

# On Tailoring the Nanocrystalline Structure of ZnO to Achieve Low Friction

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**Editor's Note:** For a closer look at Hamidreza's poster abstract, be sure to check out his short video presentation in the January digital version of TLT (*available at [www.stle.org](http://www.stle.org)*).



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## ABSTRACT

Cross-sectional high-resolution transmission electron microscopy (HR-TEM) inside worn surfaces coupled with density functional theory (DFT) calculations reveal atomistic origins of low friction and nanocrystalline plasticity when sliding on ZnO {0002}-textured nanocolumnar grains. The atomic layer deposited (ALD) sub-

stoichiometric ZnO film was structurally tailored to achieve low surface energy and low growth stacking fault energy basal planes. Sliding on this defective ZnO structure resulted in an increase in both partial dislocation and basal stacking fault densities through intrafilm shear/glide of partial dislocations on the {0002} planes. This shear accommodation mode mitigated friction and brittle fracture frequently observed in microcrystalline and single crystal ZnO. These results have potentially broad implications to other defective nanocrystalline ceramics.

## INTRODUCTION

ALD ZnO/Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> nanolaminates are good candidates for providing low friction and wear and potentially high thermal (oxidation) resistant surfaces and interfaces in moving mechanical assemblies such as carbon-carbon composite (CCC) bushings that experience fretting wear.<sup>1,2</sup> Significant reduction in the sliding wear factor ( $2.3 \times 10^{-5}$  to  $4.8 \times 10^{-6}$  mm<sup>3</sup>/Nm) and friction coefficient (0.22 to 0.15) was achieved compared to uncoated CCC [2]. This improvement was attributed to intrafilm shear (slip) of partial dislocations along the {0002} basal stacking faults in nanocrystalline grains of ZnO by a dislocation glide process. To further elucidate the underlying crystal structure-dependent deformation mechanisms responsible for this tribological improvement, ALD ZnO with nanocrystalline

{0002}-textured grains were compared to samples of ZnO with nanocrystalline randomly orientated grains and ZnO single crystal with {0001}-basal plane orientation.

## EXPERIMENTAL

The processing of ALD trilayer ZnO (~100nm thick)/Al<sub>2</sub>O<sub>3</sub> (~20nm thick)/ZrO<sub>2</sub> (~100nm thick) nanolaminates infiltrated into CCC has been reported elsewhere.<sup>2</sup> ZnO is the topmost layer deposited on amorphous Al<sub>2</sub>O<sub>3</sub>, which determines the ZnO {0002} growth texture, and ZrO<sub>2</sub> is the bottom, load bearing layer. The friction coefficient for the ZnO samples was determined in unidirectional sliding against a stationary Si<sub>3</sub>N<sub>4</sub> ball under a normal load of 0.98 N (initial mean Hertzian contact stress of ~0.6 GPa). The linear sliding speed was 2.1 cm/s and the total sliding distance was 190 m. Tests were conducted at ambient temperature and relative humidity of ~40 to 50%. X-ray photoelectron spectroscopy revealed that the ZnO layer was sub-stoichiometric (Zn<sub>0.54</sub>O<sub>0.46</sub>). This oxygen deficiency for ALD ZnO has been linked to oxygen vacancies.<sup>3</sup> Condensation of vacancies, causing the introduction of a missing or extra ZnO (0002) plane into the lattice, along with incoherent boundaries between adjacent nanocolumnar grains, are sources for ALD ZnO growth basal stacking faults (BSF). Partial dislocations (PD) border the BSF as discussed next.

## ILLUSTRATIVE RESULTS

Figure 1 illustrates that at the end of sliding the lowest friction coefficient of  $\sim 0.15$  was observed for ALD ZnO with nanocrystalline  $\{0002\}$ -textured grains. In contrast, ZnO single crystal with the same basal plane  $\{0001\}$ -orientation exhibited a much higher friction coefficient of  $\sim 0.53$ . The noisy friction coefficient values for this single crystal ZnO sample is likely related to severe structural deformation occurring during wear, which will be discussed later. In addition, the ZnO with nanocrystalline randomly orientated grains also exhibited a higher friction coefficient of  $\sim 0.4$ , confirming that the  $\{0002\}$ -textured grains of ALD ZnO are important in achieving low friction. The same  $\{0002\}$ -growth texture was responsible for low friction in pulsed laser deposited ZnO films.<sup>4</sup>

To elucidate the underlying structural mechanisms responsible for this observed ZnO friction behavior, cross-sectional transmission electron microscopy (XTEM) analyses were performed inside the worn surfaces. Figure 2 (a) shows an SEM planar image inside the wear track center of ALD ZnO/Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> coated CCC after 190 m of sliding (Figure 1). The wear track shows evidence of a sliding-induced highly deformed layer (HDL) on the surface. Figure 2 (b) is a XTEM image taken inside the wear track shown in Figure 2 (a). There is evidence that the HDL consists of CCC and stress-induced (plastically deformed) nanocrystalline ALD coating material. However, the deeper subsurface CCC pores that were infiltrated with the nanolaminate were undeformed (denoted by red arrow in Figure 2 (b)). In addition, Figure 2 (b) shows that the HDL does not exhibit uniform thickness in the wear track, which is not surprising given the heterogeneous appearance of the wear track surface in Figure 2 (a). Energy dispersive spectroscopy revealed no Si x-ray lines indicating no Si<sub>3</sub>N<sub>4</sub> ball transfer to the wear track and making up part of the HDL. Figure 2 (c) shows a higher magnification image of the HDL and a trilayer from the box location in Figure 2 (b). There is also evidence that part of the trilayer exhibited intergranular fracture, which suggests occurrence of combined plastic deformation and fracture processes inside the wear track. Based on these images, the tribologically

