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High rate deposition of amorphous hydrogenated carbon films by hollow cathode arc PECVD

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ABSTRACT

The potential of a magnetically enhanced hollow cathode arc source for high rate PECVD processes has been evaluated for amorphous hydrogenated carbon film (a-C:H) deposition from acetylene precursor gas. The argon–acetylene plasma has been characterized by energy-resolved mass spectrometry revealing a large variety of dissociation and polymerization products as well as their kinetic energy distributions, which are related to the spatial distribution of ion generation. a-C:H layers have been deposited on flat substrates with rates of up to 1 μm/min. Depending on the deposition conditions, polymeric, graphitic, and diamond-like carbon films with a maximum nanoindentation hardness of 18.2 GPa have been produced and analyzed by Raman spectroscopy, scanning electron microscopy, elastic recoil detection analysis and Rutherford backscattering spectrometry.

1. Introduction

Amorphous carbon films exhibit a wide range of properties and are of high importance in various application fields. Dependent on deposition conditions, soft polymer-like, hard diamond-like, or graphitic film properties can be obtained [1,2]. Mostly, diamond-like carbon (DLC) layers are favored for tribological coatings in order to reduce friction and wear of components [3–5]. Further applications of a-C:H coatings are biocompatible coatings on implants [6–8] or transparent polymer-like anti-reflective layers [9]. A variety of techniques is being utilized for the deposition of carbon-based films. Radio frequency-powered plasma-enhanced chemical vapor deposition (PECVD) processes are widely used due to their technological simplicity and represent the standard technology in the DLC deposition industry; however, they suffer from a low deposition rate and limited layer properties, e.g. film hardness (typically in the range of 20 GPa [9,10]). Similar limitations hold true for magnetron sputtering of carbon [11]. Higher deposition rates have been achieved by thermal arc plasmas [12] and arc evaporation techniques [5,13], which either succeeded only on a laboratory scale or exhibited a highly complex technological assembly.

A magnetically enhanced arc hollow cathode has been developed at Fraunhofer FEP, Dresden, as a high power plasma source for vacuum processes such as plasma etching and plasma-activated evaporation or sputtering [14,15]. Detailed information about the principles of the hollow cathode device has been published elsewhere [15,16], including plasma characteristics such as high plasma densities up to 10^{12} cm^{-3} in large volumes up to 1 m^3 as well as efficient reactive gas activation. Recently, a hollow cathode arc-based PECVD process (arcPECVD) has been developed for deposition with very high rates on components or large flat areas. In this paper, the highly efficient dissociation of acetylene in the hollow cathode arc plasma is demonstrated using energy-resolved mass spectrometry. The resulting films of amorphous hydrogenated carbon (a-C:H), which have been grown at rates between 100 and 1000 nm/min, are characterized by nanoindentation, elastic recoil detection analysis (ERDA), Rutherford backscattering spectrometry (RBS), scanning electron microscopy (SEM), and Raman spectroscopy.

2. Experimental setup

Fig. 1 shows a scheme of the cylindrical vacuum chamber exhibiting a length of 150 cm and a diameter of 90 cm. A vacuum pump system consisting of a rotary vane pump, a roots pump and two turbomolecular pumps allows for base pressures of 10^{-6} mbar measured by an ionization gauge. The total process pressure is measured by a Baratron gauge.

The hollow cathode tube is made from tantalum of 70 mm, 12 mm and 4 mm length, outer and inner diameter, respectively, and is surrounded by a cylindrical copper anode. The hollow cathode circuit is floating with respect to ground potential. Around the cathode–anode configuration, an electromagnetic coil with 480 windings of copper wire is placed producing magnetic fields of typically 60 mT in the center of the cathode tube.

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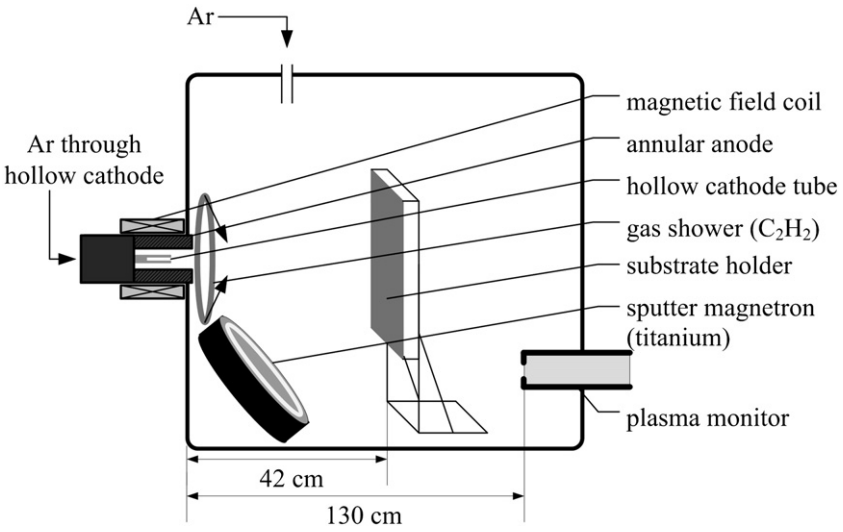

Fig. 1. Side view on the vacuum chamber. The arrows at the gas shower indicate the acetylene flow direction into the external plasma.

