

# Nanotribological properties and scratch resistance of MoS<sub>2</sub> bilayer on a SiO<sub>2</sub>/Si substrate

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**Abstract:** The tribological properties and scratch resistance of MoS<sub>2</sub> bilayer deposited on SiO<sub>2</sub>/Si substrates prepared via chemical vapor deposition are investigated. Friction force microscopy (FFM) is employed to investigate the friction and wear properties of the MoS<sub>2</sub> bilayer at the nanoscale by applying a normal load ranging from 200 to 1,000 nN. Scratch resistance is measured using the scratch mode in FFM based on a linearly increasing load from 100 to 1,000 nN. Kelvin probe force microscopy (KPFM) is performed to locally measure the surface potential in the tested surface to qualitatively measure the wear/removal of MoS<sub>2</sub> layers and identify critical loads associated with the individual failures of the top and bottom layers. The analysis of the contact potential difference values as well as that of KPFM, friction, and height images show that the wear/removal of the top and bottom layers in the MoS<sub>2</sub> bilayer system occurred consecutively. The FFM and KPFM results show that the top MoS<sub>2</sub> layer begins to degrade at the end of the low friction stage, followed by the bottom layer, thereby resulting in a transitional friction stage owing to the direct contact between the diamond tip and SiO<sub>2</sub> substrate. In the stable third stage, the transfer of lubricious MoS<sub>2</sub> debris to the tip apex results in contact between the MoS<sub>2</sub>-transferred tip and SiO<sub>2</sub>. Nanoscratch test results show two ranges of critical loads, which correspond to the sequential removal of the top and bottom layers.

**Keywords:** chemical vapor deposition (CVD)-grown MoS<sub>2</sub> bilayer; friction force microscopy (FFM); nanoscratch test; Kelvin probe force microscopy (KPFM); scratch resistance

## 1 Introduction

Molybdenum disulfide (MoS<sub>2</sub>), one of the most typical transition metal dichalcogenides, exhibits a two-dimensional (2D) layered crystalline structure with strong covalent bonds between atoms within the crystal and weak van der Waals forces between layers, thereby enabling easy shearing along its basal planes and low friction in sliding contacts. Hence, MoS<sub>2</sub> has received considerable attention as dry lubricants [1–3], a lubricant additive [4], and components of composite coatings [5–7] in various applications such

as the space industry [8, 9], and the majority of these applications are related to the use of MoS<sub>2</sub> in its bulk form or as thin films at the microscale. The use of atomically thin MoS<sub>2</sub> films for tribological applications has only received increasing attention in the last decade. Advancements in microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) have encouraged the investigation of atomically thin 2D materials as promising candidates for lubricating films on microscale and nanoscale surfaces, where conventional liquid lubricants or thick lubrication coatings cannot be supplied owing to the

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spatial constraints of MEMS and NEMS. Atomic force microscopy (AFM) can not only effectively reveal the surface image of a sample, but also the nanotribological properties of atomically thin 2D materials owing to its extremely high lateral and vertical force resolutions. Although numerous nanotribological studies regarding 2D materials based on friction force microscopy (FFM) have been performed on graphene, atomically thin MoS<sub>2</sub> films have similarly been investigated extensively [10–13]. Lee et al. [10] compared the nanoscale frictional characteristics of atomically thin sheets of graphene, MoS<sub>2</sub>, NbSe<sub>2</sub>, and h-BN exfoliated onto a weakly adherent substrate (silicon oxide) with those of their bulk counterparts. Their measurements, which involved a scale down to single atomic sheets, revealed that friction increased monotonically as the number of layers decreased for all four materials. In Ref. [11], the friction properties of chemical vapor deposition (CVD)-grown and mechanically exfoliated single-layer MoS<sub>2</sub> were compared via FFM under normal forces ranging from 0 to 20 nN. The authors demonstrated that a CVD-grown single-layer MoS<sub>2</sub> exhibited greater friction compared with a mechanically exfoliated single-layer MoS<sub>2</sub>, and conjectured that this might be related to the crystalline imperfections in the CVD-grown MoS<sub>2</sub>. The coefficient of friction (COF) of CVD-grown MoS<sub>2</sub> ranged from a value less than 0.2 to an extremely high value exceeding 1. In Ref. [12], the friction of MoS<sub>2</sub> films deposited on various substrates via atomic layer deposition was investigated. Based on an experiment using FFM under a normal load of 5–25 nN, it was discovered that friction decreased as the number of layers increased regardless of the substrate. They explained that the effect of the substrate on the friction of MoS<sub>2</sub> could be characterized by the work of adhesion as the number of layers increased. As the friction forces were not calibrated in the force units, the COFs were unknown. Cho et al. [13] compared the dry friction and wear properties of atomically thin CVD-grown graphene and MoS<sub>2</sub> films on SiO<sub>2</sub>/Si substrates under a low contact pressure (72 MPa) using a custom-developed tribometer and under high contact pressure (378 MPa) using a typical ball-on-disk tester. They claimed that mild wear occurred in a layer-by-

