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Nanotribology of pulsed direct current magnetron sputtered diamond like carbon films

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ABSTRACT

The presented research for the first time establishes the relations among nanotribological features, structural properties and deposition parameters (acetylene flow and bias voltage) of diamond like carbon films deposited by pulsed direct current magnetron sputtering. The nanotribological behaviour of hydrogen free and hydrogenated diamond-like carbon films (a-C:H) deposited by pulsed direct current magnetron sputtering was investigated using atomic force microscopy (AFM). A structural analysis with Raman spectroscopy showed that elevated acetylene concentrations in the process gas atmosphere favoured a decreased structural disorder in the a-C:H matrix, which was derived from the decreasing full with at half maximum of the G-band in the spectrum from 191 ± 3 cm^{-1} to 173 ± 1 cm^{-1}. More ordered films showed friction coefficients of ~0.001, while having still relatively high hardness. Spectroscopic data could be associated with mechanical properties: higher structural disordering of the films showed highest hardness (23.3 ± 0.3 GPa). Coatings deposited only with argon as sputtering gas have low friction coefficients ~0.002 and low wear rates ~1.2 nm. In general, the deposited films were found to be relatively free of defects and smooth, which was derived of an averaged roughness of the film surfaces of less than 1 nm.

1. Introduction

Diamond-like carbon (DLC) films are well known for tribological applications because of their high hardness [1], good thermal conductivity [2], low friction coefficient [3], excellent wear resistance [4] and chemical inertness [5]. Amorphous hydrogenated carbon films obtained by physical vapour deposition (PVD) have improved roughness along with self lubricating properties compared to nanocrystalline diamond films obtained by chemical vapour deposition [6]. Disadvantages of most of DLC films are higher internal compressive stress and poor adhesion with the substrate, which can limit its practical applications [7,8]. Thus, many studies have been carried out to reduce disadvantages by doping metal to hydrogenated amorphous carbon film. This method reduced internal stress [9], improved adhesion [10] and reduced film's sensitivity to humidity [11].

DLC can be deposited by several methods including ion beam deposition, direct current (DC) or radio frequency (RF) magnetron sputtering, plasma enhanced chemical vapour deposition (PECVD), cathodic arc deposition, electron cyclotron resonance microwave plasma chemical vapour deposition (ECR-MPCVD) and pulsed laser deposition (PLD) [12–18]. However, sputtering is still widely used due to advantages like low cost, simplicity and control of the process and film homogeneity. High power impulse magnetron sputtering (HiPIMS) is a newly developed technique which is able to provide energetic bombardment conditions necessary for deposition of DLC films with sp^3 contents achieved by state-of the art ionised PVD techniques [19]. Plasma conditions in HiPIMS allow deposition of ultra-smooth and dense films with control over the whole microstructure and phase composition in order to achieve films with superior mechanical, optical and electrical properties [20].

Further, it is to be stated that improvement of structural and mechanical properties of DLC films can be achieved by pulsing the sputtering voltage. One effect of bipolar pulsing of the magnetron voltage on the structural properties of the deposited DLC films is the additional bombardment and subsequent energy transfer of argon ions in the growing DLC film matrix: This can help to densify the film and encourage the sp^3 binding content [19,20]. An additional important advantage of pulsed DC sputtering is the suppression of arcs when using higher pulsing frequencies. When using porous graphite targets for sputtering, arc suppression is necessary to decrease the defect density in the deposited films.

Friction and wear behaviour of carbon based coatings in conventional load range have been studied by many investigators and are fairly well understood [21–26]. However, in numerous engineering applications, the applied load is substantially or even orders of magnitude lower than that employed in conventional laboratory tribological testing [27]. Over the years applications such as micro motors,

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micro pumps, micro tweezers, and micro mechanical assemblies have emerged. The applied load in these applications is in the range of nano to micro Newton.

Understanding of friction and adhesion in the nano Newton load range using an atomic force microscope (AFM) has substantially progressed [28–31]. A variety of sophisticated experimental techniques have been employed to study the nanotribological properties of DLC films. The durability of carbon films have been assessed by means of nanoindentation to measure nanohardness [32–35] and scratch testing to measure scratch resistance [36–39]. Mate [40,41] and Perry et al. [42] investigated friction and adhesion properties of a-C:H films by scanning probe microscopy. Nanotribology of carbon-based films is reported by several investigators using atomic force microscopy (AFM), and it is known that microscratch and microwear tests can be performed on these films in order to screen industrial coatings [42–45]. In view of the above, the present investigation is undertaken to evaluate the effect of varied process gas mixtures and bias voltages on nanotribological response of pulsed direct current magnetron sputtered DLC film. Although an impressive amount of work has been done in this direction, this is for the first time demonstrated, where structural factors as determined by Raman spectroscopy, have been correlated with the nanotribological properties as evaluated by atomic force microscopy. No investigator has hitherto reported such observations. Further, employing an innovative approach with force microscopy, the nature of worn surface has been characterised. Comparative studies with diamond-like carbon films deposited by other techniques having comparable structural and mechanical properties are considered as future perspective.

