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Plasma parameter investigation during plasma-enhanced chemical vapor deposition of silicon-containing diamond-like carbon films

T. Grotjahn *, Ö. Aslanbas, M. Mee, M. König, S. Meier

Fraunhofer Institute for Mechanics of Materials IWM, 79108 Freiburg, Germany

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ABSTRACT

In this work, tetramethylsilane-based plasma-enhanced chemical vapor deposition (PECVD) processes were studied, and the deposited silicon-containing diamond-like carbon (DLC) films were analyzed. The main goal was to identify correlations between plasma parameters and the film structure and properties. The electron temperature, gas temperature, and hydrogen and silicon particle densities in these plasmas were calculated using optical emission spectroscopy measurements; the electron density and elastic electron collision rate were determined using self-excited electron resonance spectroscopy. The elemental composition of the films was determined by glow discharge optical emission spectroscopy, and the hardness and Young's modulus were characterized using nanoindentation. The plasma parameters of the gas temperature and electron temperature revealed stringent correlations with the film composition and properties and thus can already monitor the resulting properties during the deposition process. Increasing the gas temperature using power variation leads to reduced incorporation of silicon and hydrogen in the diamond-like carbon films with a simultaneous increase of the film hardness. However, a gas temperature increase using a higher gas flow rate results in a decrease in the film hardness and an increase in the silicon and hydrogen contents. These results are promising concerning the use of plasma parameters for process control of CVD processes.

1. Introduction

Diamond-like carbon (DLC) films have attracted remarkable technological interest due to their unique combination of properties such as high hardness, low friction coefficient, high wear resistance, chemical inertness and high electrical resistivity [1–5]. Thus, these films are implemented in a wide range of applications, including magnetic storage disks [6], biomedical coatings [7–9], solar cells [10], automotive engineering [11] and, especially, tribological applications [2,4,12,13].

Considerable modifications of the mechanical and tribological properties as well as improved coating adhesion can be achieved by the incorporation of metallic and non-metallic elements. After the first investigations concerning metal incorporation [14,15], numerous additional studies were performed. Ultra-hard Ti or W containing a-C:H films are used for cutting tools and automotive parts. Their specific properties are reported in [16–20]. Cr relaxes the internal stresses [21,22]. F-DLC has a strongly reduced surface energy [23] and is applied for biomedical applications, where the film reduces bacterial adhesion [24], prevents cell proliferation [25] and is considered as a material for blood-contacting devices [26]. N-DLC causes improved field emission [27,28], which makes this film attractive for field-emission display panels.

Silicon amorphous hydrogenated carbon coatings are of major interest and were extensively studied in the last decades because these materials can overcome several drawbacks of pure DLC. Si incorporation reduces residual internal stress [5,29–33] and improves film adhesion [34,35]. The coating hardness can be tailored to either increase [36,37] or decrease [31,38,39]. Tribological investigations revealed reduced friction coefficients [12,31,32,40,41] connected with better wear protection [33,40,42–44] and increased abrasive wear rates [23,31,39,41,45]. The thermal stability is improved [46,47], making these films interesting for a higher range of temperature. Furthermore, Si-DLC possesses reduced surface tension [23,48], corrosion resistance [49] and is blood- [50,51] and bio-compatible [52].

Further film modification and improvement can be achieved by the simultaneous incorporation of several elements such as Si–N-DLC [53–55] and Si–O-DLC [5,23,45,55], preparation of multilayer coatings [45,56,57] or surface texturing [58].

Numerous deposition techniques are applied for synthesizing DLC coatings [2–4,12], with plasma-enhanced chemical vapor deposition (PECVD) being the most preferred technique, which is able to coat even complex substrates at low temperatures. Thus far, tailoring the film properties was achieved empirically through the variation of process parameters, such as gas flow rates, generator power or process pressure. Nevertheless, the effect of the plasma condition on the deposition process and on coating properties is not yet fully understood. Thus, this paper concerns the correlation between the plasma state and film properties.

For plasma analysis, Langmuir probes are typically used, which have the disadvantage of creating local disruptions of the plasma. Mass spectroscopy is applied for the identification of chemical species in the

* Corresponding author. Tel.: +49 761 5142 311; fax: +49 761 5142 510.
E-mail address: tobias.grotjahn@iwm.fraunhofer.de (T. Grotjahn).

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plasma. The elastic electron collision rate as well as the electron density can be determined using self-excited electron resonance spectroscopy (SEERS) [59–61]. Optical emission spectroscopy (OES) also provides information about plasma species. Furthermore, based on the first approach of *actinometry* [62] to determine the absolute particle density by comparing the spectral line intensities of the investigated species with noble gas emission lines, several approaches to calculate the densities and electron temperature have been performed [63,64]. By simulating the emission band shapes of diatomic molecules, it is possible to determine the gas temperature [65–67].

Plasma diagnostic is frequently utilized in fundamental research for the calculation of plasma parameters of inert gas plasmas [66,68–70,63]. In addition, this technique is applied in deposition plasmas to investigate the effect of the plasma parameters on the film structure and properties [71–81]. By identifying the correlation, it should be possible to modify the film properties by adjusting the plasma parameters, and the transferability of coatings should thus be improved because the generation of comparable plasma conditions, especially particle energies and fluxes, should yield comparable resulting films [78]. For physical vapor deposition (PVD), in most cases, the film properties are correlated with the particle energies and fluxes. For CVD, the situation is more complicated because the generation of plasma is performed by the substrate electrode, which is not symmetrical in most cases. Hence, the distances between the substrate surface and the counter electrode (chamber wall) are changing. This fact leads to an inhomogeneous plasma distribution in the reaction chamber.