layer manner at a low contact pressure. At a high contact pressure (378 MPa), severe wear occurred due to failure at the interface between the MoS<sub>2</sub> films and the underlying substrates. They further explained that the low friction of the MoS<sub>2</sub> film at both contact conditions was due to the transfer of the MoS<sub>2</sub> film to the counterpart, which served as a lubricant. However, these results are not comparable to any experimental results obtained using FFM, owing to the significant difference in the contact conditions (contact pressure and contact size) between the FFM and their test devices. It was discovered that studies pertaining to the nanotribological properties of atomically thin MoS<sub>2</sub> films have only addressed the friction property. Compared with the vigorous investigation of the friction and wear properties of MoS<sub>2</sub> films, the scratch resistance of atomically thin MoS<sub>2</sub> films has never been investigated. The most widely used method for quantitatively assessing the adhesion of films is the scratch test, where adhesion is measured by the critical load  $L_c$ , which is defined as the load at which the film is exfoliated or delaminated from the substrate [14, 15].

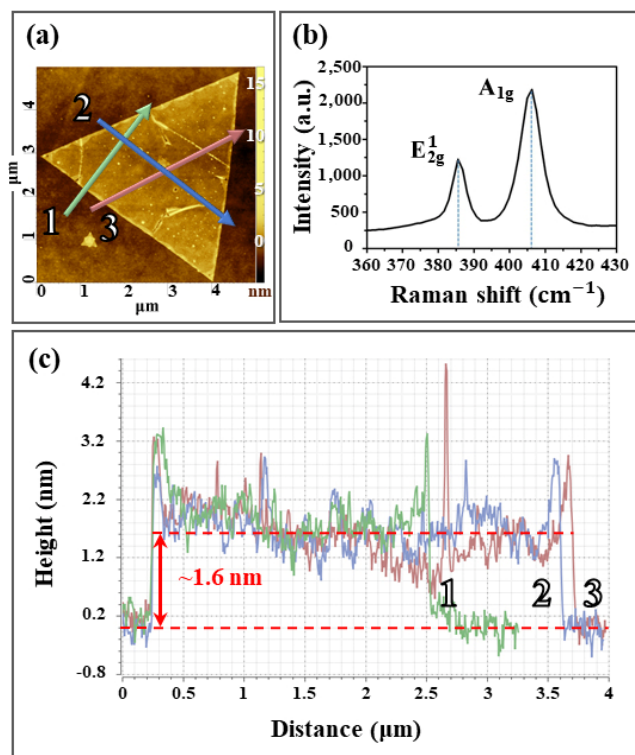
Kelvin probe force microscopy (KPFM) is a tool that measures the spatial charge distribution of various materials by measuring the contact potential difference (CPD) between the tip and the samples [16, 17]. As the surface potential and topographic image are simultaneously measured without contact to the sample surface, KPFM can provide valuable information for assessing the degradation/removal of MoS<sub>2</sub> monolayer or individual MoS<sub>2</sub> layers in cases involving a multiple-layer MoS<sub>2</sub> system. The work function of MoS<sub>2</sub> nanoflakes prepared via mechanical exfoliation was investigated using KPFM [18]. The CPDs of MoS<sub>2</sub> with monolayers and bilayers were measured to be 95 and 195 mV, respectively.

In this study, the friction and wear properties of a MoS<sub>2</sub> bilayer were investigated using FFM, and scratch resistance was investigated by employing the linear mode of FFM. The identification of critical loads (maximum contact pressure) for the degradation/removal of individual layers was prioritized. KPFM was performed to assess the failure level of the MoS<sub>2</sub> bilayer system on the tested surface.

## 2 Experimental details

### 2.1 Materials

In this study, a MoS<sub>2</sub> bilayer on a SiO<sub>2</sub>/Si substrate (2D Semiconductor, USA), which was synthesized by chemical vapor deposition (CVD) on p-doped bulk Si with an oxide layer (thickness of approximately 300 nm), was utilized in wear and scratch tests. To determine the thickness of the MoS<sub>2</sub> nanoflake, we applied AFM (SmartSPM 1000, AIST-NT, USA) with Si probes (approximately 10 nm of tip radius, Tap190Al-G, Budget Sensors, Republic of Bulgaria) in intermittent contact mode. Figure 1(a) shows a typical height image of large MoS<sub>2</sub> nanoflakes used in the wear test. The number of layers of MoS<sub>2</sub> nanoflakes was confirmed via the Raman spectroscopy (In Via Raman Microscope, Renishaw, UK) using a laser excitation of 532 nm. The Raman spectrum (Fig. 1(b)) showed two characteristic peaks: the E<sub>2g</sub><sup>1</sup> peak at 385.5 cm<sup>-1</sup> for the in-plane vibration of the S–Mo–S sandwich structure and the A<sub>1g</sub> peak at 406.3 cm<sup>-1</sup> for the out-of-plane vibration of S atoms. This Raman spectrum showed



**Fig. 1** (a) AFM height image of a MoS<sub>2</sub> nanoflake, (b) Raman spectrum of bilayer MoS<sub>2</sub> flake, and (c) surface height profile along the lines marked in Fig. 1(a).