2. Experimental details

2.1. Film deposition

For deposition of quasi non hydrogenated (a-C) and a-C:H films, a balanced industrial sized magnetron cathode (coating height: 400 mm; AJA (AJA International, North Scituate, MA, USA)) equipped with a graphite target (nominal purity >99.95%) was used. The magnetron cathode was powered with a 10 kW power supply from Advanced Energy (Advanced Energy Industries, Fort Collins, CO, USA) in the power regulation mode. The pulsing unit was set to 80 kHz, where a reverse voltage of 15% with a reverse time of 1 μs was used. A power density of ~10 W cm^{-2} was applied on the carbon target for all depositions. For deposition of a-C:H films, C_2H_2 (nominal purity >99.96%) was introduced in the coating chamber together with argon (Ar) (nominal purity >99.999%) resulting in C_2H_2/Ar ratios from 0 to 0.43. For deposition of a-C coatings, a total flow of 30 sccm Ar was used.

Boron doped Silicon wafers (100) with a thickness of 525 ± 25 μm were used as substrates. The wafers were chemically cleaned in an ultrasonic cleaner sequentially with acetone and ethanol, and were dried with nitrogen. The wafers were fixed on a grounded substrate holding carrousel situated at a distance of approximately 10 cm from the sputtering source. The diameter of this carrousel was 56 cm whereas the samples were fixed at a diameter of 40 cm on vertical columns. In order to study the influence of substrate bias, a bias power supply (Heiden, Pürgen, Germany) was connected to the carrousel. Films were deposited by oscillation of the carrousel with amplitude of 9 cm (left–right) symmetrically through the sputtering plasma. The movement was in all cases one-dimensional and perpendicular to the longitudinal axis of the magnetron cathode. The substrate temperature was monitored with an electrically insulated K-type thermocouple installed at the backside of the substrate holder. The deposition conditions are summarised in Table 1.

For plasma cleaning of the wafers prior to deposition, an ALS 340 linear ion beam source (Veeco, Woodbury, NY, USA) was operated at a voltage of 2 kV and an Ar flow rate of 20 sccm through the ion gun. For all depositions, the chamber was evacuated to a base pressure of ≤5 × 10^{-5} mbar. During deposition and plasma etching, the pressure in the chamber ranged from 1 × 10^{-3} mbar to 7 × 10^{-3} mbar. During deposition no extra heating was applied to the substrates. The coating temperature did not exceed 80 °C for all depositions.

Table 1
Deposition Condition.

Substrate	Boron doped silicon wafer (100)
Target	Graphite (99.9% pure)
Gas	C_2H_2, Ar
Pressure	1 × 10^{-3} to 7 × 10^{-3} mbar
Flow rate	20 sccm
Coating temperature	80 °C (maximum)
Substrate bias voltage	−100 V
Discharge voltage	2 kV

2.2. Structural characterisation of the film

A Raman microspectrometer (Jobin-Yvon, Villeneuve d'Ascq, France) was used to characterise the hybridization of carbon atoms in the DLC films. The instrument was operated with a laser working at an excitation wavelength of 532 nm. An Olympus 100× objective was used to focus the beam on the sample, where in all cases the power of the laser was kept well below 0.25 mW. The entrance slit to the spectrometer was set to 100 μm and a holographic grating with 1800 grooves mm^{-1} was used. A standard (100) orientated silicon wafer with a Si-peak position of 521.3 cm^{-1} was used as drift standard. A resolution of ~2 cm^{-1} could be achieved with the spectrometer. Mathematical spectrum fitting for the D- and G-bands with Gaussian functions was performed with "Peak-Fit" 4.11 (Systat, Point Richmond, CA, USA). The G-band in Raman spectra from amorphous carbon phases taken at visible excitation has its origin in the effect of bond stretching of all carbon atoms in sp^2 hybridisation in rings and chains. The D-band occurs from the breathing mode of carbon atom rings [47–49]. I_D/I_G ratios were calculated by using peak heights. Since this work focuses on the spectral features of the D and G-bands, other Raman active modes have been neglected. High resolution transmission electron microscopy was carried out to obtain the microstructural features of the deposited films. Thickness and internal stress of the films were determined using a stylus profilometer (Veeco Instruments, Tucson, Arizona, USA). Step size measurements were carried out at edges of coated and uncoated areas on the silicon substrates.

2.3. Nanohardness measurement

The hardness and the elastic modulus of the deposited films were determined with an instrumented depth sensing indenter (Triboindenter TI900, Hysitron, Inc., Minneapolis, MN, USA) without AFM attachment equipped with a Berkovich three sided pyramidal diamond indenter with a nominal angle equal to 63.5°. The instrument was placed in a vibration isolated chamber. A maximum load of 4 mN was applied for the indentations. The load was selected in a fashion to keep the deformation confined within the film. The holding time during indentation was 5 s for all measurements. Loading and unloading was performed within 10 s for all measurements. The experimental results were corrected for the thermal drift of the equipment and for the uncertainty in the zero position. The reported hardness and elastic modulus were averaged of 10 indentations for each sample on different surface positions separated by ~50 μm. The elastic modulus was determined using the procedure described elsewhere [50]. The elastic modulus was calculated employing Eq. (1) as given below.

$$\frac{1}{E_r} = \frac{\left(1-\upsilon^2\right)}{E} + \frac{\left(1-\upsilon_i^2\right)}{E_i} \tag{1}$$