In the present work, argon–tetramethylsilane (TMS; SiC_4H_{12}) plasmas were used for Si-containing DLC film growth by PECVD. The film properties and composition were determined using nanoindentation, Raman and glow discharge optical emission spectroscopy (GDOES). The non-invasive plasma diagnostic methods of SEERS and OES were used to analyze the discharge conditions. By comparing emission line intensities, the absolute particle densities and energies were calculated with the aid of the *corona model* [64]. The gas flow rates and the generator power were varied to study their effects on the resulting discharge condition and coating properties. Correlations between the plasma parameters and film properties were investigated, and an approach for enhanced reproducibility was introduced.

2. Experimental details

2.1. Chamber set-up and discharge conditions

The schematic diagram in Fig. 1 illustrates the geometry and dimensions of the cylindrical deposition system. The aluminum chamber wall and the cover plate represent the grounded counter electrode. To prevent arcing during DLC film deposition, the inner chamber wall was lined with a 10 mm thick insulation sheet. This insulator interrupts the electric circuit between the matchbox, plasma and chamber wall, such that a DC bias measurement is not possible. The water-cooled radio frequency (RF) steel electrode (13.56 MHz) was located at the chamber bottom on the opposite of the gas inlet. The gas flow rates were adjusted using mass flow controllers. A rotary vane pump (Pfeiffer DUO 65C) and a turbo molecular pump (Leybold Turbovac 450) were used to pump the gas through the exhaust ring to create the process pressure. The OES adapter and the Hercules probe were mounted at a height of 40 mm above the substrate electrode.

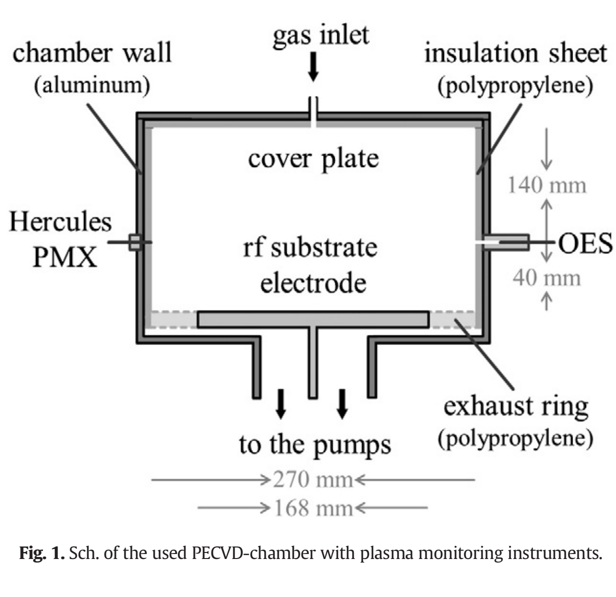

Fig. 1. Sch. of the used PECVD-chamber with plasma monitoring instruments.

The films were deposited on flat steel rings (100Cr6; outer diameter = 35 mm, inner diameter = 20 mm, height = 2 mm), previously polished in multiple steps using diamond particle suspensions with particle sizes ranging from 15 μm to 3 μm. Substrate cleaning and activation were performed using argon plasma. For the film deposition process, argon and TMS with a fixed Ar:TMS gas flow ratio of 2.5 were used for all experiments. Furthermore, molecular nitrogen and neon were added for diagnostic purposes with a flow rate of approximately 5% of the flow rate of argon and TMS. During the deposition time, Si-DLC films of approximately 5 μm thickness were deposited.

The total gas flow rate and the generator output power were varied to investigate the effect of these parameters on the plasma parameters, film microstructure and mechanical properties. The correlation between the plasma parameters and the film properties was of particular importance. Two different total gas flow rates of 10.8 sccm (7.0 sccm argon, 2.8 sccm TMS, 0.5 sccm neon, 0.5 sccm nitrogen) and 24.6 sccm (16.0 sccm argon, 6.4 sccm TMS, 1.1 sccm neon, 1.1 sccm nitrogen) were used. Both these flow rates are commonly used for depositing films for industrial applications. The generator output power was varied from 100 W to 200 W in 20 W steps, which is the range in which films are producible with the used set-up.

2.2. Characterization of film structure and properties

A portion of the substrate surface was covered during the deposition process to determine the coating thickness. The film thickness was measured using a profilometer (Hommel Tester T8000) by moving a diamond needle laterally across the step from the film to the covered area. The vertical position of the tip was recorded during these 4.8 mm line scans.

Surface roughness measurements were performed with an atomic force microscope (AFM; Veeco diDimension V). A cantilever (spring constant of 40 N/m) with a silicon tip was operated in tapping mode. The average surface roughness values were calculated from the height data using the built-in software of the AFM.

A nanoindenter (Fischerscope H100C XYp) equipped with a diamond pyramid (Vickers standard; face angle of 136°) was used to perform the indentation tests. The average surface roughness of all the deposited films fluctuated between 3 and 6 nm. Based on these results, reliable nanoindentation results are guaranteed with a penetration depth of 500 nm (approximately 10% of the film thickness). In total, 15 indentations per sample were performed with a loading and an unloading time of 30 s. By measuring the load force as a function of the penetration depth, the film hardness and Young's modulus were calculated using the Oliver and Pharr method [82].

To determine the film composition, the coatings were analyzed using a glow discharge optical emission spectrometer (LECO GDS 850A). An RF source was used for plasma excitation and for removing the electrically isolating coating from the sample surface. To calculate quantitative mass information from the measured spectral intensities, four different Si-DLC coatings with known element distribution were used to define the calibration curves. The composition of these four coatings was determined at the Fraunhofer Institute for Surface Engineering and Thin Films using secondary ion mass spectrometry (SIMS). The carbon content of these films varied from 48 to 54 at.%,