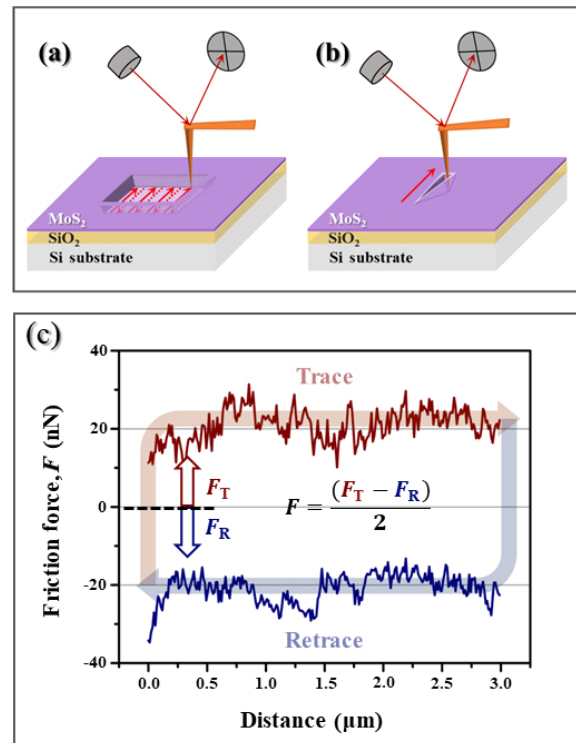
that the MoS<sub>2</sub> sample contained two layers, which agreed well with the previous measurement by Choi et al. [18]. The gap between the two peak frequencies was approximately 20.8 cm<sup>-1</sup>, which is consistent with the range of 21.0–21.5 cm<sup>-1</sup> previously reported for the MoS<sub>2</sub> bilayer [19, 20]. The spacing between the two peak frequencies for monolayer MoS<sub>2</sub> was reported to be 20.1 [18] or 19.7 cm<sup>-1</sup> [21]. The height profiles across the MoS<sub>2</sub> nanoflakes along the marked lines in Fig. 1(a) are shown in Fig. 1(c); they further confirm that the sample is a MoS<sub>2</sub> bilayer. The thickness of the MoS<sub>2</sub> nanoflake was measured to be approximately 1.6 nm, which is similar to that of the MoS<sub>2</sub> bilayer.

### 2.2 Nanoscale wear and nanoscratch test

Nanotribological characterization of the MoS<sub>2</sub> bilayer was conducted using FFM. A schematic illustration of the FFM apparatus is shown in Fig. 2(a). In FFM, a diamond tip slides over the sample surface with a constant normal load parallel to the fast scan axis. In this study, the scan rate was set to 5 Hz, and 256 test scans were conducted over an area measuring 3 μm × 3 μm. The normal load ranged from 200 to 1,000 nN, at an increment of 100 nN. We employed single-crystal diamond probe tips (D300, SCDprobes, Republic of Estonia) to conduct FFM. Probe tips with radii within the range of 10–15 nm were selected to avoid a considerable deviation in the contact pressure exerted on the sample surface by the diamond tip. The approximate tip radii were measured using the field-emission scanning electron microscope (FE-SEM; JSM-6700F, JEOL Corp., Japan), and five tips were selected from more than twenty single-crystal diamond probe tips (see the Electronic Supplementary Material (ESM) for detailed SEM images of the tips). In FFM, an accurate normal spring constant value should be used to calculate the normal load imposed on the sample surface as a load is applied through the bending of the cantilever. However, the nominal normal spring constant values supplied by the manufacturer span a wide range (some products fabricated in a single batch vary by one order of magnitude between the highest and lowest values). Therefore, the normal spring constant of each probe must be measured to apply an accurate normal load. Additionally, the torsional spring constant should be determined such

that the friction force generated from the tip-sample sliding contact can be calculated accurately. Both the normal and torsional spring constants of the cantilever were determined using the built-in calibration module in the AFM system, where the refined unloaded resonance method (Sader method) was applied [22]. The geometrical characteristics of the cantilever and tip were measured using FE-SEM and used for spring constant calibration (video clips of the measurement procedures for normal and torsional spring constants are introduced in the ESM). The test was repeated three times to obtain results with statistical information and to verify the reliability. A new diamond probe tip was used for each test, and the normal spring constants of the used cantilevers were measured to be 32.3, 33.5, and 38.5 N/m, whereas the torsional spring constants were 6.07, 5.77, and 5.89 nN·m, respectively. Frictional forces were converted into units of Newton from the voltage values corresponding to one-half the difference between the trace and retrace signals from plots of the detector voltage signal generated by the torsional deflection of the tip during scans. A representative plot of the frictional forces ( $F$ ) in the voltage signal vs. the lateral displacement is shown in Fig. 2(c). The upper ( $F_T$ ) and lower ( $F_R$ ) curves indicate the trace and retrace friction force profiles, respectively. Topography images of the degraded surface were acquired using a silicon tip (Tap190Al-G, Budget Sensors, The Republic of Bulgaria) in the intermittent contact mode. Energy dispersive X-ray spectroscopy (EDS) was employed to identify the chemical composition of the apex of the tips used to verify the transfer of degraded MoS<sub>2</sub> nanoscale debris.

