

# Characterization of nanometer scale wear and oxidation of transition metal dichalcogenide lubricants by atomic force microscopy

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(Received 9 September 1991; accepted for publication 23 October 1991)

Atomic force microscopy has been used to characterize wear and oxidation of transition metal dichalcogenide surfaces. Sequential images recorded on molybdenum disulfide ( $\text{MoS}_2$ ) and niobium diselenide ( $\text{NbSe}_2$ ) surfaces show that wear proceeds at defects, and that  $\text{MoS}_2$  wears at least five times more slowly than  $\text{NbSe}_2$ . Images of thermally treated  $\text{MoS}_2$  and  $\text{NbSe}_2$  further demonstrate that oxidation creates surface defects on both materials. However, for similar oxidation conditions,  $\text{NbSe}_2$  surfaces show extensive degradation, while  $\text{MoS}_2$  surfaces only exhibit isolated defects. The implications of these results to understanding the tribological properties of the transition metal dichalcogenides are discussed.

Molybdenum disulfide ( $\text{MoS}_2$ ) stands out as a prototypical solid lubricant by virtue of its successful use in a number of demanding technological applications.<sup>1,2</sup> The effective lubricating properties of this quasi-two-dimensional material is typically ascribed to the facile interlayer shear of the van der Waals bonded layers.<sup>3,4</sup> However, factors other than this layered structural motif must also be important since, in general, the structurally similar transition metal dichalcogenide materials are not good lubricants. In the case of  $\text{MoS}_2$  and niobium diselenide ( $\text{NbSe}_2$ ), the inferior tribological properties of  $\text{NbSe}_2$  have been attributed to the less facile interlayer shear that results from the different electronic configuration of Nb(IV) vs Mo(IV).<sup>4,5</sup> Direct support of this proposal, and more generally a detailed microscopic understanding of friction and wear in these materials are, however, not yet available. A new technique that has shown promise in addressing microscopic details of lubrication is atomic force microscopy (AFM). AFM has now been used to study the tribological properties of several interfacial systems.<sup>6-10</sup> Herein, we utilize this technique to characterize surface wear and reactivity of metal dichalcogenide materials. We show that wear on  $\text{MoS}_2$  and  $\text{NbSe}_2$  surfaces proceeds at defects, and that  $\text{MoS}_2$  wears at least five times more slowly than  $\text{NbSe}_2$ . We also show that  $\text{MoS}_2$  surfaces are more stable towards surface oxidation and defect formation than  $\text{NbSe}_2$ .

The experiments were carried out in air (relative humidity 40%–60%) using a commercial force microscope (Nanoscope, Digital Instruments, Inc.) with microfabricated, cantilever tips. Images were recorded on single crystals of  $\text{MoS}_2$  and  $\text{NbSe}_2$  in the constant force mode. The  $\text{MoS}_2$  and  $\text{NbSe}_2$  single crystals were grown by  $\text{I}_2$  vapor transport at 910 and 740 °C, respectively.

A series of AFM images, recorded as a function of time on  $\text{NbSe}_2$  and  $\text{MoS}_2$  cleaved (0001) single-crystal surfaces, are shown in Fig. 1. In these images, the feedback loop adjusts the vertical position of the sample to maintain a constant deflection of the cantilever tip (i.e., constant

force) as the sample is rastered below the tip; the images of  $\text{NbSe}_2$  and  $\text{MoS}_2$  were recorded with a similar force. Initial images recorded on all freshly cleaved  $\text{NbSe}_2$  crystal surfaces exhibit defects similar to those in Fig. 1(a). These defects are typically 7–10 nm wide at the surface, and one layer deep ( $0.65 \pm 0.03$  nm). The density of defects is about  $7 \times 10^{-5}/\text{nm}^2$ . Although all of the cleaved  $\text{NbSe}_2$  crystals exhibit surface defects, these samples are of good quality in that they exhibit sharp superconducting transitions at 7 K. In contrast, freshly cleaved  $\text{MoS}_2$  surfaces do not exhibit similar size defects. Extensive scanning of the  $\text{MoS}_2$  crystals showed no evidence of surface pits on the 10-nm scale; however, heating these crystals at 400 °C in air does lead to the formation of defects [Fig. 1(e)] similar to those observed on  $\text{NbSe}_2$ .

