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Effects of normal load on nanotribological properties of sputtered carbon nitride films

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Abstract

The nanotribological properties of amorphous carbon nitride (CN_x) films of ~380 nm thickness were investigated, in the normal (contact) load range of 2–20 mN, using a Berkovich diamond indenter. The amorphous CN_x films tested in this work were grown on Si(100) substrates by reactive sputtering and energetic ion bombardment during deposition (IBD). The dependence of the friction behavior of the CN_x films on normal load (NL) was investigated in terms of nanomechanical properties, deformation mode and Atomic Force Microscopy (AFM) images of scratched surfaces, and the intensity of IBD. In films sputtered without IBD, the increase of the normal load caused the coefficient of friction to decrease initially to a minimum value and, subsequently, to increase to a maximum value, after which, it remained constant. The dominant friction mechanism in the low-load range was adhesion, while both adhesion and ploughing mechanisms contributed to the friction behavior in the intermediate and high-load ranges. Elastic and plastic deformation (PD) and delamination of the amorphous CN_x films occurred, depending on the normal-load ranges. On the other hand, films sputtered with high-energy IBD showed a load-dependent transition in both the scratch and the friction responses. Nanoscratching below 5 mN showed mainly elastic behavior of the film, while above 10 mN, a mixed elastic–plastic behavior was identified. Testing under a normal load of 20 mN resulted in local grooving at the film surface; however, in situ profiling of the scratch trace and AFM images showed no evidence of film failure. The increased load-carrying capacity, higher hardness and elastic response obtained with films grown with high-energy IBD, and the dominant friction mechanism at each load range illustrate the normal load dependence of the nanotribological properties of the sputtered CN_x films.

Keywords: Sputtered carbon nitride films; Thin films; Nanotribology; Nanoindentation; Atomic Force Microscopy; Friction

1. Introduction

Over the last decade, carbon nitride (CN_x) films have received considerable scientific attention. Although a wide variety of techniques has been implemented, there is no clear evidence of the formation of the crystalline stoichiometric phase β-C_3N_4 [1,2]. CN_x films have been shown to exhibit higher scratching and wear resistance and low-friction properties [3,4]. Nitrogen incorporation in carbon increases the fraction of sp^2 carbon bonds, and carbon nitride coatings may become good competitors of carbon films for a wide range of sliding elements, due to their low-friction coefficients, better wear resistance, better durability, and reduced internal stresses.

Amorphous CN_x films can be synthesized by various vapor phase deposition techniques [5–7] and find applications in magnetic heads and hard disks for high-density proximity recording, due to their extremely low roughness and their excellent tribological performance. Moreover, the fact that CN_x films are based on carbon makes them good candidates for biomedical applications [8]. Another attractive application of CN_x films lies in their use as protective films on transparent antireflective coatings. This wide range of applications is driving further research and development of CN_x films with the goal of improving their performance

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in current applications, as well as in advancing their functionalities for future applications in emerging fields. One of the important aspects of these applications is their tribological properties and the factors affecting their friction behavior.

Advances of microelectromechanical system technology in the past decade make understanding of scale effects in tribology especially important, because surface to volume ratio grows with miniaturization and surface phenomena dominate. Microscale and nanoscale friction force measurements can be obtained with various instruments, such as friction force microscope [9,10], atomic force microscopy [11,12], and scratch test [13] with apparatus able to make finely controlled low-load scratches.