The hollow cathode is powered by a d. c. source with an ignition stage delivering maximum voltage peaks between cathode and anode of 800–1400 V, which are used to ignite the discharge within some seconds. In this way, any preheating of the cathode is not required. In the presented experiments, the discharge current was set to 100 A resulting in discharge voltages of 30–100 V. Argon was used as working gas of the hollow cathode discharge being injected through the cathode tube at flow rates ranging from 10 sccm to 100 sccm. Furthermore, additional argon is introduced diffusely into the vacuum chamber to keep the argon partial pressure constant during variation of the argon flow rate through the hollow cathode tube. The gas flow rates are controlled by mass flow controllers.

In front of the hollow cathode arc device, an annular gas shower injects the acetylene gas into the dense plasma flame in the vicinity of the cathode orifice (Fig. 1). The flow rates were between 200 and 1000 sccm. Below the gas shower, a sputter magnetron source PPS 5 is placed, which is equipped with a titanium target and operated in unipolar pulsing mode with a power of 2 kW. At a distance of 42 cm from the plasma source, a water-cooled substrate holder is mounted, to which a d. c. bias voltage of up to 200 V can be applied. In this paper, all bias voltages are negative with respect to ground potential, thus attracting positively charged ions from the plasma onto the substrates. The substrates are mounted on the hollow cathode's axis face to face with its orifice, and their temperature is measured by a thermocouple; due to electrical disturbance during the plasma process, only the final substrate temperature can be estimated upon completion of the process.

Prior to the deposition experiments, the plasma has been examined by an energy-resolved ion mass spectrometer in order to obtain information about the ion species and energies. The so-called plasma process monitor PPM 422 from Balzers Instruments is based on a quadrupole mass spectrometer combined with an electrostatic energy filter and has a mass range of 1–512 amu and an energy range of 0–512 eV (with respect to ground potential). For these measurements, the substrate holder and the sputter magnetron have been removed from the vacuum chamber, and the plasma monitor has been installed at a distance of 130 cm from the hollow cathode and at a distance of 20 cm from the hollow cathode axis.

Various analytical methods have been applied in order to characterize the a-C:H films. The film thickness has been determined by a profilometer Dektak 3 (Veeco Instruments, Inc.). The hardness has been measured by a nanoindenter XP (MTS Systems Corp.) [17]. The morphology has been investigated by a scanning electron microscope SU8000 (Hitachi Ltd. Corp.). Raman spectra have been obtained with the Raman microscope Renishaw 3000 (Renishaw GmbH) at a wavelength of 514.5 nm in order to draw conclusions regarding the relative content of sp^3 sites in the a-C:H films [18]; since the sp^3 content can be only indirectly detected by Raman spectrometry in the visible range via interpretation of sp^2-based Raman shifts, it has not been quantified in this paper. The film composition has been measured by ERDA (with 35 MeV Cl^{7+} and 1.7 MeV He^+ ions) and RBS (1.7 MeV He^+) [19,20] while the stoichiometry calculations were done with the program NDF [21].

3. Results and discussion

3.1. Plasma diagnostics

The hollow cathode arc discharge consists of two plasma regions: the internal and the external plasma. Within the hollow cathode tube, a dense plasma column (internal plasma) based on the flowing working gas provides ions, which are accelerated in the plasma sheath onto the cathode wall; the latter is heated to high temperatures by the ion bombardment. As a consequence, electrons are thermionically emitted by the cathode and accelerated by the cathode sheath potential into the plasma sustaining the discharge. A fraction of these electrons with energies of some tens of eV reaches the cathode orifice and drifts into the vacuum chamber, where they generate the technologically usable plasma by collisions with the gas particles (external plasma). As shown previously [15,16], the magnetic field allows for reduction of the working gas flow rate through the hollow cathode tube resulting in a strongly enhanced cathode fall voltage drop and higher discharge power. Consequently, the plasma density, dissociation rates, or charge carrier energies in the external plasma can be drastically increased due to the higher kinetic energy of the electrons emitted by the hollow cathode.

In the present experiments investigating the acetylene activation in the hollow cathode plasma, the gas flow rates both of argon and acetylene have been varied. The mass spectra in Fig. 2 show the effect of higher dissociation rates in the external plasma due a reduction of the argon flow rate injected through the cathode tube, while, as mentioned above, the total argon flow rate into the chamber was kept constant by balancing with the diffuse argon inlet. The discharge power increased from 3.6 to 8.3 kW during the reduction of the hollow cathode argon flow rate from 100 to 10 sccm. Simultaneously, the number of detected ions rises over several orders of magnitude