The scratch response of the MoS<sub>2</sub> bilayer was investigated using the linear scratch mode of the AFM system, as illustrated in Fig. 2(b). The diamond probe tips (D300, SCDprobes, Republic of Estonia) used for the nanoscratch test had a tip radius of approximately 15 nm, as measured via FE-SEM (see the ESM for the detailed SEM images of the tip before and after the test). The nanoscratch test was performed by increasing the normal load linearly from 100 to 1,000 nN at a scratch speed of 6 μm/s for a scratch distance of 3 μm. The normal and torsional spring constants were measured to be 45.1 N·m<sup>-1</sup> and 8.12 nN·m, respectively. The test was repeated 10 times with a 100 nm space between adjacent scratch tracks to obtain a result with



**Fig. 2** Schematic diagram of experiments for evaluating the tribological properties of MoS<sub>2</sub> nanolayer on Si substrate: (a) wear test and (b) nanoscratch test. (c) A representative plot of the frictional force vs. the lateral displacement.  $F_T$  and  $F_R$  denote the average friction force at trace and retrace, respectively.

statistical information and to verify the reproducibility of the scratch behavior. Scratched surfaces were observed via AFM using a sharp probe tip (nominal tip radius of less than 2 nm, SSH-NCHR-50, NanoSensors, Switzerland). However, the height images did not provide a clear image that was sufficient for distinguishing scratch tracks and failure locations.

Although both AFM height and friction force images obtained in the nanoscale wear and nanoscratch tests provided information regarding damage to the MoS<sub>2</sub> layers, they were insufficient for determining whether only the top layer was removed or whether both layers were completely degraded. Therefore, KPFM was conducted under ambient conditions to better distinguish the removal of the top and bottom MoS<sub>2</sub> layers for both tests and the load range corresponding to film failures. A conductive Pt-coated tip (25Pt200-H, Rocky Mountain Nanotechnology, USA) with a radius of less than 20 nm and a resonance frequency of 100 kHz was used for the KPFM. The distance between the tip and sample was 10 nm, and the tip bias voltage was 3 V.

### 3 Results and discussion

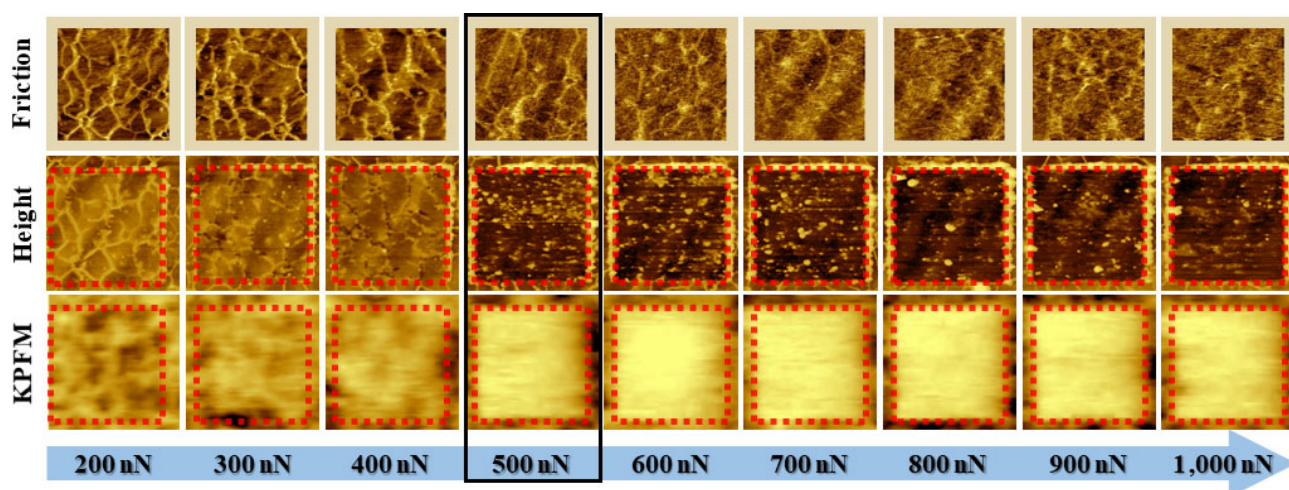
Figure 3 shows representative images corresponding to various AFM modes for a set of nanoscale wear tests. The friction images allowed us to classify the frictional behavior into three stages: low friction (from 200 to 400 nN), transitional friction (from 500 to 600 nN), and steady friction (from 700 to 1,000 nN) stages. The height images generally supported this observation.

The frictional behavior is presented in Fig. 4 in terms of the COF vs. applied load. In the first stage (from 200 to 400 nN), a diamond tip slid against the MoS<sub>2</sub> layer, and the low COF was due to the presence of either the bilayer or bottom layer of MoS<sub>2</sub>, which served as a lubricious film. However, after the bottom layer began to degrade at a load of 500 nN, and was completely removed from the underlying SiO<sub>2</sub> at 600 nN, the contact between the diamond tip and SiO<sub>2</sub> caused the COF to increase rapidly and reach the highest value (transition stage). By contrast, at a higher load of 700 nN, the COF was lower than the highest value observed in the transition stage, and the COF decreased continuously until it stabilized as the load further increased until the maximum load applied. We attributed this stable and comparatively lower COF, compared with that in the transition stage, to the transfer of lubricious MoS<sub>2</sub> debris to the tip apex, which resulted in contact between the MoS<sub>2</sub>-transferred tip and SiO<sub>2</sub>.

