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Characterisation of the interface region in stepwise bias-graded layers of DLC films by a high-resolution depth profiling method

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Abstract

The stepwise graded layer concept solves the problem of high internal compressive stresses in diamond-like carbon (DLC) films by adjusting a graded constitution by stepwise increasing the ion energy, i.e., the bias voltage, during sputter deposition. In order to optimize this concept, the detailed characterisation of the interface zones between the layers sputtered with different bias voltage plays a key role. The small-angle cross-section method (SACS) has been developed as a special nanoindentation (NI) technique to perform a high-resolution depth-profiling of the mechanical properties on the nanometer scale in multilayer or nanolaminated composite systems and especially to characterise their interfacial regions. Using improved area correction functions, by varying the maximum load, and by separating the instrumental broadening from the measured hardness profiles, it was possible to significantly improve the sensitivity and the resolution of the SACS. This allowed for the first time to investigate the dependence of the expansions of the interface zones between the graded layers on measuring and processing parameters. By using SACS, depth profiles of hardness and elastic modulus in dependence of applied load and layer thickness ratio have been measured.

Keywords: Diamond-like carbon (DLC); Stepwise bias-graded layer design; Interface characterisation; Depth-profiling; Mechanical properties

1. Introduction

Due to their high hardness, chemical inertness and excellent tribological properties, amorphous carbon coatings with significant fractions of sp^3 bonds, often called diamond-like carbon (DLC) coatings, are of great interest for technological applications such as wear-resistant coatings in magnetic storage disks [1,2] or protective coatings in the food industry [3], friction-reducing coatings in micro-electromechanical systems [4], or biocompatible coatings [5,6]. In sputter deposition, a strong ion bombardment of the growing carbon film is applied in order to provide a strong densification of the amorphous carbon network [7,8], which is necessary to increase the fraction of diamond-like sp^3 bonds. The sputter deposition mechanism differs from that, when the films are grown from energetic C^+ ions using filtered cathodic vacuum arc (FCVA) [9] or mass-selected ion-beam (MSIB) deposition method [10]. During sputtering, the Ar^+ ions act only to bombard the growing DLC film and are not incorporated into the film in contrast to the C^+ ions in FCVA and MSIB which are energetic enough to enter subsurface sites. The Ar^+ ions displace C atoms into subsurface positions (knock-on subplantation), densify the surface, and provide conversion from sp^2 to sp^3 bonds by a high local compressive stress. Because the three different mechanisms have different process parameters, the sp^3 content does not vary linearly with stress as in FCVA [9] but remains constant until a certain threshold is reached, and then increases rapidly [7]. Thus, the high internal compressive stresses in DLC films limits either their maximum thickness or their maximum sp^3 bond fraction. The stepwise bias-graded layer design was shown to be successful for solving this problem [11,12]: in order to improve the adhesion and to manage the internal stresses, a graded constitution of the growing DLC films is adjusted by a

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stepwise increase of the ion energy, i.e., the bias voltage, during deposition. While the ion bombardment provides a high density and a high hardness, the modification of the interface regions between the substrate and the graded layers ensures a good adhesion. By using the stepwise bias-graded layer design, it has been possible to deposit stable adherent DLC films with a maximum thickness of 10 μm and a maximum hardness of 5300 HV0.05. However, to optimize this concept, a depth profiling of the mechanical properties particularly at the interfaces between the layers deposited with different bias voltage is of great interest. Combining experimental investigations of the mechanical properties at the nanoscale with theoretical work on this field by Monte-Carlo [13] or molecular dynamics simulation [14,15] will result in a deeper understanding and a better optimization of amorphous layer systems.

