Mechanical Properties of Molybdenum Disulfide and the Effect of Doping: An in Situ TEM Study

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Supporting Information

ABSTRACT: Direct observations on nanopillars composed of molybdenum disulfide (MoS2) and chromium-doped MoS2 and their response to compressive stress have been made. Time-resolved transmission electron microscopy (TEM) during compression of the submicrometer diameter pillars of MoS2- and Cr-doped MoS2 (Cr: 0, 10, and 50 at %) allow the deformation process of the material to be observed and can be directly correlated with mechanical response to applied load. The addition of chromium to the MoS2 changed the failure mode from plastic deformation to catastrophic brittle fracture, an effect that was more pronounced as chromium content increased.

KEYWORDS: antifriction films, tribology, in situ electron microscopy, transition metal dichalcogenides

INTRODUCTION

Molybdenum disulfide (MoS2) is a ubiquitous solid lubricant1 along with graphite.2 These two materials have been used for decades and centuries, respectively, and the concept that they reduce friction because of their intrinsic two-dimensional nature has long been widely appreciated. Lubrication by thin solid films has been studied by macroscopic methods such as tribology, but measurements of their mechanical behavior at the atomic scale are recent.3,4 Such studies of the interactions between the two-dimensional layers in MoS2 have, in part, been driven by a burgeoning interest in studies of the interactions between the two-dimensional layers of graphene-like materials. Ex situ studies on MoS2 tend to suggest the validity of these studies, as crystallites have been observed to become oriented by the shear forces experienced in tribological wear.10,11 Doping of MoS2 with other transition metals is also of interest and is known to increase the wear resistance of the material without dramatic loss of superlubricity.12 The effect this transition metal inclusion has on the mechanical failure mode of MoS2 is unknown. We have studied the effects of the incorporation of chromium into the crystal lattice of molybdenum disulfide. It was found that the highly ordered laminar MoS2 lattice contracts in the c direction and is more disordered upon addition of chromium, decreasing crystal grain size and presenting a network of “cross-linked” lamellae as-evidenced by electron microscopy measurements.7 The benefit of this morphological change is often an increase in hardness or material persistence at surfaces, which should lead to an increase in wear resistance in tribological applications.13

We have also been interested in the compression of novel mechanical cleavage of two-dimensional crystals has also been studied.3 These two studies probe the material at the atomic level providing useful information for the study of exfoliation of graphene-like materials. Ex situ studies on MoS2 tend to suggest the validity of these studies, as crystallites have been observed to become oriented by the shear forces experienced in tribological wear.10,11 Doping of MoS2 with other transition metals is also of interest and is known to increase the wear resistance of the material without dramatic loss of superlubricity.12 The effect this transition metal inclusion has on the mechanical failure mode of MoS2 is unknown. We have studied the effects of the incorporation of chromium into the crystal lattice of molybdenum disulfide. It was found that the highly ordered laminar MoS2 lattice contracts in the c direction and is more disordered upon addition of chromium, decreasing crystal grain size and presenting a network of “cross-linked” lamellae as-evidenced by electron microscopy measurements.7 The benefit of this morphological change is often an increase in hardness or material persistence at surfaces, which should lead to an increase in wear resistance in tribological applications.13

We have also been interested in the compression of novel
materials such as metal–organic frameworks at the nanoscale using direct in situ TEM imaging.\textsuperscript{14} In this paper, we report studies of MoS\(_2\) and Cr-doped MoS\(_2\) under compressive stress in a transmission electron microscope, bridging the gap between the nanoscopic/mesoscopic and the macroscopic length scale. This work provides new information about the behavior of this important material, as although there is a precedent for in situ TEM analysis of sliding behavior, compressive experiments that simulate asperity contact in MoS\(_2\) lubricated counterfaces have not been reported. By performing a compression test on a submicrometer diameter pillar of MoS\(_2\)- and Cr-doped MoS\(_2\) generated by aerosol-assisted chemical vapor deposition (AACVD), profiles of displacement vs load can be obtained with a concurrent TEM video or image sequence clearly providing a history of how the material fails under stress. The technique simultaneously quantifies material properties (stress/strain curves) and allows a qualitative assessment of structural failure.