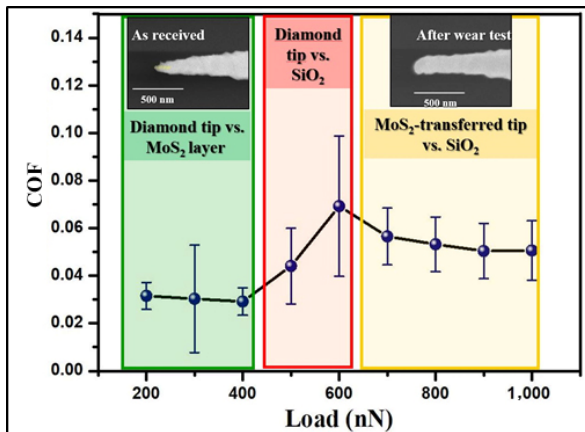
The transfer of MoS<sub>2</sub> debris to the tip apex was

confirmed using EDS. In conjunction with the SEM image of the tip used, the chemical compositions of the tip apex region (point 1) and the location distant from the tip apex (point 2) were measured via EDS, as shown in Fig. 5. The EDS spectra clearly showed the presence of Mo and S on the tip apex, indicating the transfer of MoS<sub>2</sub> wear debris. Therefore, the sliding contact pair was not a diamond tip and SiO<sub>2</sub>, but primarily the MoS<sub>2</sub>-transferred tip and SiO<sub>2</sub>. The height images in Fig. 3 show a similar surface feature with a load from 200 to 400 nN, and a change in the surface feature was recognizable between 500 and 700 nN, where the images became relatively darker with scattered bright spots. Furthermore, beyond 700 nN, the images became much darker, and the bright spots almost disappeared. By contrast, the KPFM images can be classified into two stages: less bright features with blurred brownish spots until 400 nN load and a markedly brighter feature without any spots at 500 nN and beyond. The less bright images obtained from 200 to 400 nN were associated with the presence of the MoS<sub>2</sub> layer. The brighter images beyond the 500 nN load did not exhibit any noticeable difference, indicating significant damage to both MoS<sub>2</sub> layers that ultimately extruded the SiO<sub>2</sub>/Si substrate, which had most likely occurred at extremely high loads.

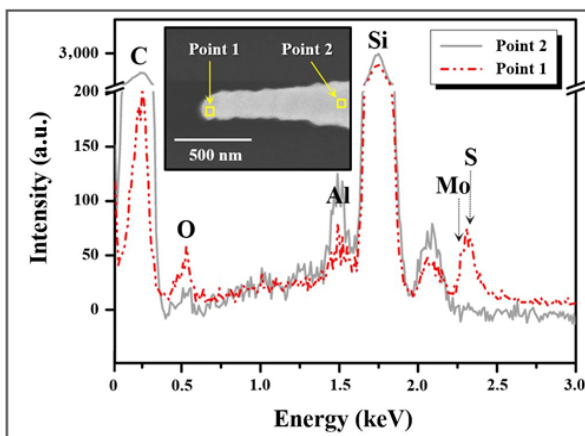
To identify whether both MoS<sub>2</sub> layers deteriorated simultaneously at a single critical load or only the top layer deteriorated first at a certain load followed by the bottom layer as the load was further increased, an



**Fig. 3** Friction images (top row), height images (middle row), and KPFM images (bottom row) of bilayer MoS<sub>2</sub> surface after wear tests at loads from 200 to 1,000 nN with a 100 nN increment. The test areas were 3 μm × 3 μm.



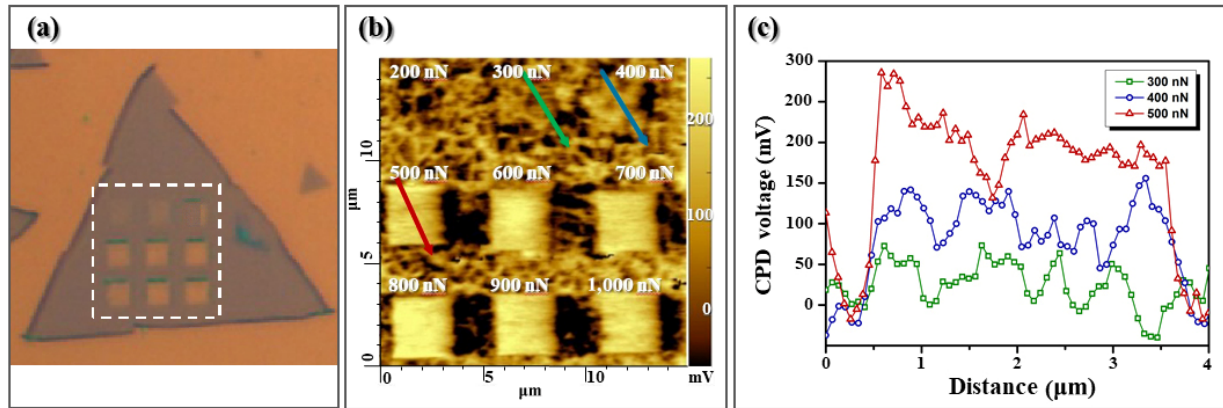
**Fig. 4** A representative plot of COF against the applied load.



