Frictional anisotropy of tilted molybdenum nanorods fabricated by glancing angle deposition

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ABSTRACT

The frictional anisotropy and deformation behavior of a nanostructured thin film (NSTF) consisting of tilted molybdenum (Mo) nanorods was investigated. The NSTF exhibited strong frictional anisotropy and the coefficients of friction were larger when sliding against the direction of nanorods tilt as compared to sliding along the tilt direction, reaching a maximum of ~35% difference. Frictional anisotropy at low loads is attributed to the anisotropy in surface roughness, whereas, at high loads, it is attributed to the difference in the deformation mechanism of nanorods when sliding along and against the direction of nanorods tilt. Furthermore, no deformation was detected after the scratch even after heavy scratches, indicating strong resistance of nanorods to plastic deformation.

1. Introduction

Friction is of great interest and has been debated and studied since the time of Leonardo da Vinci because of its complexity and numerous mechanisms involved. Today, frictional properties of various materials are extensively researched due to their great importance in practical applications such as bearings in machine components, piston and rings in car engines, and tool bits in cutting tools. It has been shown that, for some crystals, friction force is anisotropic with respect to the crystallographic direction [1–6]. For example, when a single crystal diamond slide in air against itself on the [001] plane, coefficient of friction exhibited anisotropy, and it was larger in the [100] direction than in the [110] direction [1]. The frictional anisotropy was attributed to the preferred slip system during plastic deformation. For the single crystal muscovite mica, the friction forces were found to be anisotropic with respect to the lattice misfit angle which was interpreted from the perspective of lattice commensurability [2]. Other materials such as Cu, Ni, Pd, and NaCl have also been researched due to their anisotropic frictional properties [3–6]. Frictional anisotropy has also been observed in case of a lipid monolayer on mica where the anisotropy in frictional behavior was attributed to molecular tilt [7].

Frictional anisotropy is also observed in nature. Geckos, snakes, and glaciers all display anisotropic friction, and have been researched to better understand this phenomenon [8–14]. Surface structural anisotropy at small length scale, as in the case of geckos and snakes, or at large scale, as in the case of glaciers, is the main reason for the frictional anisotropy. For example, gecko’s ability to strongly attach to smooth vertical walls and rapidly and easily detach from the walls was attributed to the directional orientation of millions of adhesive setae on their toes [8–11]. In the case of snakes, the nanostructured design of snake skin helps in locomotion due to its frictional anisotropy [12].

Nature’s marvels have stimulated investigations on bio-inspired surfaces, such as gecko-inspired adhesives that use vertically aligned plastic microfibers to mimic gecko’s toe to enable sticking when sliding on a surface [11,15–17]. Such gecko-inspired adhesives could be useful for climbing robots, sporting goods, or medical equipment where a controllable and reusable adhesive is needed. Recent studies have shown that angled polypropylene microfiber arrays [15] and tilted polydimethylsiloxane (PDMS) half-cylinder micron-scale fibers [16–17] exhibit directional adhesion similar to that found in gecko, suggesting tilted/angled microstructures/nanostructures as a promising direction in developing gecko-inspired adhesive surfaces.

Nanostructured thin films created using a glancing angle deposition (GLAD) technique, which is also named oblique angle deposition [18–24], provide opportunities to study frictional anisotropy for a large variety of material systems. GLAD involves
an obliquely incident flux of atoms/molecules in a typical vapor deposition system such as sputtering or thermal evaporation. At high oblique deposition angles without substrate rotation, GLAD can produce tilted nanorods with very pronounced structural anisotropy, which forms the basis for many interesting physical properties. The structural anisotropy could also lead to anisotropy in frictional properties. For example, Eric et al. observed anisotropic friction coefficient and contact depth of GLAD produced nanostructured parylene films during sliding contact [25]. However, they did not study the deformation of the film after sliding, which is important for understanding the long term performance of the polymer films. Hirakata et al. performed experiments and used Finite Element Modeling (FEM) to study the frictional anisotropy in oblique nanocolumn arrays of Ti grown by GLAD [26]. In the study, the observed frictional anisotropy was attributed to the difference in the deformation mode of tilted Ti nanocolumns with and against the tilt direction. They also investigated the effect of tip shape by using indenter tips of different shapes. Another recent study on nanosculptured thin films of chromium grown by GLAD method showed that the tribological behavior is strongly influenced by the growth mechanism and sputtering parameters [27].