Scratch test is increasingly used for the evaluation of the functionality of the film–substrate compound, because it can provide fast qualitative, semiquantitative, and quantitative information on the adhesion of the film onto the substrate [12,13], the friction and wear behavior. Adhesion, elastic, and plastic deformation (PD) on nano- to microscale contributes to friction, while the scale dependence of deformations has to be considered. Actually, load effect on friction has been an interesting aspect of the tribological study of thin films, but few studies have been devoted to the effect of consecutive load on friction process especially for amorphous CN_x films. As far as we know, several groups have studied the nanoscratch performance of carbon-based thin films. The coefficient of friction and deformation response of diamondlike carbon (DLC) films with thickness between 100 and 500 nm were found to vary with contact load in the range of 10–300 mN [13,14], in scratch experiments conducted with a Berkovich diamond tip. Ma et al. [15] studied the effects of normal load (NL; 10–1200 μN) on the nanotribological properties of thin amorphous carbon (a-C) films by performing nanoscratch tests. By increasing the normal load, the coefficient of friction was found to decrease initially to a minimum value, subsequently to increase to a peak value, and, finally, to either decrease slightly or remain constant. The coefficient of friction obtained with diamond pins slid against amorphous CN_x films was found to increase to a maximum value (0.22) and subsequently to decrease to 0.1 with increasing film thickness without exhibiting a dependence on normal load in the range of 10–250 mN [16]. Different deformation responses, such as elastic and plastic deformation, fracture, and delamination, have been reported in scratching tests with DLC films grown on titanium alloy [14], CN_x films, and single (multi)-layer a-C films grown on Si substrates [13,17]. Miyoshi [18] proposed an empirical relation of coefficient of friction (μ), $\mu=kL^b$ (k, b are constants) for diamond sliding on a ceramic film, under the condition that only plastic deformation was produced without fracture damage. This relation has been also applied to describe the rise of μ with increasing normal load for CN_x films with the normal load in the range 10–150 [17] and 2–20 mN [19,20]. The friction behavior of very thin (20 nm) amorphous CN_x films deposited on Si substrates by magnetron sputtering has also exhibited load dependence [12]. The aforementioned studies illustrate a significant influence of the normal load on the tribological performance of CN_x, a-C and DLC films.

Despite the important insight into the tribological properties of carbon and amorphous CN_x films derived from previous studies, relatively less attention has been paid on the friction behavior and films deformation mode dependence on the applied normal load, especially in the case of CN_x films subjected to low normal loads. The objective of this work is the investigation of the nanotribological performance of CN_x films deposited onto Si(100) by reactive sputtering and energetic ion bombardment during deposition (IBD), which varies from low to higher values due to the applied bias voltage onto the substrate. Nanoindentation and nanoscratching tests were performed in order to study the effects of normal load and hardness on the friction behavior of amorphous CN_x films. The study is mainly focused on the deformation mode and the friction behavior of the films at different normal loads and aims to the better understanding of the mechanisms governing the failure of thin CN_x films. Atomic Force Microscopy (AFM) was also used in the quantification of morphological and tribological properties of the CN_x films revealing a fair agreement of the occurred material deformations with those in situ monitored by the nanoscratch apparatus.

2. Experimental details

2.1. Specimens

Amorphous CN_x films were deposited onto Si(100) substrates by reactive RF magnetron sputtering using a graphite target of 99.999% purity in a deposition chamber with a base pressure better than 1×10^{-7} mbar applying sputtering power of 100 W and by applying different bias voltage (V_b) on the substrate, ranging from −250 to +16 V. As sputtering gas N_2 of 99.999% purity was used at a partial pressure of 4×10^{-3} mbar. The cleaning procedure of the substrates included chemical and dry etching with low-energy Ar^+ ions before deposition. Films with a thickness of ~380 nm were grown at room temperature to minimize substrate deformation under the maximum Hertz applied contact pressure.

Nitrogen has the ability to form with C several bonding configurations [21]. These include the sp^3 (tetrahedral, C–N), sp^2 (trigonal, C=N), and the chain terminating sp^1 (linear, –C≡N and –N≡C) bonds. The properties of the CN_x films depend on the distribution of N atoms among the possible bonding configurations as determined by a variety of factors, such as the deposition system geometry, the sputtering gas partial pressure, and the sputtering power. However, the bonding structure of the deposited films is mainly affected by the intense ion bombardment [N^+, N^{2+}, CN^+ $(CN)_n^+$, etc.], which is a consequence of the plasma