**Fig. 5** EDS mapping of the tested tip shows the differences in chemical composition at different locations.

in-depth analysis of the CPD profiles was conducted based on the KPFM images at loads ranging from 300 to 500 nN. Figure 6(b) shows a KPFM image of a set of degraded surfaces obtained from another set of test trials (Fig. 6(a)) and the line profiles of the CPD (Fig. 6(c)) along the lines marked in Fig. 6(b). The KPFM images consistently showed a noticeable difference beyond 500 nN load, as described earlier based on Fig. 3. However, Fig. 6(c) shows that the line profile of the CPD values at 500 nN load ranged from 150 to 250 mV, whereas that tested at 400 nN was between 50 and 150 mV. Based on surface potential measurement via KPFM, Choi et al. [18] indicated that CPD values with respect to a SiO<sub>2</sub>/Si substrate were approximately 95 and 195 mV for a MoS<sub>2</sub> monolayer and bilayer, respectively. The degraded surface tested at 300 nN indicated a CPD value of less than 40 mV, which was similar to that obtained from

the untested surface. Therefore, CPD values similar to or less than 40 mV indicate that the MoS<sub>2</sub> bilayer remained on the SiO<sub>2</sub>/Si substrate. Based on the observations from not only the line profiles of the CPD but also the friction and height images, it is conceivable that the damage to the MoS<sub>2</sub> layers occurred in a layer-by-layer manner. The top layer degraded first at a load of 400 nN, and the bottom layer degraded partially at a load of 500 nN. The removal of the top or bottom layer has been explained in terms of the applied normal load thus far. It is noteworthy that the critical loads defined in this experimental study, in relation to the separate degradation of the top and bottom layers, were restricted to the radius of the diamond tip used. This is because the contact pressure, which is more relevant for evaluating the failure of MoS<sub>2</sub> layers than the load, varies with the tip radius. Moreover, in the Hertzian contact model, the maximum contact pressure in the circular contact is inversely proportional to the tip radius to the power of two-thirds [23]. The maximum contact pressures were calculated by assuming that the contact reflected the Hertzian model, and the contact occurred between a single-crystal diamond with a 15 nm tip radius and a flat thermally grown SiO<sub>2</sub> layer. The maximum contact pressures at loads of 400 and 500 nN corresponding to the degradation of the top and bottom MoS<sub>2</sub> layers, respectively, were calculated to be 11.7 and 12.6 GPa, respectively. Furthermore, in the Hertzian model based on the typical approach, where the maximum depth of deformation occurred at the center of contact, the thicknesses were 1.09 and 1.27 nm, which were much smaller than that of the SiO<sub>2</sub> substrate (100 nm). Although these values were approximated based on the aforementioned assumption, the actual values of the maximum contact pressure and the values obtained from the typical approach will not deviate significantly from these values if the diamond tip has a similar tip radius, and the top substrate (SiO<sub>2</sub> film) is sufficiently thick such that the thickness of the atomically thin MoS<sub>2</sub> layer is negligible. Cho et al. [13] compared the dry friction and wear properties of atomically thin CVD-grown graphene and MoS<sub>2</sub> films on SiO<sub>2</sub>/Si substrates using a typical reciprocating ball-on-disk tester at contact pressures of 72 and