Repetitive scanning of  $\text{NbSe}_2$  and  $\text{MoS}_2$  surface regions that contain defects leads to dramatic wear and material removal (Fig. 1). There are, however, several important differences in the details of the wear on  $\text{MoS}_2$  and  $\text{NbSe}_2$ . First, for similar imaging forces ( $10^{-8}$ – $10^{-7}$  N), we find that it takes at least five times longer to wear a similar size area on  $\text{MoS}_2$  compared to  $\text{NbSe}_2$  [e.g., Fig. 1(d) and 1(h)]. We thus suggest that the wear rate is  $\approx 5$  times faster on  $\text{NbSe}_2$  versus  $\text{MoS}_2$ . This difference in rate, which was observed on a number of independent samples, indicates that  $\text{MoS}_2$  is more stable than  $\text{NbSe}_2$ . Despite the more rapid rate of material removal from  $\text{NbSe}_2$  surfaces, wear occurs in a relatively controlled layer by layer manner for both materials; i.e., the depth of the surface depressions correspond to the Se-Nb-Se or S-Mo-S repeats of 0.650 and 0.615 nm, respectively. Material removal is also remarkably selective on  $\text{MoS}_2$  compared to  $\text{NbSe}_2$  surfaces. The initial defect on the  $\text{MoS}_2$  surface [Fig. 1(e)] grows preferentially in a triangular shape from a size of 10–200 nm on edge. Atomic resolution images demonstrate that wear occurs preferentially along the three equivalent crystal-lattice directions, and not along the scan direction, as observed for  $\text{NbSe}_2$ . Selective wear of  $\text{MoS}_2$  surfaces has been found in all of our AFM images. The observation of highly selective wear and significantly lower wear rate for  $\text{MoS}_2$  indicate that this surface is intrinsically more stable than that of  $\text{NbSe}_2$ . Notably, previous studies, addressing

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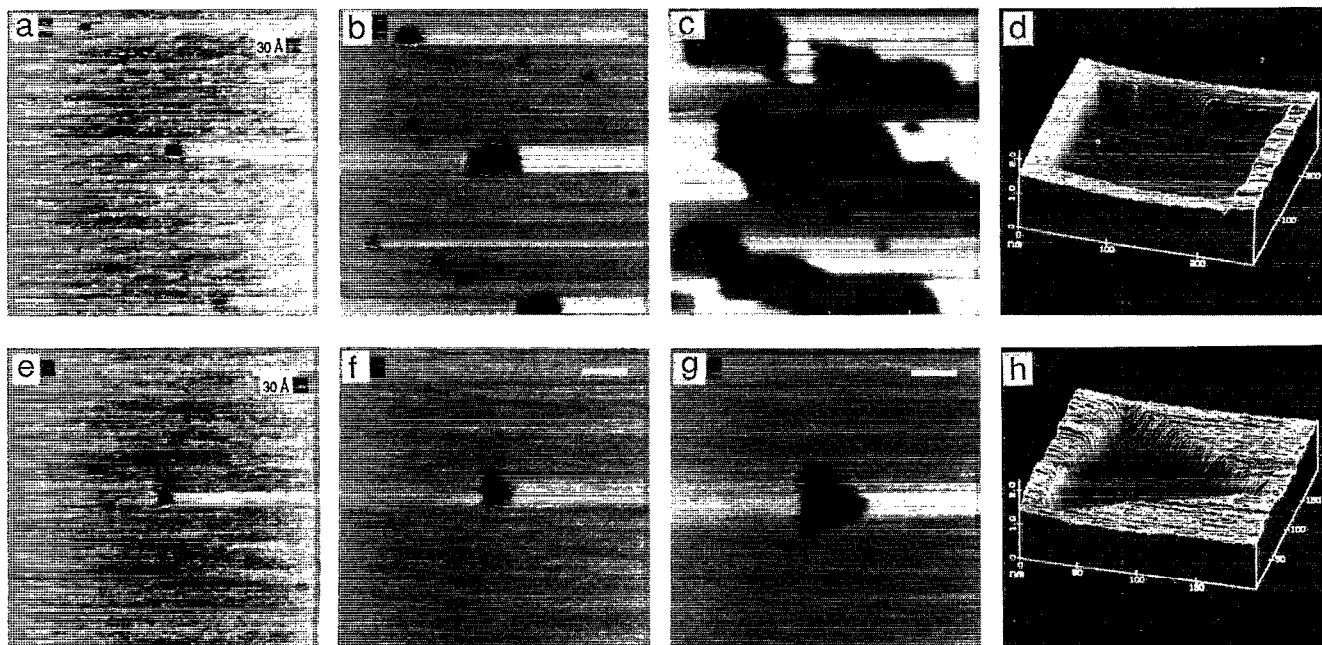


