High rate PECVD of a-C:H coatings in a hollow cathode arc plasma

Burkhard Zimmermann, Fred Fietzke, Heidrun Klostermann, Jan Lehmann, Frans Munnik, Wolfhard Möller

Abstract
Amorphous carbon films deposited by plasma-based processes are of increasing importance for tribological applications, e.g. as protective coatings on components or in order to reduce their friction. However, most plasma-activated CVD and PVD techniques suffer from their poor deposition rate and low economic efficiency. At Fraunhofer FEP, a hollow cathode-based plasma source has been established as a versatile, reliable, and highly efficient tool for plasma pretreatment, plasma-enhanced PVD processes, and reactive gas activation in large volumes. As a further application field, this plasma source has been evaluated for PECVD of amorphous hydrogenated carbon films (a-C:H).

1. Introduction
At Fraunhofer FEP, a magnetically enhanced arc hollow cathode has been established as a large volume plasma source (plasma density of $10^{10} - 10^{12}$ cm$^{-3}$ in a volume of several 100 l) for applications such as plasma etching, plasma-assisted evaporation (e.g. Al) as well as reactive magnetron sputtering (e.g. CrN) [1,2]. The magnetic field allows for drastic reduction of the working gas flow rate through the hollow cathode resulting in strongly increased plasma density and range [3]. In this paper, the hollow cathode arc plasma has been evaluated for plasma-enhanced chemical vapor deposition (arcPECVD) of amorphous hydrogenated carbon (a-C:H) films with very high rates up to 1 μm/min. a-C:H coatings can exhibit polymeric, graphitic, or diamond-like properties and are typically used as tribological coatings reducing wear or friction of components, or as biocompatible coatings e.g. on implants [4].
2. Experimental setup

The hollow cathode consists of a tantalum tube (length 75 mm, inner and outer diameter 4 and 12 mm, respectively) which is surrounded by a cylindrical anode. The discharge current was 100 A throughout the presented investigations. A magnetic field coil produces a magnetic field, which is axial within the cathode tube, where it reaches typically 60 mT. Whereas the working gas argon flows through the hollow cathode tube, the PECVD precursor acetylene (C\textsubscript{2}H\textsubscript{2}) is injected by a gas shower into the hollow cathode plasma. Furthermore, additional argon can be introduced into the vacuum chamber to maintain a certain argon partial pressure when reducing the gas flow through the hollow cathode. Below the hollow cathode plasma source, a sputter magnetron PPS5 equipped with a titanium target is installed. The substrates are mounted on a water-cooled substrate holder face-to-face with the orifice of the hollow cathode tube. The plasma has been characterized by an energy-resolved mass spectrometer (plasma process monitor PPM 422, Balzers Instruments).

3. Plasma characterization

The reduction of the working gas flow rate (argon through hollow cathode tube) leads to enhanced energies of the electrons emitted by the hollow cathode and generating the plasma [3]. In the case of arc-PECVD, working gas flow rate reduction resulted in strongly increased acetylene dissociation. In the mass spectrum depicted above, signals recorded at three different values of gas flow rate through the hollow cathode tube are shown. Signals of dissociation and polymerization products as well as of hydrogenated residual gas and working gas can be identified (constant total argon flow rate of 100 sccm, acetylene flow rate of 200 sccm). The signal intensity increases with decreasing flow rate through the hollow cathode. The ion energy distributions (see poster) consist of a low energy peak and high energy tails up to 100 eV. The low energy peak dominates the energy distribution of polymerization products and is related to the bulk plasma potential. In contrast, the high energy tails are based on ions generated in the vicinity of the hollow cathode plasma source at elevated potential, and have been mainly observed for products of acetylene dissociation. It can be derived that whereas dissociation is stimulated by high energy electrons near to the hollow cathode orifice, polymerization predominantly takes place in the bulk plasma.
4. Deposition and analysis of a-C:H films

a-C:H films have been deposited on glass, stainless steel, and n-doped silicon substrates. After hollow cathode-based plasma treatment, a 100-200 nm titanium sublayer has been sputtered in order to enhance the a-C:H layer adhesion. As a third step, arcPECVD of a-C:H (argon flow rate through the hollow cathode tube: 15 sccm) with different additional argon and acetylene flow rates as well as varied substrate bias voltage has been carried out.

The deposition rate is found to depend on the acetylene gas flow rate and reaches values between 100 and 1000 nm/min. Various analysis techniques have been applied for film characterization. The highest nanoindentation hardness of 18.2 GPa has been reached in the case of substrate cooling and high substrate bias voltage (diamond-like a-C:H, substrate temperature up to 290°C). The content of hydrogen measured by elastic recoil detection analysis and Rutherford backscattering spectrometry (ERDA/RBS, with 1.7 MeV He+ ions, H content ca. 31 at.-%) as well as of the sp³ sites obtained by Raman spectroscopy has been found to be medium. Scanning electron microscopy (see poster) reveals a dense microstructure and a smooth surface of the coatings.

Without substrate bias, soft polymer-like films have been produced with high hydrogen and sp³ contents, respectively, as the hydrogen atoms are predominantly bonded by sp³ sites to carbon atoms. Without substrate cooling, high substrate temperatures of about 500°C were reached due to thermal load at high bias voltages resulting in graphitic film properties. The values of hardness, hydrogen and sp³ content are low in this case.

5. Conclusions

arcPECVD has been found to be a versatile PECVD technique with very high deposition rates and simple technological assembly. Energy-resolved mass spectrometry reveals plenty of dissociation and polymerization products in the argon acetylene plasma; the energy distribution of the ions depends on the spatial distribution of their origin. a-C:H layers with a film hardness up to 18.2 GPa have been deposited. First deposition experiments on small components treated as bulk good have been carried out successfully and will be published elsewhere. The presented results will be described in detail in a paper submitted to Surface and Coatings Technology.

References


394