 layers (2L, 11L, 13L, 14L, and 15L, respectively), situated on a SiO_2 substrate. (b) Friction on Re-doped MoS_2 areas with different number of layers. Friction is normalized to the value obtained on the 14L area.

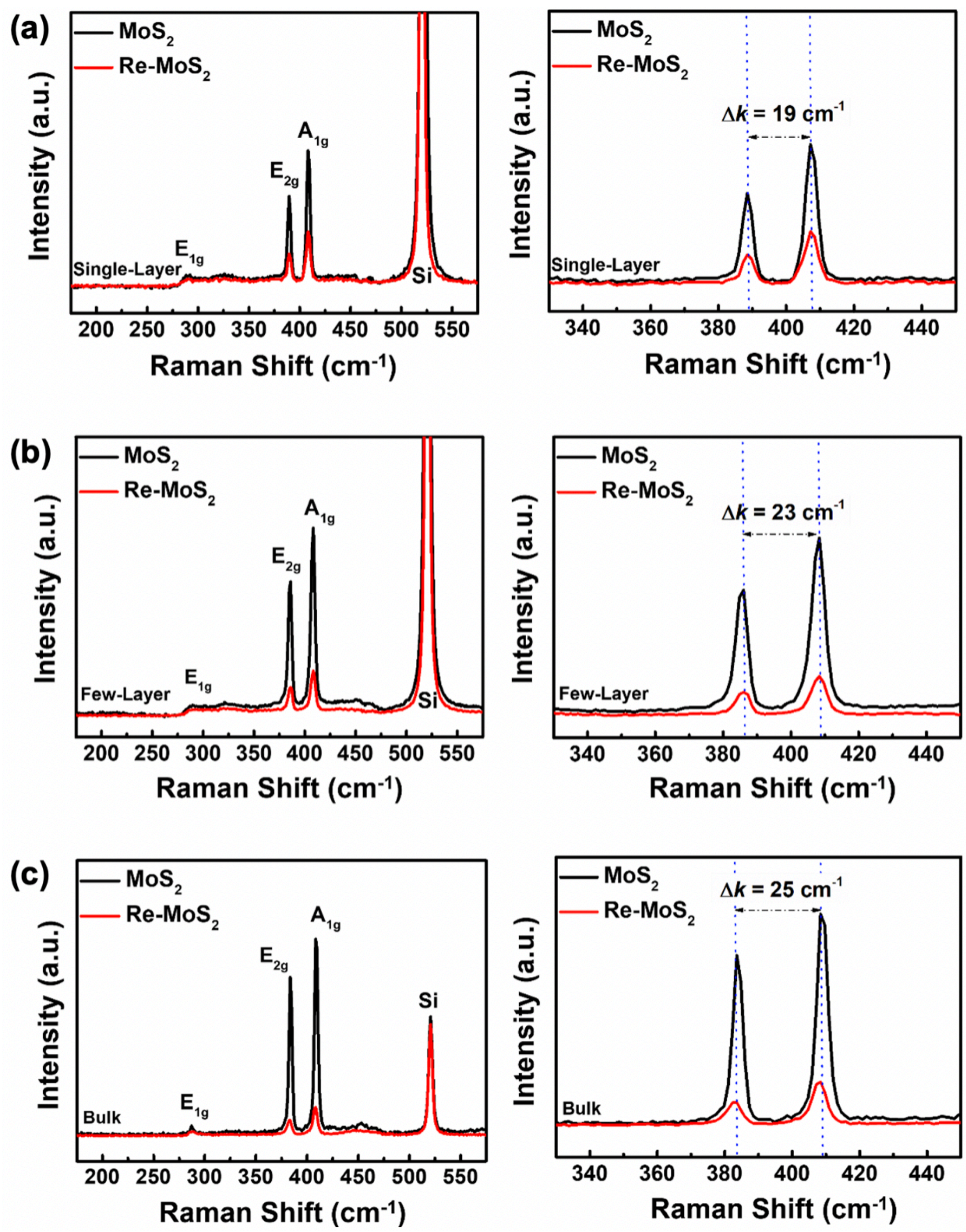

FIG. 3. Raman spectra of (a) single-layer, (b) few-layer and (c) bulk samples of undoped and Re-doped MoS_2. The panels on the right are zooms on the regions that contain the E_{2g} and A_{1g} peaks of MoS_2. Δk indicates the wavenumber spacing between the E_{2g} and A_{1g} peak positions, which are themselves highlighted by the dotted blue lines.

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Supplemental Material

Inverse Layer Dependence of Friction on Chemically Doped MoS_2

Ogulcan Acikgoz,[1*] Alper Yanilmaz,[2*] Omur E. Dagdeviren,[3] Cem Çelebi,[2†] and Mehmet Z. Baykara[1‡]

[1]Department of Mechanical Engineering, University of California Merced, Merced, California 95343, USA

[2]Department of Physics, Izmir Institute of Technology, Izmir 35430, Turkey

[3]Department of Physics, McGill University, Montréal, Québec H3A 2T8, Canada

[4]Department of Mechanical Engineering, École de Technologie Supérieure, University of Quebec, Quebec H3C 1K3, Canada