FIG. 1. A time series of AFM images recorded on cleaved NbSe<sub>2</sub> [(a)–(d)] and MoS<sub>2</sub> [(e)–(h)] crystals; the MoS<sub>2</sub> sample was also heated for 5 min in air at 400 °C prior to imaging. Images (a)–(d) were recorded after 0, 487, 1722, and 3345 s, respectively, of continuous scanning over a 200×200 nm<sup>2</sup> area. Images (e)–(h) were recorded after 0, 586, 1763, and 8499 s, respectively, of scanning over a 200×200 nm<sup>2</sup> area. All of the images except (d) are 200 nm on edge; image (d) of NbSe<sub>2</sub> is 260 nm on edge, and illustrates the 200×200 nm<sup>2</sup> wear defect that was created by scanning. The white bars in these images correspond to 30 Å.

the tribological properties of MoS<sub>2</sub> and NbSe<sub>2</sub>, have not considered relative wear and stability to explain the superior properties of MoS<sub>2</sub>.<sup>3–5</sup> Our studies strongly suggest that the intrinsic stability of the MoS<sub>2</sub> surface must play an important part in its effectiveness as a lubricant.

It is also interesting that the surface wear observed in these AFM studies is similar to “etching” and surface modification reported in several scanning tunneling microscopy (STM) studies of metal dichalcogenides carried out in air.<sup>11–13</sup> The similarity of these results to our AFM data suggests that the STM tip is in contact with the surface in air, and that scanning causes abrasive wear. In support of this proposal, we note that ultrahigh vacuum STM studies of these materials demonstrate that no etching occurs for true vacuum tunneling, when the tip and sample are not in contact.<sup>13</sup>

In addition, we have characterized other details of the wear process. First, the rate of material removal for a given transition metal dichalcogenide material depends directly on the scan speed, 600–8000 nm/s, as expected for a tip-induced surface wear process. Furthermore, the wear rates are remarkably insensitive to changes in the imaging force between 10<sup>–8</sup> and 10<sup>–7</sup> N. This result indicates that the force per unit area is constant over this range. A constant force/area would be readily achieved if the tip (radius = 20–40 nm) deforms the surface, and increases the tip-surface contact area with increasing load. Indeed, recent experimental and theoretical work strongly suggests that the tip-surface contact area in AFM exceeds a single atom, and will increase with increasing force due to deformation of the surface.<sup>7,14</sup> Alternatively, it is possible that deforma-

tion of a contamination layer between the tip and surface may yield a constant force per unit area for the conditions used in this study.<sup>9</sup>

While the atomistic details of wear in these systems is not yet known, it is important to consider possible mechanisms. Molecular dynamics (MD) simulations of a Ni tip in contact with a Au substrate show that the maximum compressive stress occurs five layers below the surface, and that a similarly large magnitude tensile stress (negative pressure) exists at the periphery of the tip-surface contact.<sup>7</sup> Although MoS<sub>2</sub> and NbSe<sub>2</sub> are more anisotropic and have lower surface free energies than Au, it is nevertheless interesting to speculate whether tensile stress at the surface might break chemical bonds and lead to wear. In this case, the relative wear (for imaging at a constant force) should reflect the strength of the bonding in MoS<sub>2</sub> vs NbSe<sub>2</sub>. MD simulations of a metal tip in contact with a metal dichalcogenide material should help to understand better these microscopic details.

