Materials Letters 142 (2015) 207–210

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Characterization of nanofriction of MoS_2 and WS_2 nanotubes

Dave Maharaj, Bharat Bhushan *

Nanoprobe Laboratory for Bio- & Nanotechnology and Biomimetics (NLBB), The Ohio State University, 201 West19th Avenue, Columbus, OH 43210-1142, USA

ARTICLE INFO

Article history:
Received 23 October 2014
Accepted 4 December 2014
Available online 13 December 2014

Keywords:
MoS_2
WS_2
Friction
Wear
Nanotubes

ABSTRACT

MoS_2 and WS_2 nano-objects have been studied in tribological applications and increasingly in other applications where nano-objects come into sliding contact with each other. Fundamental friction studies on a single nano-object are of interest. In this research atomic force/friction force microscopy (AFM/FFM) studies have been conducted on MoS_2 and WS_2 nanotubes to study scale effects and analyze the contributions of surface topography and orientation effects on friction. Variations in friction force due to topography were determined to be as a result of the ratchet mechanism and "collision" effect. There were no orientation effects on coefficient of friction on either of the nanotubes.

1. Introduction

MoS_2 and WS_2 nano-objects have been studied in tribological applications on the macro- to nanoscale in dry and liquid environments and increasingly in other applications such as catalysis and as hosts for storing hydrogen and lithium. In these applications the nano-objects come into contact with each other and the surfaces in which they are used [1–5]. Detailed knowledge of their interfacial friction as well as the influence of environmental conditions on the friction mechanism is needed to determine their suitability for various applications. MoS_2 and WS_2 both have a lamellar structure in which there are strong covalent bonds between atoms of the same layer and weak van der Waals forces between the layers. During sliding on these materials, the weakly bonded layers shear past each other, which results in reduced friction and wear [6]. To understand the frictional behavior of theses nano-objects on the nanoscale, AFM/FFM studies on single nano-objects made of MoS_2 and WS_2 are carried out. These studies can provide useful information on scale effects and local changes in friction due to topographic effects and material effects related to surface chemistry and nano-object orientation [7–10].

In this paper MoS_2 and WS_2 nanotubes were chosen to investigate friction by comparing topography and friction maps of various features on the nanotube surfaces. Studies were also conducted to determine effects of friction with regard to nanotube orientation.

2. Experimental

Si (100) silicon wafers with a native oxide layer (University Wafers, Boston, MA) were ultrasonically cleaned in deionized (DI) water, followed by isopropyl alcohol (IPA) and finally acetone for 15 min each.

Fig. 1 shows representative images of the nanotubes used for the experiments performed with magnified images of defects. MoS_2 nanotubes were obtained from Josef Stefan Institute, Slovenia, and WS_2 nanotubes from Weizmann Institute, Israel. Fig. 1a shows representative transmission electron microscopy (TEM) micrographs of a MoS_2 nanotube with a broken edge (Top) and a magnified image showing broken surface layers (Right). Fig. 1b shows agglomerated WS_2 nanotubes (Left) and a magnified image with an arrow pointing to exfoliated layers (Right). The diameters of the nanotubes used were at least 200 nm and lengths no less than 5 μm for both MoS_2 and WS_2 nanotubes. The nanotubes suspended in isopropyl alcohol were deposited onto Si (100) substrates using a syringe. The substrate was then placed on a hot plate and heated to a temperature of about 70–80 °C and left until the liquid evaporated. Topography and friction maps were obtained with an AFM (Dimension 3100, Bruker, Santa Barbara, CA). A sharp silicon nitride tip (Orc8 series, Bruker, Camarillo, CA) with cantilever stiffness $k=0.1$ N/m and a nominal radius of 15 nm was used.

Friction maps were obtained at a constant normal load over scan sizes of 2 μm × 2 μm, 500 nm × 500 nm and 5 nm × 5 nm. For coefficient of friction, voltage data obtained were converted to forces by using an established calibration method [10,11]. The tip was first calibrated on a silicon surface by scanning along the cantilever axis to obtain the coefficient of friction and then orthogonal to the axis to obtain a conversion factor to change the friction signals to forces. The coefficients of friction for the

* Corresponding author.
E-mail addresses: maharaj.1@osu.edu (D. Maharaj), Bhushan.2@osu.edu (B. Bhushan).

http://dx.doi.org/10.1016/j.matlet.2014.12.024
0167-577X/

nanotubes were then obtained by plotting the friction force obtained during orthogonal scanning as a function of normal load from five random spots over a scan length of 5 nm and velocity of 9 nm/s. The scan length is very small compared to the minimum diameters of the nanotubes (200 nm) and removes any curvature effects on friction. Normal loads were determined by multiplying the cantilever vertical deflection by the cantilever stiffness (Bhushan, 2011) [9]. The vertical deflection in turn was obtained by operating the cantilever in force calibration mode, in which the deflection sensitivity obtained from the force curve was multiplied by the change in setpoint voltage.