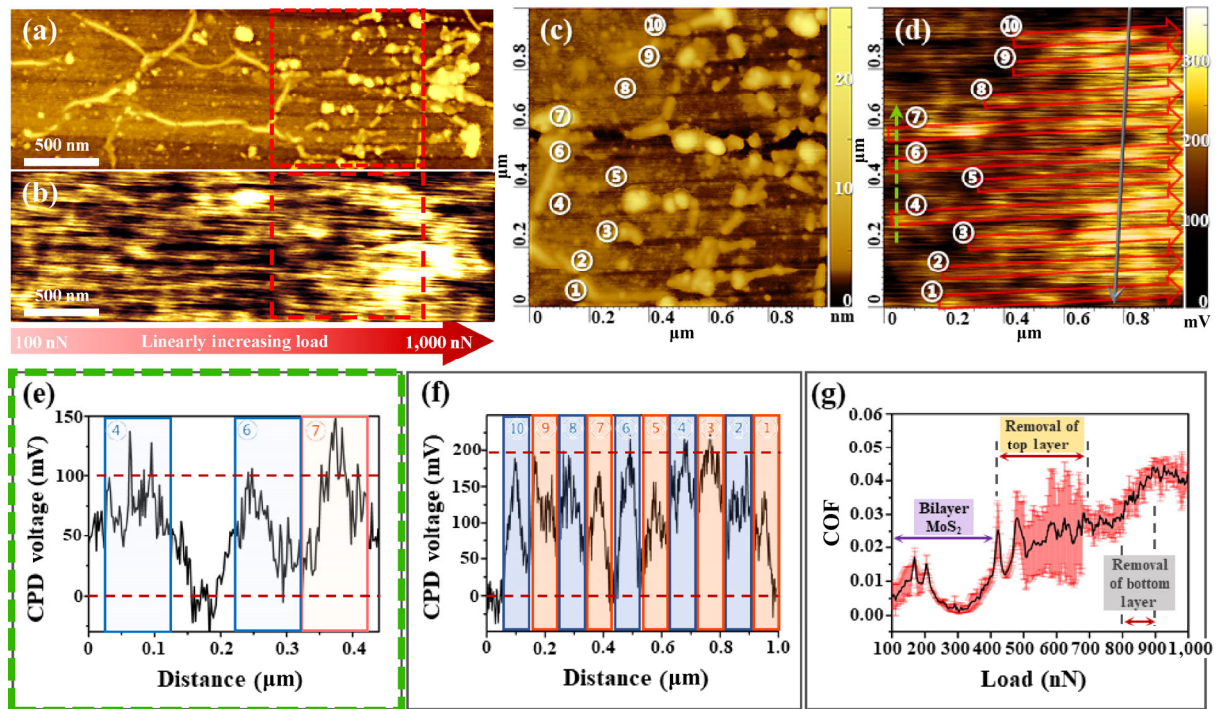
**Fig. 6** (a) Optical microscopy image of the sample surface with inset square showing MoS<sub>2</sub> nanoflakes used for wear tests; (b) KPFM image of worn surfaces for a set of test runs (the region marked with white square in Fig. 6(a) and the scan size of 15 μm × 15 μm); and (c) contact potential difference profile along the lines marked in Fig. 6(b).

378 MPa and at an average speed of 50 μm/s with a stroke of 2 mm. They claimed that mild wear occurred in a layer-by-layer manner only at a low contact pressure (72 MPa). At a high contact pressure (378 MPa), the MoS<sub>2</sub> layers were completely removed after 50 cycles of sliding. The COF of the MoS<sub>2</sub> bilayer system at stable conditions was 0.1–0.2 with low contact pressures and 0.18–0.24 with high contact pressures. It is noteworthy that this test scheme differs significantly from the FFM used in this study. In their study, sliding contacts were repeated on the same site of the surface in a reciprocating motion with a constant contact pressure (load), whereas in our FFM, the site of sliding contact changed only after one reciprocating motion. Therefore, the maximum contact pressures associated with the damage of layers obtained from our FFM were much higher than those obtained from the mesoscale reciprocating ball-on-disk tests.

Figures 7(a)–7(c) show the height and KPFM images of the scratch tested surface of the MoS<sub>2</sub> bilayer by increasing the normal load linearly from 100 to 1,000 nN. The scratch marks in the height image (Fig. 7(a)) were not clearly distinguishable at this low resolution, and the related KPFM images in Fig. 7(b) show recognizable bright marks corresponding to the scratch tracks, where the intensity increased rapidly beginning at a distance of approximately 1 μm (scratch load of 700 nN) prior to the location where the test was terminated at 1,000 nN load. The higher resolution height and KPFM images of the surface

shown in Figs. 7(c) and 7(d) are from the red squares parts in Figs. 7(a) and 7(b), respectively. The height image (Fig. 7(c)) shows 10 well-distinguished scratch tracks that were numbered on the left side of the image, indicating partial or full removal of the MoS<sub>2</sub> layers. Figure 7(c) further reveals the presence of soft particulate contaminants on the surface, which did not affect the scratch behavior of the MoS<sub>2</sub> layers. Few investigations have mentioned these particulate contaminants of various unreacted species those adhered to the surface during the growth process, which involved a reaction between MoO<sub>3</sub> and S<sub>2</sub> in the CVD route [24].

The KPFM image in Fig. 7(d) provides a better understanding of the damage level based on the brightness degree, which increased with the scratch load. The extremely bright long patches on the scratch tracks in the region of the highest scratch load were associated with the complete removal of the MoS<sub>2</sub> layers, whereas the less bright patches in the region of the 700 nN load implied the partial removal of the MoS<sub>2</sub> layers. These hypotheses were confirmed by the line profiles of CPD related to these two regions. Figure 7(e) shows the variation in the CPD values obtained across the dotted green arrow in Fig. 7(d). The three CPD peaks were associated with tracks 4, 6, and 7 in Fig. 7(d), and the CPD values ranged between 100 and 150 mV, which are related to the presence of only one layer on the surface. Therefore, the top MoS<sub>2</sub> layer degraded primarily at a scratch load of 700 nN. The CPD profile shown in Fig. 7(f)



**Fig. 7** Nanoscratch test: (a) AFM height image of the tested region (scan size of  $3.2 \mu\text{m} \times 1.2 \mu\text{m}$ ); (b) KPFM image of the test region; (c) high magnification height image of the region marked with red square in Fig. 7(a) (scan size of  $1 \mu\text{m} \times 1 \mu\text{m}$ ); (d) KPFM image of the region marked with red square in Fig. 7(b) (10 scratch tracks are expressed with red arrow to compare with the surface potential measurement); (e) CPD profile along the green arrow marked in Fig. 7(d), whose top layer began to be removed; (f) CPD profile along the grey arrow in the region of the total failure of  $\text{MoS}_2$  layers; (g) variation of the COF as a function of the scratch load.

