

Tribological Properties of Ultrananocrystalline Diamond Films in Inert and Reactive Tribo-Atmospheres: XPS Depth-Resolved Chemical Analysis

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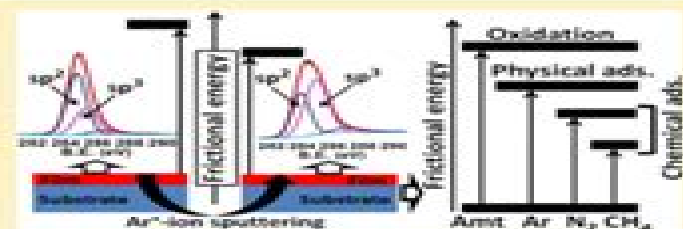
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Supporting Information

ABSTRACT: Tribological properties of diamond films are sensitive to the chemically reactive and inert tribo-atmospheric media, and therefore, it is difficult to understand the underlying tribological mechanisms. In the present work, tribological properties of surface-modified ultrananocrystalline diamond (UNCD) thin films were investigated in four distinct tribo-environmental conditions of ambient humid-atmosphere, nitrogen (N_2), argon (Ar), and methane (CH_4) gases. The in situ depth-resolved X-ray photoelectron spectroscopy (XPS) showed the desorption of oxygen and oxy-functional additives and sputtering of weakly bonded amorphous carbon species from the UNCD film surface after the Ar^+ -ion sputtering process. After desorption of these chemical entities, friction and wear were decreased and run-in regime cycles became shorter in UNCD films. Friction in the ambient humid-atmosphere was higher compared to other tribo-environmental conditions, and it was explained by the oxidation mechanism of the sliding interfaces and the formation of the oxidized carbon transferfilm. However, low friction and wear in the N_2 atmosphere was associated with the adsorption of N_2 species, forming nitrogen-terminated carbon bonds at the sliding interfaces. This was directly investigated by XPS and energy dispersive X-ray spectroscopy techniques. Furthermore, low friction in the Ar atmosphere was explained by the physical adsorption of Ar gaseous species, which tend to avoid the covalent carbon bond formation across the sliding interfaces. Moreover, ultralow friction in the CH_4 atmosphere was governed by the passivation of dangling carbon bonds by dissociative CH_4 complexes, which creates hydrogen-terminated repulsive sliding interfaces. More importantly, a shorter run-in regime with low friction and wear in Ar^+ -ion-sputtered UNCD films were explained by desorption of the oxygen and oxy-functional groups, which are inherently present in the UNCD films.



1. INTRODUCTION

Carbon-based functionalized two-dimensional (2D) nanomaterials^{1,2} and carbon/carbon nanocomposite thin films^{3,4} are useful in tribological applications. Properties of diamondlike carbon (DLC) and diamond thin films are chemically and mechanically exceptional, which are significantly useful for various mechanical and tribological applications.^{5–8} Tribological stability and tribo-performance of these films depend on several factors. For DLC, it is mainly associated with the sp^3 / sp^2 phase fraction and hydrogen concentration in the films.^{9,10} However, the grain size and grain boundary volume fraction with distinct chemical properties are the main internal associates for tuning the tribological behavior of crystalline diamond films.^{11–13} Recently, nanocrystalline diamond (NCD)

and ultrananocrystalline diamond (UNCD) films with a distinct morphology, microstructure, and phase composition showed improved and sustainable tribological properties.^{1,14–16} This is specifically explained by the densely packed morphology, ultrasmall sp^3 -bonded grain size, and sufficiently high volume fraction of the short-ranged sp^2 crystalline phase occupying the grain boundaries of these films.^{12,17} The UNCD films showed a superlow friction coefficient after the run-in regime and a negligible wear.¹⁸ However, adverse wear from the ball counterbody was observed because of the high friction in the

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Ultrananocrystalline Diamond Olga A. Shenderova, Dieter M. Gruen, 2012-09-11 Ultrananocrystalline Diamond Synthesis Properties and Applications is a unique practical reference handbook Written by the leading experts worldwide it introduces the science of UNCD for both the R D community and applications developers using UNCD in a diverse range of applications from macro to nanodevices such as energy saving ultra low friction and wear coatings for mechanical pump seals and tools high performance MEMS NEMS based systems e g in telecommunications the next generation of high definition flat panel displays in vivo biomedical implants and biosensors This work brings together the basic science of nanoscale diamond structures with detailed information on ultra nanodiamond synthesis properties and applications The book offers discussion on UNCD in its two forms as a powder and as a chemical vapor deposited film Also discussed are the superior mechanical tribological transport electrochemical and electron emission properties of UNCD for a wide range of applications including MEMS NEMS surface acoustic wave SAW devices electrochemical sensors coatings for field emission arrays photonic and RF switching biosensors and neural prostheses etc Ultrananocrystalline Diamond summarises the most recent developments in the nanodiamond field and presents them in a way that will be useful to the R D community in both academic and corporate sectors Coverage of both nanodiamond particles and films make this a valuable resource for both the nanotechnology community and the field of thin films vacuum deposition Written by the world s leading experts in nanodiamond this second edition builds on its predecessor s reputation as the most up to date resource in the field

Science and Technology of Ultrananocrystalline Diamond (UNCD) Thin Films for Multifunctional Devices, 2000 MEMS devices are currently fabricated primarily in silicon because of the available surface machining technology However Si has poor mechanical and tribological properties and practical MEMS devices are currently limited primarily to applications involving only bending and flexural motion such as cantilever accelerometers and vibration sensors However because of the poor flexural strength and fracture toughness of Si and the tendency of Si to adhere to hydrophylic surfaces even these simple devices have limited dynamic range Future MEMS applications that involve significant rolling or sliding contact will require the use of new materials with significantly improved mechanical and tribological properties and the ability to perform well in harsh environments Diamond is a superhard material of high mechanical strength exceptional chemical inertness and outstanding thermal stability The brittle fracture strength is 23 times that of Si and the projected wear life of diamond MEMS moving mechanical assemblies MEMS MMAs is 10 000 times greater than that of Si MMAs However as the hardest known material diamond is notoriously difficult to fabricate Conventional CVD thin film deposition methods offer an approach to the fabrication of ultra small diamond structures but the films have large grain size high internal stress poor intergranular adhesion and very rough surfaces and are consequently ill suited for MEMS MMA applications A thin film deposition process

has been developed that produces phase pure nanocrystalline diamond with morphological and mechanical properties that are ideally suited for MEMS applications in general and MMA use in particular The authors have developed lithographic techniques for the fabrication of diamond microstructure including cantilevers and multi level devices acting as precursors to micro bearings and gears making nanocrystalline diamond a promising material for the development of high performance MEMS devices

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