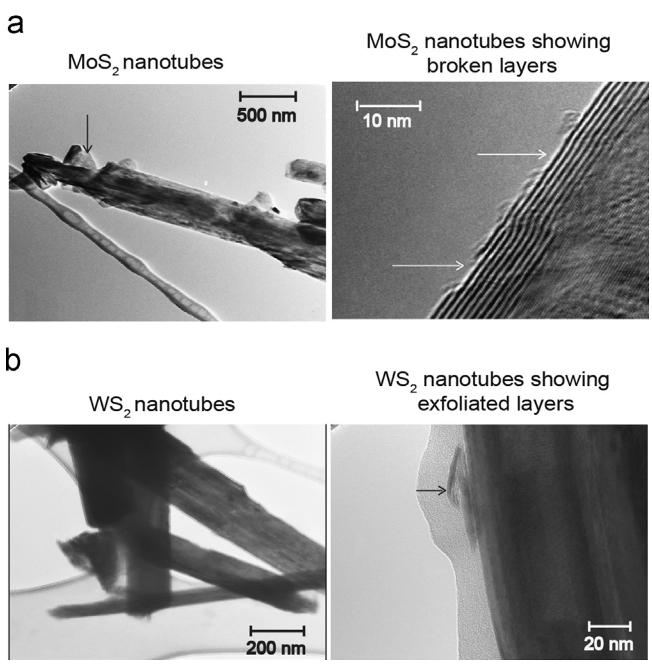

Fig. 1. TEM images of (a) MoS_2 nanotube with a broken edge (Top), magnified image showing broken surface layers (Right), (b) agglomerated WS_2 nanotubes (Left), a magnified image with an arrow pointing to exfoliated layers (Right) and a magnified image of a nanotube showing ordered layers (Maharaj and Bhushan, 2014).

3. Results and discussion

Fig. 2 shows corresponding topography and friction force maps for both MoS_2 and WS_2 nanotubes over a 2 μm × 2 μm scan area (Top). The areas highlighted within the dashed squares (500 nm × 500 nm) were imaged and are shown in the bottom row.

From the magnified images it can be observed that the features seen in the topography maps correspond to changes in the friction maps. The lighter regions on the friction maps correspond to higher friction and darker regions, lower friction. These changes in friction occur where there are changes in the slope of the topography map as a result of the ratchet mechanism [12–15]. As the AFM tip is scanned up a slope it experiences a higher lateral force and the friction force is a combination of the material friction and the slope of the asperity. Conversely, the friction force is lower when descending as the slope term is subtracted out. These variations in friction do not occur due to the nanotube curvature as the change in the slope of the tube is negligible compared to the features on the tube. Sundararajan and Bhushan (2000) [15] found that there is also a contribution to friction due to the collision of the tip when ascending a slope. This produces an additional torsion to the tip and contributes to the friction force being higher than when descending the slope. The magnitude of this force is dependent on the applied normal load and scanning velocity. The "collision" force is not present when descending the slope and only the ratchet mechanism is at work. These effects can be minimized by scanning on a flat surface where slope and "collision" contributions would be negligible which allows for isolating the material induced effects of friction.

Fig. 3 shows representative topography and friction force maps for MoS_2 (Top) and WS_2 nanotubes (Bottom) taken over a 5 nm × 5 nm area to minimize roughness effects, as the surface asperities at this

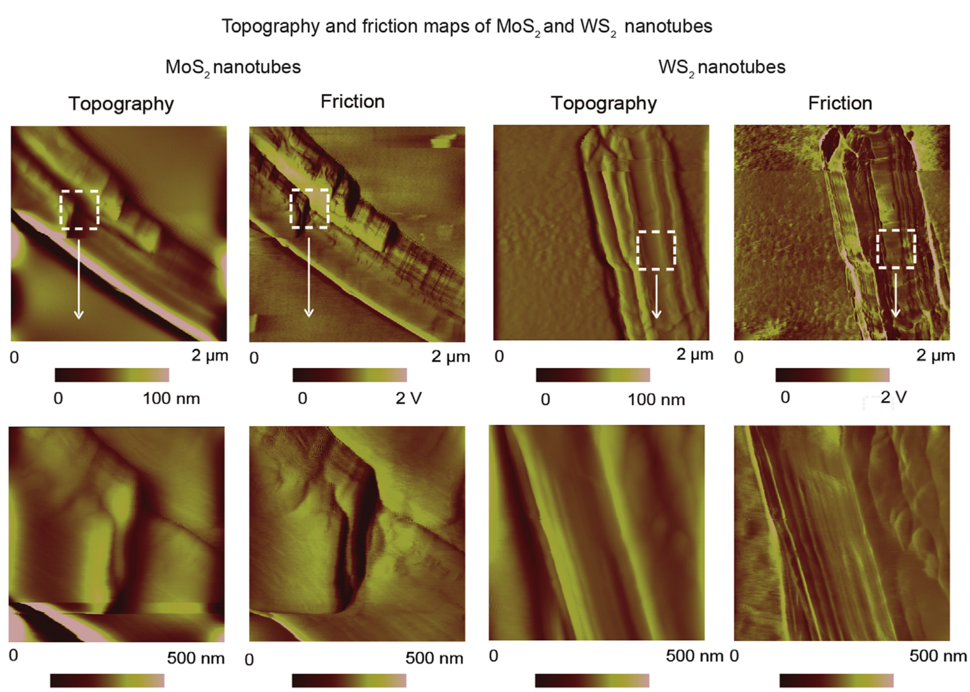

Fig. 2. Examples of topography and friction maps of MoS_2 (Left) and WS_2 nanotubes (Right) with arrows pointing to magnified images of the areas highlighted by dashed squares.