From our AFM studies, it is apparent that wear proceeds at surface defect sites, and thus one can speculate that such sites are critical in determining the overall stability and lubricating properties of these materials. Since many technological applications of transition metal dichalcogenide lubricants require their use in oxidizing environments and at elevated temperatures,<sup>2,15</sup> it is important to characterize how such conditions affect surface defects and wear. AFM provides unique insight into this problem, and further highlights the distinct differences between MoS<sub>2</sub> and NbSe<sub>2</sub>. While room-temperature cleaved MoS<sub>2</sub> crystals rarely exhibit surface defects of the type observed on NbSe<sub>2</sub>,

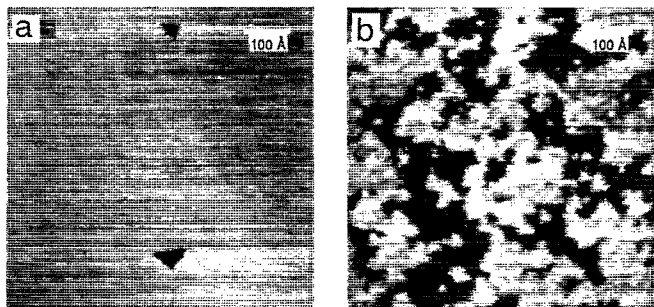


FIG. 2.  $660 \times 660 \text{ nm}^2$  grey-scale AFM images of (a)  $\text{MoS}_2$ , and (b)  $\text{NbSe}_2$ , recorded after thermal oxidation in air. The  $\text{MoS}_2$  sample was heated at  $400^\circ\text{C}$  for 5 min, and the  $\text{NbSe}_2$  sample was heated at  $200^\circ\text{C}$  for 5 min. The two triangular defects on the  $\text{MoS}_2$  surface are one layer deep; the defects on the  $\text{NbSe}_2$  surface range from 1 to 3 layers in depth.

[Fig. 1(a)], oxidation of  $\text{MoS}_2$  surfaces in air at  $400^\circ\text{C}$  for 5 min produces defects [Fig. 2(a)] with a size and density similar to that found on *in situ* cleaved  $\text{NbSe}_2$ . In contrast, oxidation of  $\text{NbSe}_2$  at  $200^\circ\text{C}$  for 5 min ( $200^\circ$  lower than the  $\text{MoS}_2$  treatment) causes extensive surface degradation [Fig. 2(b)]. The defects on oxidized  $\text{NbSe}_2$  extend over large areas of the sample and are several layers deep. Previous x-ray photoelectron spectroscopy measurements have shown that  $\text{MoS}_2$  and  $\text{NbSe}_2$  surfaces can be oxidized at elevated temperatures,<sup>16</sup> and thus we believe that these data represent the first nanometer scale structural view of the oxidation process.

These results, obtained at elevated temperatures, further support our conclusion that  $\text{MoS}_2$  surfaces are more stable than  $\text{NbSe}_2$  surfaces. Since wear occurs preferentially at surface defects, our data also show why  $\text{NbSe}_2$  would be a poor choice for a lubricant at elevated temper-

atures, and  $\text{MoS}_2$  could be acceptable. In summary, this work shows the importance of surface stability in wear, and how AFM can be used to assess processes (wear and surface reactivity) critical to tribology. Future AFM investigations of wear, reactivity, and friction at elevated temperatures in  $\text{MoS}_2$  and modified metal dichalcogenide materials should lead to further development of these solid lubricants.

C.M.L. gratefully acknowledges support of this work by the Air Force Office of Scientific Research, and the David and Lucile Packard, Camille and Henry Dreyfus, and A. P. Sloan Foundations.

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