Diamond & Related Materials 78 (2017) 12–23

Contents lists available at ScienceDirect

Diamond & Related Materials

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

Tribofilm formation in ultrananocrystalline diamond film

Revati Rani[a], K.J. Sankaran[b,c], Kalpataru Panda[d,e], N. Kumar[a,*], K. Ganesan[a], S. Chakravarty[f], I-Nan Lin[g]

[a] Indira Gandhi Centre for Atomic Research, HBNI, Kalpakkam 603102, Tamil Nadu, India
[b] Institute for Materials Research (IMO), Hasselt University, 3590 Diepenbeek, Belgium
[c] IMOMEC, IMEC vzw, 3590 Diepenbeek, Belgium
[d] Center for Nanomaterials and Chemical Reactions, Institute for Basic Science, Daejeon 305-701, Republic of Korea
[e] Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea
[f] UGC-DAE CSR, Kalpakkam Node, Kokilamedu 603104, Tamil Nadu, India
[g] Department of Physics, Tamkang University, Tamsui, Taiwan

ARTICLE INFO

Keywords:
Friction and wear properties
Ultrananocrystalline diamond films
High resolution microstructure
Boundary phase
Tribofilm formation

ABSTRACT

Friction and wear properties of ultrananocrystalline diamond (UNCD) films are found to be superior, and therefore it could be useful for various applications. However, understanding of the tribological properties with respect to boundary phase composition in this material is not yet well understood. Here, the grain boundary phases such as graphite and amorphous carbon (*a-C*) of UNCD films were tailored during the chemical vapor deposition process by altering the Argon and Nitrogen gases in CH_4 plasma medium. The significance of these grain boundary phases in UNCD film was discussed to explain the tribological properties. In run-in, friction coefficient was high in $UNCD_{Ar}$ film deposited in CH_4 (1%)/Ar plasma condition and it was decreased to lower value after longer sliding distance. However, ultrahigh wear resistance of this film was observed. Here, graphite and *a-C* phases were insignificant in the grain boundary region as evident from high resolution transmission electron microscope (HRTEM). Further, chemical bonding of these phases was quantitatively described by electron energy loss spectroscopy (EELS). In contrast, ultralow value of friction coefficient with significantly shorter run-in high friction regime was observed in $UNCD_N$ film deposited in CH_4 (6%)/N_2 plasma. Such a unique characteristic was described by the nanographite phase encasing the needle-like diamond grain of $UNCD_N$ film, forming core-shell granular structure. Atomic force microscopy (AFM) showed nucleation of two dimensional (2D) nanographite particles in the deformed wear track after run-in. This was possible due to the presence of core-shell granular structure in $UNCD_N$ film. Graphitic nature of the shell for needle-like diamond grains in the wear track was investigated by micro-Raman spectroscopy. Moreover, graphite and *a-C* tribofilm phase in the wear track was investigated by X-ray photoelectron spectroscopy (XPS) having spatial resolution micrometer scale. Needle-like diamond grains and graphite phase of tribofilm could be one of the primary reasons for the marked reduction in the friction coefficient.

1. Introduction

Extreme friction and wear problem at the nanoscale are becoming critical issues, in particular, when real machine system works in macroscopic contact condition [1,2]. This problem can be resolved if one can understand the mechanism by which friction and wear take place. At microscale, the friction force may disrupt normal performance by overcoming driving force of the sliding devices [3,4]. Furthermore, extreme wear can damage individual components and thus significantly reduces the lifetime of the machine systems. Therefore, it is necessary to understand and further quantify the friction and wear behavior at the nanoscale when system functions in macroscopic contact condition. Such analysis could be helpful to improve the design aspect of materials for the sustainable application.

Tribological properties of materials depend mostly on the orientation of the crystalline phase, hardness, elastic modulus, fracture toughness, roughness, grain size and grain boundary phase composition [5–10]. The last two factors become important to understand the friction and wear behavior in nano/ultrananocrystalline diamond films [8,11]. Tian et al. showed that the tribological properties were found to improve with the decrease in the grain size of diamond [10]. This was related to the decrease in roughness and enhancement of amorphous

* Corresponding author.
E-mail address: niranjan@igcar.gov.in (N. Kumar).

http://dx.doi.org/10.1016/j.diamond.2017.07.009
Received 10 March 2017; Received in revised form 19 June 2017; Accepted 13 July 2017
Available online 14 July 2017