In this work, we present a detailed investigation of frictional anisotropy and deformation properties of a very stiff nanostructured material – tilted molybdenum nanorods. Compared to the polymer films investigated previously [15–17,25], metals are much stiffer, having about two orders of magnitude larger elastic moduli, which could lead to better deformation resistance than polymers. Since molybdenum (Mo) is a commonly used material for tribological applications, we studied nano-structured thin film (NSTF) of tilted Mo nanorods grown on a silicon substrate by the GLAD technique. We used a much bigger tip than those used by Hirakata et al. [26] to simulate tip in contact with many nanorods where frictional anisotropy can be most utilized. The NSTF demonstrated large frictional anisotropy as well as strong resistance to deformation that has not been reported previously.

2. Experimental

Tilted Mo nanorod NSTF sample was fabricated by using DC magnetron sputter GLAD technique. Films were deposited on [100] oriented silicon wafer pieces of size about 2 × 2 cm² by sputtering 99.95% pure 5.08 cm diameter Mo target (i.e. source). Sample was mounted at 20 cm distance from the target at an 85° off angle with respect to incoming Mo vapor flux. After reaching base pressure of 1.0 × 10⁻⁶ mbar, ultra high purity argon gas was introduced into the deposition chamber and working pressure was set to 2.5 × 10⁻³ mbar during the deposition. Deposition was carried out by applying 150 W DC power to the Mo target and deposition rate was monitored by a quartz crystal microbalance. Sample was neither heated nor rotated during the deposition. NSTF sample was investigated for frictional anisotropy and compared with a conventional Mo thin film sample, which was fabricated at the same deposition conditions as the NSTF except the sample was mounted facing directly towards the Mo target (i.e. normal angle deposition).

Friction/scratch tests were performed on the tilted Mo nanorod NSTF sample and conventional Mo thin film sample in air at a relative humidity of about 45% using a Tribolindenter (Hysitron, Inc.). The friction force and normal displacement of the samples were measured during the friction/scratch test, while the deformation of the samples after the scratch was characterized using scanning electron microscope (SEM, Philips/FEI XL30).

The Tribolindenter has force and displacement sensing capabilities in both vertical and lateral directions. A 90° conical diamond tip with 100 µm tip radius of curvature, mounted on the force/displacement transducers of the Tribolindenter, was used to make scratches. Fig. 1 shows the schematics of the tip scratching a NSTF under an applied normal load. The friction/scratch tests were conducted at a sliding speed of 1 µm/s with 8 µm scratch lengths. As illustrated in Fig. 2, the friction/scratch tests consisted of the following seven steps: (1) the tip engaging the sample surface at a contact force of about 1 µN in the midpoint of the expected scratch (A), (2) the tip sliding toward one end of the expected scratch in 4 s under zero normal load (A and B), (3) the tip staying at this end of scratch for 5 s while the normal load is increased to a targeted normal load, this load is 2000 µN in Fig. 2 (B and C), (4) the tip scratch toward the other end of the expected scratch in 8 s under the targeted normal load (C and D), (5) the tip staying at the end of the scratch for 5 s while the normal load is reduced to zero (D and E), (6) the tip moving back to the middle of the scratch under zero normal load (E and F), and (7) the tip withdrawing from the sample surface. The purpose of employing steps (1) and (2) is to properly account for the sample tilt in the measured normal displacement data. The normal and lateral forces and displacements were recorded simultaneously and continuously as a function of time during sliding for each test by the force/displacement sensor of the Tribolindenter. The coefficient of friction (COF) at any time during the scratch was calculated as the ratio of the measured lateral force and applied normal force.