\section*{EXPERIMENTAL SECTION}

\textbf{General.} All chemicals and were purchased from Sigma-Aldrich and used without further purification. All reactions were performed in a nitrogen environment using standard Schlenk techniques.

\textbf{Synthesis of Tetrakis(N,N-diethylthiodicarbamato)-molybdenum(IV), MoL\(_4\).} Tetrakis(N,N-diethylthiodicarbamato)-molybdenum(IV) was synthesized as described previously.\textsuperscript{7} Briefly, to a stirred suspension of molybdenum hexacarbonyl (1.0 g, 3.8 mmol, 1.0 equiv) in acetonitrile (degassed) under N\(_2\), tetraethylthiuram disulfide (2.25 g, 7.6 mmol, 2.0 equiv) was added and brought to reflux for 2 h. After slow cooling to room temperature, a black microcrystalline product precipitated, and was isolated by vacuum filtration, followed by washing withpentane (3 \times 20 mL). Mp 119–124 °C. ES-TOF+ m/z: 689 [M+H]\(^+\); FT-IR (solid) \(\nu_{\text{max}}/\text{cm}^{-1}\): 2970 (w), 2930 (w), 2869 (w), 1517 (m), 1490 (m), 1454 (m), 1427 (m), 1374 (m), 1352 (m), 1269 (m), 1211 (m), 1145 (m), 1094 (m), 1074 (m), 1001 (m). Anal. Calcd for C\(_{15}\)H\(_{30}\)N\(_3\)S\(_6\): C, 37.0%; H, 6.6%; N, 8.3%. Found: C, 37.0%; H, 6.6%; N, 8.3%.

\textbf{Synthesis of Tris(N,N-diethylthiodicarbamato)chromium(III), CrL\(_3\).} The chromium(III) complex was synthesized as described previously. Briefly, to a green solution of chromium trichloride flux for 2 h.

\textbf{Figure 1.} Fabrication scheme for stratified nanopillars. (a) As-supplied silicon substrate, (b) trenches are cut by FIB, (c) creation of angle in central ridge by FIB to induce shear (inset SEM image of an angled pillar), (d) deposition of thin films: thermal silicon oxide growth followed by nickel sputtering and finally MoS\(_2\) by AACVD, (e) creation of nanopillar by FIB, (f) flattening of pillar tip (inset: SEM image of finished pillar), (g) compression by picoindenter tip, as-imaged by TEM.
A Hysitron PI 95 TEM PicoIndenter sample holder was used in conjunction with a JEOL 2010 LaB₆ transmission electron microscope to perform micromechanical measurements of frictional materials. The materials of interest were deposited by AACVD onto nickel sputtered silicon substrates with a 1 μm wide central ridge (Hysitron), and a stratified pillar of diameter 250−500 nm was fabricated by focused ion beam milling (FIB) from the ridged section of the substrate (Figure 1). FIB was conducted with a Helios Nanolab 600i system. The pillar was compressed by the diamond punch of the PicoIndenter to generate load vs displacement curves and concurrently imaged to give a video of the pillar through the duration of the compression test. Substrates were mounted in the PicoIndenter with Crystalbond (Agar Scientific). Traditional TEM samples were also prepared by FIB and imaged in the JEOL 2010 LaB₆.

**RESULTS AND DISCUSSION**

Deposition of Doped and Undoped Transition Metal Dichalcogenide (TMDC) Thin Films. The general scheme to produce the stratified pillars for in situ transmission electron microscopy (TEM) imaging of MoS₂ under compressive stress is given in Figure 1. Deposition of molybdenum disulfide onto Si:SiO₂:nickel stratified substrates was achieved by aerosol-assisted chemical vapor deposition (AACVD). Nickel was chosen as the top-layer to simulate the metallic nature of counterfaces commonly found in tribological applications, e.g., engine parts. To prevent nickel reacting with the underlying silicon substrate during MoS₂ growth at 450 °C,15 we grew a thermal silicon oxide layer on the silicon surface prior to sputtering of a metallic nickel film onto the substrate. A thin film of MoS₂ was subsequently deposited by AACVD from the tetakis(N,N-diethylthiodithiocarbamato)molybdenum(IV), and characterized by scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) and Raman spectroscopies and powder X-ray diffraction (pXRD) (Figure 2). Inclusion of chromium dopant ions was achieved by including tris(N,N-diethylthiodithiocarbamato)chromium(III) in the AACVD precursor solution at the appropriate molar ratio for the desired level of dopant atoms. Thin films (200−500 nm thick) of molybdenum disulfide with 0, 10, and 50 mol % Cr dopant were created.