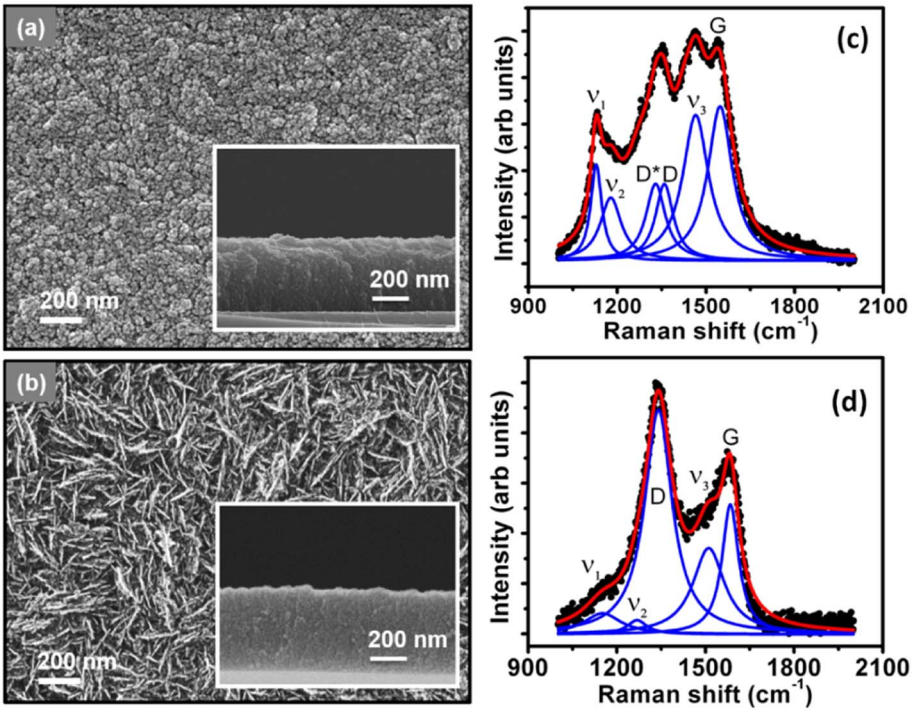

Fig. 1. Morphology of: (a) $UNCD_{Ar}$ and (b) $UNCD_N$ films, and Raman spectra of: (c) $UNCD_{Ar}$ and (d) $UNCD_N$ films, respectively.

carbon (*a-C*) and graphite phase in the grain boundary. Particularly, graphite phase provides low shear strength due to layered lattice structure of weakly bonded intra-graphite planes and therefore shows low sliding resistance. There are many other factors, including chemical transformation in tribo-contact which complicate the friction and wear mechanism in carbon materials [12–14]. Moreover, such transformation is sensitive to contact stress, temperature, test environment and chemical affinity of the sliding bodies [11–13,15–20]. It is shown that the tetrahedral diamond-like carbon (DLC) and diamond phase convert into *a-C*, graphite and short-ranged tetrahedral amorphous carbon (*ta-C*) under tribo-contact conditions [7,13,19–23]. These tribolayer phases largely influence the friction and wear characteristic of tribo-system. Normally, friction and wear reduce when diamond or DLC film's surface graphitizes, which provides layered lattice structure of crystalline graphite at the sliding interface [13,19,21–25].

However, tribological behavior of diamond materials depends largely on their microstructure. Primary reason for high friction and wear in macro and microcrystalline diamond film is possibly high roughness, large grain size, dangling bonds and high energy of specific orientation of crystalline plane [5,6]. In contrast, ultralow value of friction coefficient and high wear resistance in nanocrystalline diamond (NCD) and ultrananocrystalline diamond (UNCD) films were explained by *a-C* and graphite phases present in the grain boundary [8,11,26]. Furthermore, ultralow friction behavior in UNCD film was described by surface chemical inertness and passivation mechanism [27–29]. It was noticed that ZrO_2 ball was severely deformed while wearless characteristic of UNCD film deposited in Ar/CH_4 plasma was observed. In contrast, wear loss from the UNCD film deposited in N_2/CH_4 plasma was found to be higher and ZrO_2 ball was marginally deformed during sliding [9]. Extremely high friction coefficient and high wear loss at the beginning of the sliding cycles were observed for the diamond film deposited using Ar/CH_4 plasma. This was explained by the presence of surface contamination of carbon-oxygen functional complexes [16,30]. These complexes are easily formed because of the high chemical affinity of atmospheric composition towards dangling carbon bonds present at the UNCD film surface. However, as soon as the run-in lapsed, friction coefficient was reduced to the super-low value 0.008 with extremely high wear resistance. The mechanistic aspect of such a unique characteristic of UNCD film is not fully explained so far. In addition, tribolayer characteristic with respect to grain boundary phase is also not known in the UNCD films.

Present paper investigates the influence of grain boundary phases on tribological properties of UNCD films. Nanoscale wear characteristic of UNCD films formed during macroscopic tribological contact condition was studied. Atomic force microscopy (AFM) was used to analyze the nanoscale topographical changes in wear track. Furthermore, nucleation of secondary particles under the tribo-stressed condition was investigated. Chemical structure and chemical composition evaluation of deformed ultrananno diamond particles in the wear track were carried out by micro-Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDX). During the tribology test, in-situ electrical contact resistance (ECR) measurement was performed to describe the tribolayer formation. These results were inter-correlated to investigate the friction and wear behavior of UNCD films. Here, it is important to mention that the tribolayer is one of the most significant aspects for the determination of friction and wear properties. The investigation of this issue is relevant for understanding the tribology mechanism in UNCD films.

2. Experimental

The UNCD films were grown on silicon (100) substrates in microwave plasma enhanced chemical vapor deposition (MPECVD) system (2.45 GHz 6″ IPLAS-CYRANNUS). Two different types of UNCD films were deposited for the comparative tribological studies. In first condition, CH_4 (1%)/Ar plasma with a microwave power of 1200 W, a pressure of 120 Torr and a substrate temperature of 450 °C was used. The other UNCD film was deposited employing CH_4 (6%)/N_2 plasma with a microwave power of 1200 W, a pressure of 50 Torr and a substrate temperature of 700 °C. These were optimized parameters used for the deposition of UNCD films. For simplicity, films deposited in CH_4 (1%)/Ar and CH_4 (6%)/N_2 plasma medium will be further designated in the text as $UNCD_{Ar}$ and $UNCD_N$ films, respectively. More detail deposition procedure is published elsewhere [9]. UNCD film morphology was characterized by field emission scanning electron microscopy (FESEM, Zeiss Supra 55). The microstructure and local bonding