Different values of normal loads ranging from 100 µN to 8000 µN were applied in the scratch tests. Friction results for the scratch tests performed at 8000 µN are not reported as the data had significant noise. However the scratches are used for studying the nanorods deformation. Five scratches were made at each applied normal load in each direction. Scratches were arranged in matrix pattern consisting of rows and columns. Each column of the matrix contained five scratches (five rows) made at a
particular normal load and in the same tilt direction. Since it is hard to locate the very short scratches made by the 100 μm tip during SEM characterization after the scratch test, especially the ones made using low normal loads that may not cause detectable deformation, two sets of two-column reference scratch marks were made with a relatively sharp conical diamond tip with radius of curvature of 1 μm. These columns sandwiched the scratch matrix formed by the scratch tests at various applied normal loads using the 100 μm tip. The reference scratches allowed easy identification of the scratched area during the SEM characterizations after the scratch test.

To locate the test matrix in the SEM, a crosshair was also manually scribed onto the sample surfaces using a diamond scriber prior to the scratch test. A quadrant was then chosen relative to the scribed crosshair for performing the scratch test matrix based on the cleanliness of the quadrant and the alignment of the scribed crosshair to the Tribolindenter coordinate system. Once a quadrant was chosen, an origin was defined at the corner of the quadrant where the scribed lines cross. This origin was used to define a starting point for the scratch matrix. Once the scratches on the NSTF and conventional thin film surfaces were completed, SEM micrographs were taken at different magnifications to characterize the deformation of the films by identifying the crosshair first and then the test matrix.

3. Results and discussion
3.1. Surface topography

Fig. 3 shows SEM micrographs of top down and cross-sectional views of the Mo NSTF and conventional Mo thin film. It can be seen from Fig. 3(a) and (b) that the nanorods on the NSTF surface are randomly distributed and have different diameters and heights. The nanorods are tilted at an angle of about 45° to the surface of the substrate. The tops of these nanorods are flat and elliptical in shape with rod diameters of about 70–200 nm. The spacing between the nanorods along the nanorods tilt direction ranges from 90 nm to 360 nm. In comparison, it can be seen from Fig. 3(c) and (d) that the conventional Mo thin film surface is much smoother with no high aspect ratio isolated surface nanostructures as in the case of GLAD NSTF morphology.

3.2. Coefficient of friction

Fig. 4 shows plots of the normal displacement for the NSTF surface (for both along and against the direction of nanorods tilt) and the conventional thin film surface as a function of the applied normal load. The plotted normal displacement at each applied normal load is the average of five averages calculated from five scratches. The error bar is twice the average of five standard
deviations calculated from five scratches. From Fig. 4, it can be seen that the normal displacement was the highest for the NSTF along the tilt direction, in between for NSTF against the tilt and the lowest for conventional thin film. Higher normal displacement for NSTF than conventional thin film at each applied load is expected because the nanorods are not tightly packed and will deform easily as compared to conventional thin film. It is also seen that the normal displacements were higher along the tilt direction at each load when compared to against the tilt. This can be explained by comparing the difference in deformation modes in two directions as illustrated in Fig. 5. The nanorods will bend easily in the tilt direction while scratching along the tilt but will provide significant resistance while scratching against the tilt. During scratching along the tilt direction (Fig. 5(b)), the net force (summation of normal force and lateral force vectors) on the nanorods will be in a direction more perpendicular to the rod axis causing bending in the nanorods. On the other hand, when scratched against the tilt direction (Fig. 5(c)), this net force will be more along the rod axis leading to minimal bending and more resistance when the tip moves from rod to rod. Because of this anisotropic behavior, the mode and amount of deformation in the nanorods will be different in each direction, with less deformation against the direction of nanorods tilt.

