



Protective double-layer coatings prepared by plasma enhanced chemical vapor deposition on tool steel



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ABSTRACT

Hydrogenated diamond-like carbon films were prepared on high-speed steel substrates using low pressure radio-frequency capacitively coupled discharge (13.56 MHz) using methane mixed either with hydrogen or argon. A dc self-bias was induced by the rf discharge and accelerated the ions towards the substrates during the whole deposition process. Prior to the carbon film deposition and to improve the adhesion, the substrates were subject to plasma nitriding and coated with a silicon oxide layer using the same reactor. The deposited films were optically characterized (UV-IR) and by using a combination of Rutherford backscattering spectroscopy and elastic recoil detection the atomic composition was determined. The carbon films high hardness (~18 GPa) was assessed from indentation tests. Adhesion tests revealed critical loads up to 13.6 N for the carbon films deposited on steel substrates using silicon oxide interlayer. Friction coefficient varied from 0.02 against diamond and 0.23 against steel counterpart. The results suggest that hard carbon films can be deposited on steel substrate using a silicon oxide intermediate layer deposited by the same plasma process with commercial potential.

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1. Introduction

The stainless steels (SS) and high-speed steels (HSS) widely used in industry are limited by their poor tribological characteristics, mainly high wear rate associated with high friction coefficient and low hardness. Therefore, the surface properties of SS and HSS have to be improved by a surface coating. Diamond-like carbon (DLC) coatings are attractive industrial coatings from tribological point of view because of their outstanding properties such as low friction coefficient, high thermal conductivity, high hardness and chemical inertness against corrosive agents [1–4]. They can be prepared by plasma enhanced chemical vapor deposition (PECVD) offering a high degree of control regarding the film properties due to variability of gas feeds used, the accurate control of a coating conformity and the applicability to large substrates. Different hydrocarbon gases can be used for PECVD of DLC and the deposition rate was clearly related to the type of the hydrocarbon

molecule [4,5]. The H/C ratio in the molecule affects the hydrogen content in the films and their density. Therefore, the DLC films produced from acetylene (C_2H_2) tend to be hard than from CH_4 [6]. A disadvantage of C_2H_2 lays in the impossibility to obtain it in higher purity and its tendency to form dusty particles [7]. Hydrocarbon gases are often mixed with other gases like H_2 , Ar or He. Tomasella et al. [8] concluded that addition of Ar or He to CH_4 led to an increase of graphitization and a decrease of the stress in the films. In this paper the samples were prepared from CH_4 mixed with Ar or H_2 (the most used dilution gases in both laboratory and industry). In CH_4/H_2 mixtures hydrogen etching is a significant competitor to the deposition process [9]. For CH_4 /Ar mixture the sputtering by Ar ions does not play an important role because of its low sputtering yield [10] but the ions bring higher momentum than for H_2 . Ar ion bombardment has low efficiency in the densification of the carbon films but induces a thermal spike which enhances the mobility of carbon atoms. For intense Ar bombardment stress points are created in the film by recoil implantation which favors the creation of sp^3 sites. Therefore, these mixtures were chosen for a detailed comparison of the film structure and functional properties.

DLC films have an intrinsic problem with a good adhesion to steel substrates [11]. In case of steels, the iron and nickel (the most common elements used for carbon nanotubes production) act like catalysts for

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graphitization. Carbon diffusion in steel [12] is another process which can result in a bad adhesion of DLC layers on steel substrates. Since DLC films possess high intrinsic stress the toughness of the film-substrate interface is a critical parameter for their applications. Some of the strategies for improving it are:

- the use of a carbide layer (usually WC) but it is easily combined only with magnetron sputtering deposition of DLC [13,14],
- employing high ion beams to deeply implant carbon into the substrate creating a mixed interface [4,15] with enhanced adhesion,
- plasma nitriding for long periods and at elevated temperatures [16],
- deposition of an intermediate metallic layer [11] or silicon based interlayer [17], with a good adhesion to substrate that promotes a stress free DLC layer,
- deposition of an inhomogeneous or graded multi-layers using either PVD or CVD technique [18].

Another technique requires the incorporation of elements like N and Si to form a composite material with better adhesion on steel substrates [19–21] but sometimes with a decrease of hardness [22].

Most of the high performance DLC coatings on steel substrates prepared by PECVD require an Al, Cr, Ti or Ni adhesion layer produced by a PVD method and the composite/doped films are not always on the same level as the DLC films in terms of hardness, wear resistance and friction coefficient. Thus the motivation of the work was to prepare at ambient temperature hard DLCH coatings with a good adhesion to high speed steel using an interlayer compatible with PECVD technology based on a relative safe precursor.

2. Experimental details

2.1. Preparation of samples

DLCH films with SiO_x interlayer were prepared onto 1.3343 high-speed steel (HSS) HS6-5-2 (0.94% C, 0.45% Si, 0.40% Mn, 0.03% S, 0.03% P, 4.50% Cr, 5.20% Mo, 2.00% V, 6.70% W) in capacitively coupled discharges in parallel plate PECVD reactor. The bottom electrode, 420 mm in diameter, was coupled via blocking capacitor and matching unit to the RF generator working at 13.56 MHz. The upper electrode and reactor walls were grounded. The distance between the electrodes was 55 mm. Technical details of the reactor chamber can be found in [23]. The reactor was pumped with a turbomolecular pump to a base pressure of 2×10^{-4} Pa. The total pressure was controlled using a throttle valve.