Only recently, three methods for a depth-resolved measurement of hardness and Young's modulus in the nanometer range were developed: the load variation method, the constant load method (CLM) and the cross section method. The basis of all methods is depth-sensitive nanoindentation (NI). Here, a diamond tip is pressed into the sample as an indenter and removed again after reaching a maximum load or depth, while the load F and the displacement or penetration depth h_t of the indenter are recorded. The simplest method to obtain depth profiles is a stepwise increase in load, and thereby increasing the probed depth, during indentation in vertical direction to the surface. Therefore, the depth resolution available with this load variation method (LVM) decreases with increasing load [16]. In the constant load method (CLM), the layers are removed in a stepwise manner by ion sputter etching. Indentation takes place vertically to the surface at constant load. Resolution is somewhat better than for the LVM, as the measurements can always be performed at the same small load. On the other hand, this method is destructive and modifications of the specimen properties by ion bombardment have to be taken into account. In case of the cross-section method (CSM) developed by Kunert et al. for studying carbon implantation into Ti–6Al–4V steel [16], indentations take place at constant load along an appropriately prepared specimen cross section. In principle, this method provides the best depth resolution. However, its use for studying thin nanoscale films and in particular interface regions in stepwise bias-graded layers of DLC films is limited, as the minimum possible distance between two indentations required is 2 μm in a CSIRO UMIS2000 system and 100 nm in a HYSITRON TriboScope® system. Therefore, the small-angle cross-section method (SACS) has been developed as a special nanoindentation technique, which allows to significantly increase the number of measurement points in the single layers and to use the high-resolution capacity of scanning probe methods [17]. The SACS has been optimised by varying the maximum load, using improved area correction functions and subtracting the instrumental broadening from the measured hardness profiles.

Using the SACS on a UMIS2000 system, the mechanical properties of two different bias-graded DLC films were examined at the nanoscale. This allowed for the first time to investigate the dependence of the expansions of the interface zones between the graded layers on measuring and processing parameters. By using SACS, depth profiles of hardness and elastic modulus in dependence of applied load and layer thickness ratio have been measured.

2. Experimental

2.1. Deposition and characterisation of stepwise bias-graded DLC films

The DLC films were deposited onto polished commercial M15 hard metal cutting inserts (88.5 wt.% WC, 11 wt.% Co, 0.5 wt.% Ta(Nb)C; 12×12×4.5 mm) by nonreactive d.c. magnetron sputtering of a pure C target in an argon atmosphere. Prior to the deposition the recipient was evacuated to a residual pressure of less than 5×10^{-4} Pa and the substrates were cleaned by ion etching at a r.f. substrate bias of −800 V for 15 min in argon. The constant deposition parameters applied were a d.c. sputtering power of 500 W, which corresponds to a power density of 11.32 W/cm^2, an argon pressure of 0.6 Pa and a target–substrate distance of 5 cm. Following the graded layer concept developed by Stüber et al. [18], stepwise bias-graded DLC films composed of three layers with different properties were realized by increasing the ion energy, i.e., the substrate bias voltage U_B in three steps as shown in the schematic presentation in Fig. 1. The deposition started with a bias voltage of 0 V to initiate a high adhesion of the growing film. Then, the bias voltage was increased stepwise to −150 V and finally to −300 V to produce a hard film surface. To investigate the influence of the thicknesses D_i of the three graded layers on the expansion of the interface regions d_{12} between 1. and 2. layer and d_{23} between 2. and 3. layer, two different layer deposition time characteristics and thus thickness ratios D_1:D_2:D_3 of the three graded layers were adjusted. The two samples with reversed ratio of layer

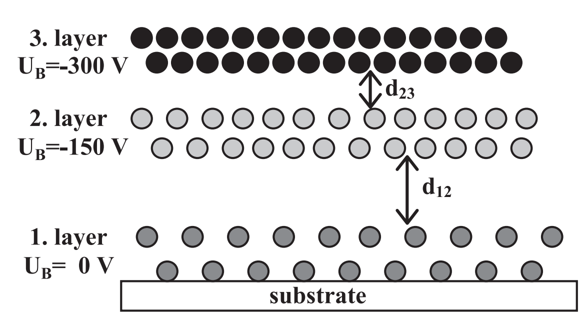

Fig. 1. Bias-graded layer design of DLC films with the expansions of the interface regions d_{12} between 1. and 2. layer and d_{23} between 2. and 3. layer.