Fig. 6 shows plots of the coefficient of friction (COF) for the NSTF surface (for both along and against the direction of nanorods tilt) and the conventional thin film surface as a function of the applied normal load. The plotted COF at each applied normal load is the average of five averages calculated from five scratches. The error bar is twice the average of five standard deviations calculated from five scratches. Table 1 summarizes the obtained COF at different normal loads for the NSTF and conventional thin film samples. Difference (in %) in the COF between against the tilt direction and along the tilt direction is also given in the table, as well as the difference (in %) in COF between the conventional thin film and along the tilt direction. From Fig. 6 and Table 1, it is clearly observed that COF values are consistently higher while sliding against the tilt as compared to sliding along the tilt at all applied normal loads. These observations are in agreement with

![Fig. 5](image_url) A schematic showing the behavior of nanorods when the tip interacts with the NSTF sample. (a) At low normal load, (b) scratching along the tilt at high normal load and (c) scratching against the tilt at high normal load (not to scale).

<table>
<thead>
<tr>
<th>Load (µN)</th>
<th>NSTF along the tilt</th>
<th>NSTF against the tilt</th>
<th>Thin film</th>
<th>Difference (%) against along</th>
<th>Difference (%) thin film – along</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.34 ± 0.03</td>
<td>0.39 ± 0.03</td>
<td>0.76 ± 0.03</td>
<td>13.5</td>
<td>55.5</td>
</tr>
<tr>
<td>500</td>
<td>0.20 ± 0.01</td>
<td>0.25 ± 0.01</td>
<td>0.29 ± 0.01</td>
<td>25.0</td>
<td>31.1</td>
</tr>
<tr>
<td>1000</td>
<td>0.17 ± 0.01</td>
<td>0.22 ± 0.01</td>
<td>0.21 ± 0.01</td>
<td>26.7</td>
<td>19.0</td>
</tr>
<tr>
<td>2000</td>
<td>0.15 ± 0.01</td>
<td>0.19 ± 0.01</td>
<td>0.17 ± 0.005</td>
<td>29.1</td>
<td>11.9</td>
</tr>
<tr>
<td>4000</td>
<td>0.13 ± 0.01</td>
<td>0.17 ± 0.01</td>
<td>0.14 ± 0.004</td>
<td>34.9</td>
<td>6.9</td>
</tr>
</tbody>
</table>
the study on oblique Ti nanocolumns [26] and opposite to that of nanostructured polymeric films where the friction was higher along the tilt direction than against the tilt [25]. The difference in COF values is ~14% at the lowest applied load (i.e., 100 μN) and ~35% at the highest load of 4000 μN. From the results, it is also seen that the percentage difference in COF increases with increase in normal load. This is because molybdenum is very stiff and highly resistant to deformation due to which nanorods undergo minimal deformation at lower normal loads as can be seen in Fig. 4. Moreover, the tip is very large as compared to the diameter of nanorods and spacing between nanorods, which causes the tip to slide over the nanorods with little resistance from the deflection of nanorods against the tilt direction. Therefore the friction at lower loads will be mainly adhesion based. So at lower loads, the frictional anisotropy arises because of the directional anisotropy of the surface roughness in NSTF between along and against the tilt, similar to that of a saw-tooth wave. Whereas at higher normal load, when the scratch is performed along the direction of nanorods tilt, the nanorods underneath the indenter tip bend in the direction of tilt as illustrated in Fig. 5(b) and when the scratch is performed in the reverse direction against the direction of nanorods tilt, there is a higher resistance as the nanorods beneath the indenter tip deflect against the tilt direction as shown in Fig. 5(c). Similar observation has also been reported by Hirakata et al. in case of tilted Ti nanocolumn arrays [26].

From the results in Fig. 6, two different trends in variation of COF values are observed when comparing the frictional behavior of NSTF and conventional thin film samples. When the applied normal load is smaller than 1000 μN, the thin film sample has a larger COF than the NSTF sample both along and against the tilt direction. However, when the load is larger than 1000 μN, the COF of the thin film surface is lower than that of the NSTF surface when sliding against the tilt direction and higher than the NSTF surface when sliding along the tilt direction. The difference in COF values of along the tilt of NSTF and thin film decreases with increase in normal load and when the load is 4000 μN, the COF value of the thin film surface is close to that of the NSTF surface. A maximum of ~55% reduction in COF values is seen under the smallest applied normal load of 100 μN, suggesting the NSTF surface can significantly reduce the COF at low loads.