was obtained along the grey arrow marked in Fig. 7(d) in the region of the high scratch load ( $\sim 900 \text{ nN}$ ). The CPD values across the 10 scratch tracks ranged between 140 and 220 mV clearly indicated the removal of the entire  $\text{MoS}_2$  layer. The frictional behavior with respect to the increase in the scratch load is shown in Fig. 7(g), where the standard deviations of the COF are included with the average values marked by black dots. Figure 7(g) shows that the COF obtained from the nanoscratch test can be classified into three stages. In the first stage (up to 400 nN), the COF was maintained at a low level as the  $\text{MoS}_2$  bilayer remained on the surface. As the scratch load increased to the range of 500–700 nN, the COF increased rapidly with a significant fluctuation, which was attributed to the partial removal of the top  $\text{MoS}_2$  layer, as evidenced by the measurement of CPD values (Fig. 7(e)). In the third stage, beyond the load of 800 nN, the COF increased further. The CPD values in Fig. 7(f), which were approximately 200 mV, measured on the scratch tracks after the 900 nN load, indicated the conspicuous removal of the bottom  $\text{MoS}_2$  layer, and the high COF

was due to the direct sliding contact between the diamond tip and  $\text{SiO}_2$  substrate.

The maximum contact pressures corresponding to the critical scratch loads associated with the removal of the top and bottom layers were calculated based on the Hertzian model, where the same material properties as those used for the wear tests were assumed. The tip radius measured via FE-SEM after the nanoscratch test increased by approximately 2.5 nm from 15 nm measured in the as-received state. The maximum contact pressure was calculated based on the increased tip radius. The maximum contact pressure at the first critical load in the range of 500–700 nN, which corresponded to the removal of the top layer, was calculated to be 11.3–12.7 GPa, whereas that at the second critical load in the range of 800–900 nN, which is associated with the full removal of the bottom layer, was in the range of 13.2–14.8 GPa. It is noteworthy that compared with the wear tests, the maximum contact pressures at the two critical loads in the nanoscratch test were relatively higher. This discrepancy is attributable to the intrinsic



difference between the two test procedures, as illustrated in Fig. 2. The sliding contact in FFM was subjected to more severe conditions. The tip under constant load slid on an identical surface twice (trace and retrace) and shifted to the next location, which was 11.7 nm away from the previous track as 256 scans existed in the 3  $\mu\text{m}$  width. As the contact diameter was in the range of 6.8–11.6 nm for the load range of 200–1,000 nN (as calculated using the Hertzian model), the damage on a single track might be increased by the effect of adjacent tracks, thereby resulting in the failure of the MoS<sub>2</sub> layer at lower critical loads than those of the nanoscratch test.

## 4 Conclusions

We investigated the tribological properties and scratch resistance of CVD-grown MoS<sub>2</sub> bilayers at the nanoscale via FFM and nanoscratch tests, respectively. We demonstrated the effectiveness of KPFM in the evaluation of separate degradation/removal of the top and bottom MoS<sub>2</sub> layers by measuring the local CPD between the tip and the sample surface. In the nanoscale wear tests, three stages of frictional behavior were observed in association with the presence/removal of MoS<sub>2</sub> layers: a low friction stage at a low maximum contact pressure (less than 11.7 GPa) with the presence of the bottom MoS<sub>2</sub> layer, a transitional friction stage (12.6–13.4 GPa) after the degradation of the bottom MoS<sub>2</sub> layer, and a steady friction stage at the high maximum contact pressure (above 14.1 GPa), where friction was reduced owing to the contact between the MoS<sub>2</sub>-transferred tip and SiO<sub>2</sub> surface. The nanoscratch test results of the MoS<sub>2</sub> bilayer deposited on a SiO<sub>2</sub>/Si substrate revealed two critical loads associated with the removal of individual layers in the MoS<sub>2</sub> bilayer system. The scratch resistance of the monolayer MoS<sub>2</sub> was explained in terms of the critical scratch load and the corresponding maximum contact pressure. In the first critical scratch load (500–700 nN, equivalent to the maximum contact pressure of 11.3–12.7 GPa), only the top MoS<sub>2</sub> layer was removed, accompanied by a rapid increase in the COF. Successive removal of the bottom layer occurred at the second critical scratch load (800–900 nN, equivalent to the maximum contact pressure of 13.2–14.8 GPa with a high COF). The CPD values

measured using KPFM enabled the identification of degraded/removed MoS<sub>2</sub> layers. The CPD values of approximately 200 mV indicated the complete removal of MoS<sub>2</sub> layers, whereas those of approximately 100 mV were associated with the degradation of the top layer.

This investigation pertaining to the tribological properties and scratch resistance of MoS<sub>2</sub> bilayer can facilitate a better understanding of the durability of CVD-grown MoS<sub>2</sub> on a SiO<sub>2</sub>/Si substrate system, and provide valuable information for enhancing the design and reliability of micro- and nano-devices involving atomically thin MoS<sub>2</sub> films.

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