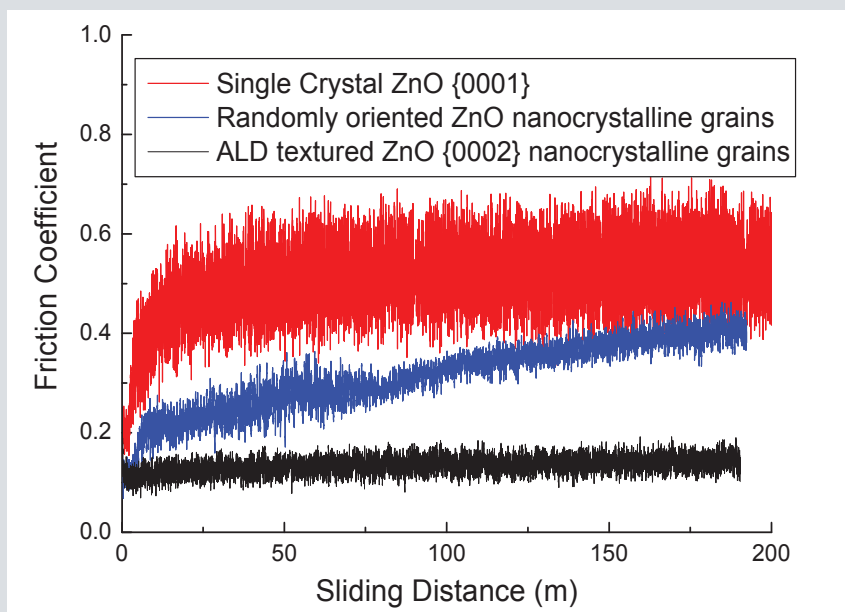


Figure 1 | Friction coefficient as a function of sliding distance for ALD textured ZnO  $\{0002\}$  nanocrystalline grains, single crystal ZnO  $\{0001\}$  orientation, and randomly oriented ZnO nanocrystalline grains.

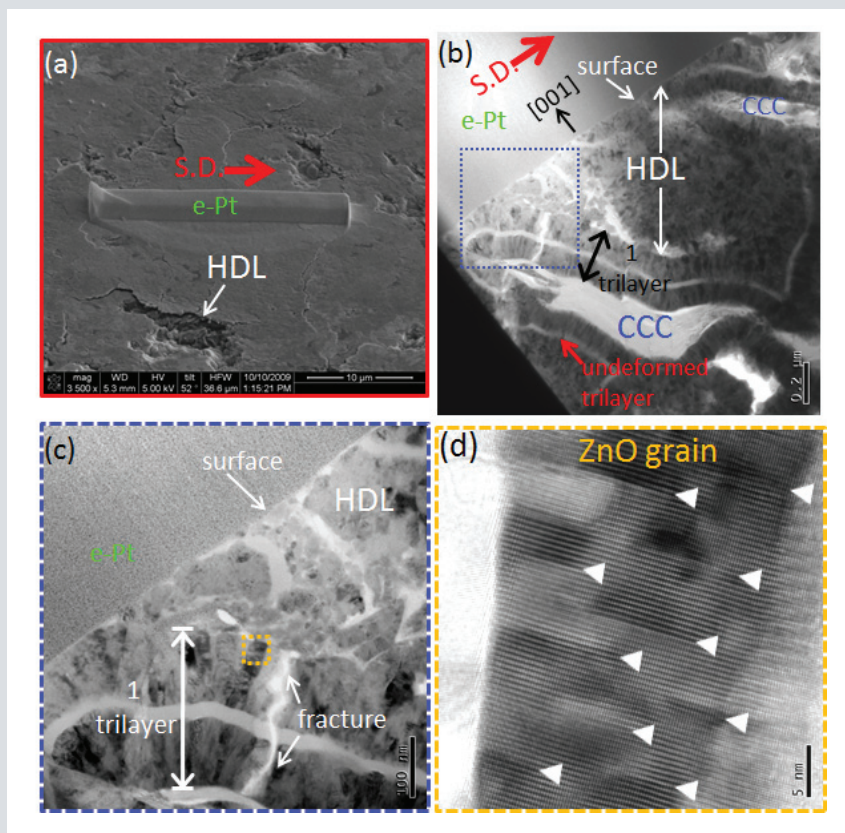


Figure 2 | (a) SEM image inside the ALD trilayer ZnO/Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> nanolaminate wear track after 190 m of sliding. S.D. = sliding direction. The rectangular bar is e-beam evaporated Pt deposited in the SEM to protect the surface during FIB-milling. XTEM images (b) inside the wear track showing HDL and undeformed trilayer, (c) HDL taken from the box location in (b), and (d) plastically deformed ZnO  $\{0002\}$ -orientated grain taken from the box location in (c). The arrows point to a high density of sliding (shear)-induced basal stacking faults inside a nanocrystalline ZnO grain.