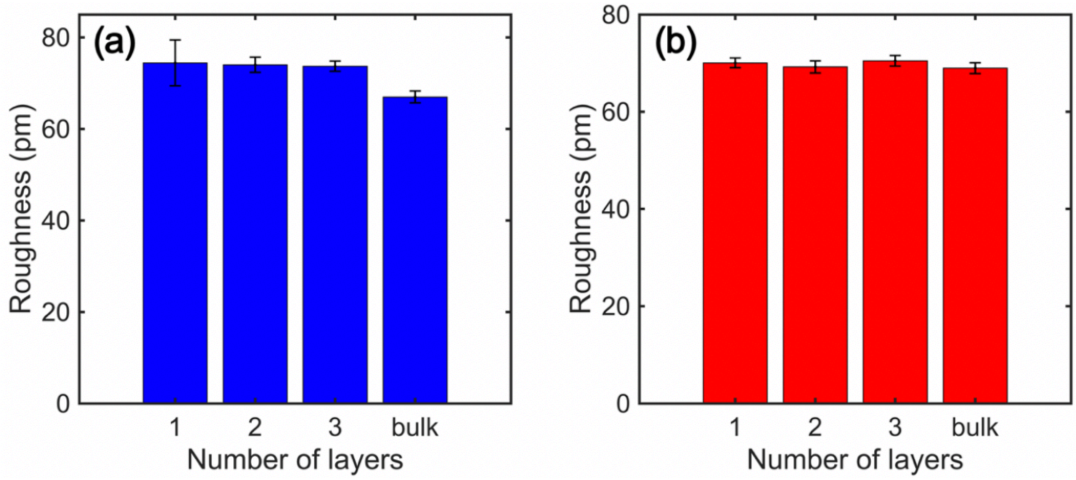
* These authors contributed equally to this work.

† Corresponding author. cemcelebi@iyte.edu.tr

‡ Corresponding author. mehmet.baykara@ucmerced.edu

Roughness Measurements

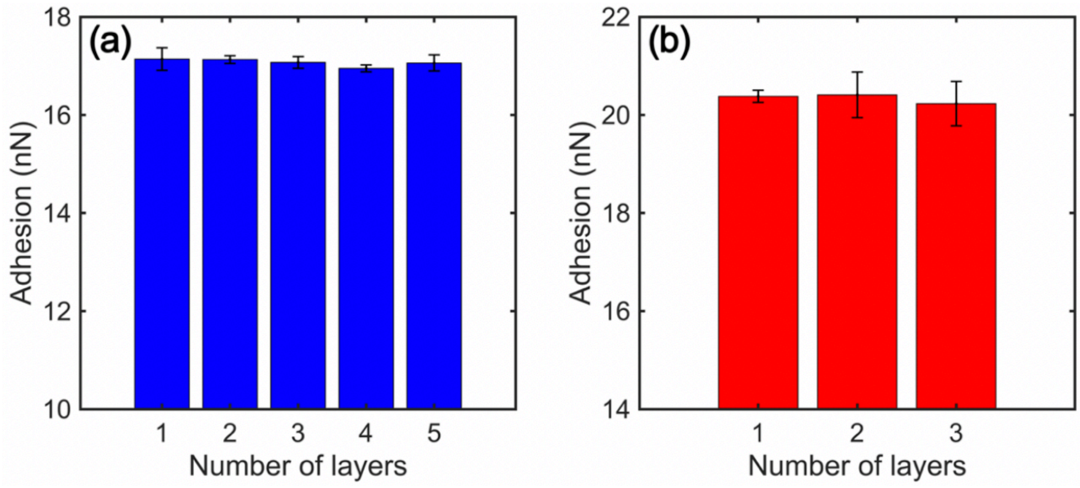
In order to try and identify the physical mechanism responsible for the observation of inverse layer-dependence of friction on Re-doped MoS_2 samples, we performed AFM-based roughness measurements in contact mode. In particular, Supplemental Fig. 1(a) shows roughness measurements on undoped MoS_2. While mean roughness values recorded on 1-, 2- and 3-layer regions are nearly identical, the mean roughness of the bulk region is ~11% lower, in accordance with previous studies that proposed reduced roughness at increasing number of layers as an alternative / complementary mechanism to the puckering effect [1]. On the other hand, the roughness measurements performed on Re-doped MoS_2 (reported in Supplemental Fig. 1(b)) show no significant change between different regions, with the difference between mean roughness values on different number of layers being less than ~2.2%. These findings demonstrate that changing roughness with increasing number of layers cannot be the reason behind the observation of anomalous layer-dependence of friction on Re-doped MoS2 samples.



Supplemental Fig. 1. Roughness values measured on 1-, 2-, 3-layer and bulk regions of (a) undoped MoS_2, and (b) Re-doped MoS_2 extracted from 10 nm × 10 nm scans.

Adhesion Measurements

An alternative physical mechanism potentially responsible for the observation of anomalous layer-dependence of friction on Re-doped MoS_2 samples could involve increasing adhesion (and thus, friction) at increasing number of layers. In order to probe whether there is any effect of number of layers on adhesion force, we performed force spectroscopy experiments on undoped and Re-doped MoS_2 samples to extract adhesion values. In particular, adhesion maps consisting of 256 × 256 pixels were recorded on the samples areas presented in Fig. 1(a) and Fig. 1(c) to extract adhesion values with high statistical significance. As demonstrated in Supplemental Fig. 2, no significant difference in adhesion forces exist between single-layer and few-layer regions of the flakes for both undoped and Re-doped MoS_2 samples, as previously reported for a number of 2D materials [2]. Consequently, adhesion trends cannot explain the anomalous friction trend observed on Re-doped MoS_2.



Supplemental Fig. 2. Adhesion force values measured on (a) 1-, 2-, 3-, 4- and 5-layer regions of undoped MoS_2, and (b) 1-, 2-, and 3-layer regions of Re-doped MoS_2.

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