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Nanomechanical and nanotribological properties of carbon based films

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Abstract

Submicrometer-thick hard amorphous carbon (a-C) and carbon nitride (CN_x) films were deposited on Si and stainless steel (SS) substrates by rf magnetron sputtering (MS) and reactive MS, respectively. a-C films were synthesized by either sputtering alternating ultrathin layers of soft and hard a-C on Si or by using a Cr interlayer between a-C and SS substrate. The main purpose of this work is to investigate and to compare the nanomechanical, adhesion and nanotribological properties of the CN_x and a-C films. Hardness (H) and elastic modulus (E) were obtained from indentation experiments performed with a nanoindenter using the continuous stiffness method. The H of a-C films was found to be equal to ~25 GPa, and the corresponding values of a single-layer amorphous CN_x films were found to be equal to ~12 GPa. Nanoscratch tests of the films were performed by a Nano Indenter XP system with a lateral force measuring attachment. Ultralow load scratch tests were performed in the load range from 2 to 20 mN. Below 5 mN, nanoscratching showed mainly elastic behavior of the CN_x and a-C films, 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 showed no evidence of film failure. The coefficient of friction was found to vary in the range 0.15–0.3, being lower for a-C films. The higher elastic properties, no permanent damage and higher elastic recovery under the same normal load imply that a-C films grown on both SS and Si substrates sustain higher scratch-induced stresses and can be more effective as protective coating material.

Keywords: Amorphous carbon; Hardness; Elastic modulus

1. Introduction

Amorphous carbon (a-C) films possess a unique and adjustable combination of properties such as high hardness (H) and wear resistance, chemical resistance and good tribological performances [1,2]. They have low friction coefficients and provide protection for the counterparts [3]. Therefore, these films show good prospects for a wide range of applications such as machining, metallurgical, pharmaceutical or computer industry. However, the main restriction for the full commercialization of a-C films is attributed to the poor adhesion to steel substrates, which is caused mainly by high diffusion of carbon and high residual stresses in the films. Generally, a-C films are hard (about 18–70 GPa) but brittle. They may cause problems for high loading applications such as automotive parts and high-precision ball bearings. Particularly, when applied on soft substrates with low load-carrying capacity, severe plastic deformation can occur. To overcome these difficulties and to tailor the film properties, various techniques have been adopted to provide better adhesion and load-carrying capacity. Introducing an interlayer such as Cr, Ti, etc. [2,4] has been found to be an effective way to promote the adhesion. Stress levels can also be reduced by the design of periodically repeated multilayers [5,6]. In addition, some researchers have found that a series of functionally graded underlayers can effectively equalize the stress and improve the adhesion [7,8]. Recently, the pretreatment of substrates with ion implantation prior to deposition has been proved to be successful to provide adherent a-C films [9–11].

Nitrogen incorporation in carbon increases the fraction of sp^2 carbon bonds, and thus carbon nitride (CN_x) coatings

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may become good competitors for 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 [12–15] and may serve in potential 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 [16]. This wide range of applications is driving further research and development of CN_x films and their tribological properties. The aim of this paper is to compare adhesion, mechanical and tribological properties of a-C and CN_x films by investigation of the nanomechanical properties and the scratch performance. The study is mainly focused on the analysis of the nanoscratching processes at low loads to obtain quantitative analysis, the comparison of their elastic/plastic deformation response and nanotribological behavior.

2. Experimental

2.1. Specimens

The a-C films were deposited by rf magnetron sputtering (MS) on c-Si(100) and stainless steel (SS) substrates using a 6" hot-pressed graphite target (99.999% pure, density 1.9 g/cm^3). The films presented in this work were deposited at room temperature, the substrate to target distance was 65 mm, the sputtering power 100 W, and the argon partial pressure was 2×10^{-2} mbar. The energetic particle bombardment of the growing film is known to be a major factor controlling the compressive stress in the film. In sputtering, the energetic species are the argon ions, which impinge on the growing film when a negative bias voltage (V_b) is applied to the substrate. The a-C films were deposited in one layer (single layer—SL) or in sequential thin layers (A and B) with alternating positive (layer A) and negative (layer B) V_b during deposition (multilayer—ML), d_A~10 nm with positive V_b=+10 V and d_B~20 nm with negative V_b=−20 V. We present here results for films with a total thickness of about 90 nm.

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 negative bias voltage (V_b) on the substrate. The applied V_b controls the ion energy. Negative bias promotes the high-energy ion bombardment during deposition (IBD). 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. The surface roughness of the CN_x films grown with high-energy IBD was about 0.5 nm, and the average compressive internal stress of the film was ~900 MPa as it was estimated by AFM and a commercial cantilever laser beam apparatus [16], respectively.

2.2. Nanoindentation test

The elastic properties of the films were measured by using a Nano Indenter XP system placed in a vibration-free isolated cabinet. The hardness (H) and elastic modulus (E) of the films were measured with a Berkovich three-sided pyramidal diamond indenter with a nominal angle (defined by the tip axis and faces) equal to 65.3°. Tests were performed in clean air environment with a relative humidity of approximately 40%, while the temperature was constantly kept at 22 °C. Tip shape calibration was carried out before testing by producing indentations at different contact depths on fused silica of hardness and elastic modulus approximately equal to 10 and 73 GPa, respectively. The H and E of the films were conducted using continuous stiffness measurements (CSM) [17], with a load and displacement resolution of 50 nN and <0.01 nm, respectively. In all CSM tests, a total of 10 indents on different surface positions with a spacing of 50 μm were averaged to determine the mean H and E values for statistical purposes.

2.3. Nanoscratch test

Nanoscratch tests were performed on a-C and CN_x films deposited onto SS substrates using an interlayer of Cr with thickness of about 10 nm to promote the adhesion of the film to the substrate to compare their scratch performance. A Berkovich diamond tip of nominal radius of curvature approximately equal to 100 nm was used to scratch the film surfaces. The detailed description of the system used and the calibration and testing methodology were presented elsewhere [18]. The displacement velocity was constant for all the tests (10 μm s^{-1}), while scratching was carried out with ramping normal loads of 0.02–5 mN. To avoid deformation effects from neighboring scratches, the distance between sequential scratches was set to 15 μm. The general profile of all scratch testing presented in this work has been presented elsewhere [18]. Briefly, first, the entire length of the scratch (700 μm) was profiled under a constant load of 0.02 mN, after which the stage direction was reversed, and a small segment of the scratch line was profiled again. Then, a ramp load scratch test was performed. The indenter was then unloaded back to 0.02 mN to profile the last small segment of the scratch line. Finally, the entire length of the scratch line was profiled one more time. The evolution of the scratch depth was in situ measured by profiling the surface of the film before, during and after testing, with a total test length of 700 μm, while the scratch length was 500 μm. The load for initial and postscratch scanning was 0.02 mN, a value sufficiently low not to produce any damage or permanent deformation on the films.