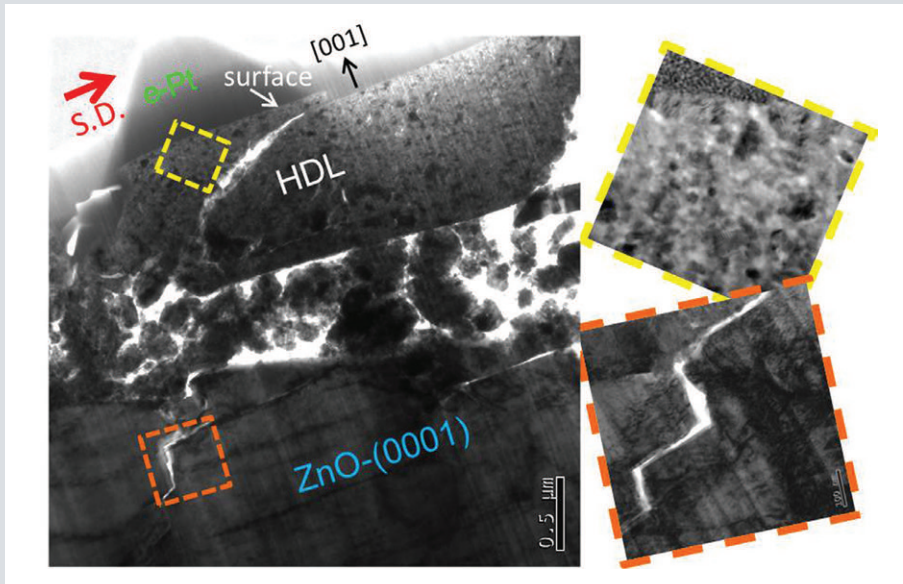


Figure 3 | XTEM images inside the wear track of a {0001}-ZnO single crystal. Insets show HDL and cleavage cracks along the ZnO basal and prismatic planes.

stress-induced HDL is a contributing factor to the improvement in the friction of the ALD ZnO/Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> nanolaminate. Also, the ZnO in the intact trilayer and HDL likely play an important role in friction. Figure 2 (d), taken from the box location in Figure 2 (c), shows an intact ZnO layer that has not fractured into smaller nanocrystalline grains, i.e., it is not part of the above HDL. Nevertheless, this ZnO layer does show evidence of extensive plastic deformation through subsurface-induced plastic shear. ZnO {0002} BSF were observed (white arrows) inside the ZnO grain and at the grain boundary suggesting that there is discernible localized plasticity in the nanocolumnar ZnO grains. This is a type-I intrinsic BSF (ABAB|CBCB). The DFT calculation of the stacking fault energy (SFE) using Vienna Ab-initio Simulation Package (VASP)<sup>5</sup> confirmed that {0002}-basal plane stacking faults with SFE of ~24 mJ/m<sup>2</sup> are thermodynamically preferred over {1-100}-prismatic stacking faults with SFE of ~427 mJ/m.<sup>2</sup> Therefore, solid lubricity of ALD ZnO is attributed to localized dislocation glide along BSF/PD that promotes intrafilm shear/slip and consequently lowers the friction. More details of this process and mechanism are in.<sup>2</sup>

In dramatic contrast to ALD ZnO, the deformation mechanism in {0001} ZnO single crystal did not involve any localized plasticity, since XTEM analysis of the features below the surface HDL (nanocrystalline ZnO) exhibited extensive cleavage fracture (Figure 3). The cleavage cracks along basal (0002) and prismatic (10-10) and (11-20) planes are responsible for brittle fracture and higher friction coefficient. Since there are no grain boundaries, there are no preexisting BSFs/PDs nucleating at low angle grain boundaries (as in ALD ZnO) to provide low friction pathways via intrafilm shear/slip. This severe deformation process accounts for the high and noisy friction coefficients in Figure 1. Lastly, the ZnO with nanocrystalline randomly orientated grains has multiple, interacting slip systems operative, which can lead to localized hardening, and consequently to a larger interfacial shear (friction), as indicated in Figure 1. In contrast, ALD ZnO has the most energetically favorable, single basal orientated slip system active during sliding.

### SUMMARY

The overall damage mechanism for bulk microcrystalline and single crystal ceramics is well-known to be brittle

(cleavage) fracture. Here, for the first time, we provide evidence of localized nanocrystalline plasticity in ALD ZnO wherein only basal slip is active. This provides enhanced solid lubrication due to intrafilm shear (slip) of partial dislocations along the ZnO {0002} basal stacking faults likely occurring via dislocation glide.

### ACKNOWLEDGMENTS

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