The difference in COF values between NSTF and thin film samples at lower loads can be explained from the difference in real contact area between the indenter tip and the surfaces. This is because adhesion is the dominant mechanism of friction at lower loads [28]. As explained previously in this section, at lower loads of less than 1000 μN, there is very little deformation in the nanorods. Due to this, the indenter tip surface is only in contact with the apex of the nanorods as shown in Fig. 5(a). Thus, the contact area between the tip and NSTF is smaller than that of the contact area between tip and conventional thin film. Since friction is proportional to real area of contact, the COF is larger for thin film surface than that of NSTF surface for both along and against the tilt at lower loads. At larger loads, the deformation becomes dominant mechanism as opposed to adhesion at lower loads [28]. This is the reason why a sharp drop in COF values is seen in case of conventional thin films. As previously mentioned in this section, at larger normal loads, there is resistance from the nanorods while scratching against the tilt direction resulting in a higher COF value for the NSTF than that of the conventional thin film surface. The nanorods bend in the direction of tilt while scratching along the tilt at larger normal loads and this in turn causes an increase in contact area as the tip tends to touch the sides of the nanorods as opposed to touching only the apex of the nanorods at lower loads. Therefore, the difference in COF values between the NSTF surface along the tilt and thin film decreases with increase in normal load. At the highest load of 4000 μN, the COF values of NSTF along the tilt direction approach that of conventional thin films. This indicates that, at higher loads, when deformation is the dominant mechanism, the NSTF along the tilt direction behaves like a conventional thin film. It seems that at higher loads along the tilt,
the nanorods bend to limit where the gaps between the nanorods disappear which causes the NSTF to behave similarly to that of a conventional thin film except the surface roughness.

3.3. Deformation

Fig. 7 shows SEM micrographs of the NSTF sample and the conventional thin film sample after being scratched by the 100 μm radius diamond tip under an applied normal load of 8000 μN. Fig. 7(a) and (b) shows the thin film sample surface at 5000 × and 20,000 ×, respectively, while Fig. 7(c) and (d) shows the NSTF sample surface, at 5000 × and 20,000 ×, respectively. The 8000 μN scratches were placed between the reference scratches made by a sharp tip with 1 μm tip radius. Fig. 7 shows that both the NSTF sample and the conventional thin film sample have no detectable deformation. The estimated Hertzian contact pressure (not considering the frictional force effect) at 8000 μN for the thin film is about 2.3 GPa, assuming 1141 GPa and 0.07 for the elastic modulus and Poisson’s ratio for the diamond indenter, and 329 GPa and 0.31 for the elastic modulus and Poisson’s ratio for the Mo thin film, respectively. The contact pressure, if we consider the frictional force effect, applied on the nanorods during scratch should be even larger due to smaller contact area between the tip and the discontinuous nanorods. Therefore, the nanorods demonstrated strong resistance to plastic deformation under high contact pressure.

4. Conclusions

The frictional and deformation behavior of a NSTF coating consisting of tilted Mo nanorods grown by GLAD technique were studied and compared to a conventional thin film made of stocks with nanorods and the way these tilted nanorods deform in each direction. Difference in COF values between the two directions were observed to increase with increase in applied normal load and a maximum difference of 35% was observed at a load of 4000 μN. The scratch direction affects the way the tip interacts with nanorods and the way the tilted nanorods deform in each direction giving rise to frictional anisotropy. The nanorods easily bend in the direction of tilt while scratching along the tilt, but provide strong resistance in the opposite direction as the nanorods need to deflect against the tilt. Therefore higher frictional force is observed against the tilt than along the tilt direction. The COF values for NSTF were significantly lower than that of conventional thin films at loads below 1000 μN indicating that NSTF can significantly reduce friction at lower loads. At higher loads, NSTF showed larger COF values against the tilt direction when compared to thin films and COF values along the tilt was similar to that of thin films. NSTF surface demonstrated strong resistance to plastic deformation because SEM micrographs did not show any visible plastic deformation. In future studies, it will be interesting to investigate the effect of tilt angle, spacing between the nanorods, shape and size of the nanorods on frictional anisotropy.

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