The Cr content of the chromium-doped MoS₂ films were found to correlate well with the films produced under the deposition conditions reported by Lewis et al.7 Crystallographic characterization was carried out by pXRD and all films indexed to the pattern of 2H-MoS₂,16 with a decrease in the intensity and broadening of the (002) diffraction peak concurrent with increasing chromium level (Supporting Information). Raman spectroscopy revealed the characteristic intense A₁g and E₂g phonon modes characteristic of MoS₂.

Fabrication of Stratified Pillars Terminated with TMDC by Focused Ion Beam (FIB) Milling of Coated Substrates. Stratified pillars of diameter 250−500 nm were fabricated by focused ion beam milling (FIB) from the ridged section of the substrate (Figure 3). A typical stratified pillar consists of a MoS₂ (undoped or Cr-doped) tip, Ni(0) layer,
silicon oxide layer, and silicon base. The layer structure of the pillar did not vary with varying chromium inclusion, as the element was exclusively doped into the layer that constitutes the MoS$_2$ tip after fabrication is complete. In order to ensure even distribution of the initial compression force, the pillar tip was flattened by FIB milling so that at the moment of contact, both surfaces were parallel.

In Situ TEM Nanomechanical Analysis of Nanopillars under Compression. Pillars were compressed by the diamond punch of a picoindenter within the TEM to generate load vs. displacement curves and videos of the pillar during the compression test. The compression test protocol can be held to simulate asperity contact in dry sliding between MoS$_2$ lubricated metal interfaces or the boundary lubrication regime of the Stribeck curve (the region in which loads and pressures between tribological interfaces are sufficient to displace any liquid lubricant present) and bring opposing counterfaces into physical contact. Boundary lubrication leads to any protruding parts of the surfaces becoming the active sites for wear as they are subjected to compression at high contact pressures, due to the small surface area of the asperity tip and high mechanical load. As no liquid lubricant is present in this compression test, the influence of adsorbed species from liquid lubricant is neglected. Compression during the test occurs in the direction of the long axis of the pillar, and the angled interfaces in the pillar serve to induce shear failure of the material if it is prone to it. The picoinidenter punch is linearly displaced at a constant rate with respect to time, and the force that is required to maintain this regime is recorded to produce curves of stress vs strain (Figure 4). The data set includes the force recorded during retraction of the picoinidenter, the rightmost part of each curve should not therefore be interpreted as representing the properties of the material being studied.

The results of nanocompression are shown in Table 1. The mean yield strength of materials increases with the amount of chromium, from $821 \pm 141$ MPa to $1017 \pm 239$ MPa for 50 at % Cr-doped MoS$_2$. The failure mode of the materials, as judged

![Figure 4](image_url)
The presented method is a stepping stone between the nanoscale, mesoscale, and macroscale and will provide further new insights into the in situ behavior of antitrust films under stress, an area that has, until now, remained elusive.

**CONCLUSIONS**

The imaging and quantification of material failure at the nanoscale is presented for the study of the solid lubricant molybdenum disulphide and its Cr-doped derivatives. The introduction of chromium was found to increase the compressive yield strength of the material potentially offering improved antitrust properties compared with MoS². Chromium inclusion dramatically altered the failure mechanism of MoS² from a plastic failure mode to a brittle failure mode, an effect that became more pronounced as Cr content increased. Tandem imaging and mechanical analysis affords insight when interpreting regions of the load vs displacement curve that ex situ mechanical testing cannot and thus could potentially be a quantum leap in the way antitrust materials are assessed under stress.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b06055.

- Powder X-ray diffraction patterns and TEM images (PDF)
- Video S1 (AVI)
- Video S2 (AVI)
- Video S3 (AVI)

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**Notes**

The authors declare no competing financial interest.

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