Previous attempts to deposit DLCH directly on HSS, even nitrided, resulted in failure of the coating. The film delamination occurred immediately after the samples were removed from the reactor. The films were not stable longer periods of time (days) despite optimization of the deposition process, including the use of plasma nitrided steel samples.

The SiO_x interlayer was prepared from the mixture of HMDSO and oxygen (O₂). The HMDSO and O₂ flow rates were set to 1 respectively 11.5 sccm. The deposition pressure was set to 6.5 Pa. The DLCH top layer was deposited from 8 sccm of methane (CH₄) mixed either with 5 sccm of hydrogen (H₂) or 5 sccm of argon (Ar). The total pressure was set to 12 and 8 Pa for CH₄/Ar (sample CH83) and CH₄/H₂ (sample CH87), respectively. The deposition conditions are summarized in Table 1.

Some HSS substrates were plasma nitrided at 150 W (–80 V bias) prior to the film deposition in the same reactor using 15 sccm of nitrogen (pressure 30 Pa). The process was performed for 3 h without any external heating the substrates. The temperature of the steel at the end of the process was below 100 °C. Apart from deposition on HSS, the films were also deposited on glass and two types of <111> silicon single crystal (N-type phosphorus doped) substrates. These samples were necessary for application of several physical diagnostic methods

Table 1

Deposition parameters for selected bottom and top layers.

SiO _x films (bottom layer)							
Sample	Q (HMDSO) [sccm]	Q (O ₂) [sccm]	Power [W]	Bias [V]	Pressure [Pa]	Time [min]	
A60	1	11.5	200	−215	6.5	45	
A64	1	11.5	200	−205	6.5	45	
DLCH films (top layer)							
Sample	Q (CH ₄) [sccm]	Q (Ar) [sccm]	Q (H ₂) [sccm]	Power [W]	Bias [V]	Pressure [Pa]	Time [min]
CH83	8	5	0	75	−110	12	120
CH87	8	0	5	60	−115	8	120

(see Section 2.2) characterizing film thickness, composition, structure and properties. Silicon substrates, both with the thickness of 381 µm, were one-side polished with the resistance of 0.043–0.09 Ω·cm and double-side polished with the resistance of 5–9 Ω·cm. The latter one was necessary for infrared (IR) spectroscopy in the transmittance mode. The films on glass were important for analysis of hardness from indentation tests. Silicon substrate was also needed for ellipsometry and reflectance measurements in UV/VIS, because stainless steel was too rough for these techniques. Although different substrates were used for the deposition, it is assumed that the properties of DLCH films were the same on all of them, because PECVD is not a substrate-dependent deposition technique except possible transition layers arising from material mixing. Part of the substrates was removed after the interlayer deposition and new ones were introduced in the reactor in order to investigate the SiO_x and DLCH films also separately.

All substrates were ultrasonically cleaned for 10 min in the 1:1 mixture of cyclohexane and isopropyl alcohol and dried in dry air flow. After this step the substrates were placed on the bottom electrode (connected to the RF generator) and prior to the deposition they were plasma cleaned using a H₂ and Ar mixture. The flow rates were set to 10 sccm for H₂ and 3 sccm Ar. The power was 100 W and self-bias –150 V corresponding to 8 Pa working pressure. The discharge was operated for 10 min.

2.2. Characterization of deposited films

The films deposited on the Si substrates were characterized by the UVISEL Jobin Yvon phase modulated ellipsometer in the NIR-UV range 0.6–6.5 eV at variable angle of incidence 55°–75°, by the PerkinElmer Lambda 45 spectrophotometer in the NIR-UV range 1.24–6.5 eV with the reflectance accessory at 6° and by the Bruker Vertex 80v Fourier transform IR spectrophotometer (0.045–0.93 eV, i.e. 370–7500 cm^{–1}) equipped with the parallel beam transmittance accessory for correct measurement of absolute transmittance. Refractive index and absorption coefficient of DLCH and SiO_x films in the range from UV to IR were obtained by fitting the ellipsometric, reflectance and transmittance data simultaneously. Besides the optical constants, the ellipsometry and spectrophotometry in UV/VIS enabled the determination of the film thickness with high precision. Electronic dielectric response of the films was constructed using parameterization of joint density of states (PJDOS) and phonon absorption in IR was modeled by Gaussian peaks in the imaginary part of dielectric function [24]. Optical constants of the Si substrate were obtained by fitting the measurements on bare Si. DLCH films were additionally investigated by Raman spectroscopy using the Renishaw inVia Raman microscope. Measurement was done with 532 nm laser wavelength, 50% laser power, 2400 grooves/mm grating and averaging 5 accumulations of 15 s.

The atomic composition of the films was determined by a combination of Rutherford backscattering spectroscopy (RBS) and elastic recoil

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