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# Deposition of silicon doped and pure hydrogenated amorphous carbon coatings on quartz crystal microbalance sensors for protein adsorption studies

Rupert Kargl [a,*], Markus Kahn [b], Stefan Köstler [b], Martin Reischl [a,b], Aleš Doliška [c], Karin Stana-Kleinschek [c], Wolfgang Waldhauser [b], Volker Ribitsch [a,b]

[a] Karl-Franzens-University Graz, Institute of Chemistry, Heinrichstraße 28, AT-8010 Graz, Austria
[b] Joanneum Research, MATERIALS, Institute for Surface Technologies and Photonics, Leobner Straße 94, A-8712 Niklasdorf/Steyrergasse 17, AT-8010 Graz, Austria
[c] University Maribor, Smetanova Ulica 17, SI-2000 Maribor, Slovenia

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ABSTRACT

In this study hydrogenated amorphous carbon films (a-C:H) and silicon doped hydrogenated amorphous carbon films (a-C:H:Si) with different hydrogen and silicon contents were deposited onto sensors of a quartz crystal microbalance with dissipation detection (QCM-D). The resulting films were investigated with regard to their structural and elemental compositions using Raman spectroscopy, elastic recoil detection analysis and Rutherford backscattering spectroscopy. Furthermore the surface free energy (SFE) of the films was determined using contact angle measurements. The polar part of SFE of the a-C:H:Si films was found to be adjustable by the silicon content in these films and increased by increasing amounts of silicon. Carbon films with a broad range of chemical composition showed similar structure and properties when deposited on QCM-D sensors as compared with the deposition on silicon wafers. Subsequently, the amorphous carbon coated QCM-D sensors were used to study the adsorption of human serum albumin. These QCM-D results were related to the surface properties of the films.



## 1. Introduction

Amorphous diamond-like carbon films (DLC) are promising as mechanically durable, low friction, smooth and biocompatible coatings for medical devices that are in contact with human body fluids and proteins [1]. The application of amorphous carbon films as a biomaterial requires not only sufficient adhesion to the substrate but also antithrombogenicity and haemocompatibility which relates to its protein adsorption [2]. Human serum albumin (HSA) accounts for approximately 50% of the proteins found in human plasma [3]. Due to its abundance ($\approx$35–52 g $L^{-1}$ in biological fluids such as blood) it is the first protein involved in the cascade adsorption of proteins on solid surfaces immersed in a biological medium, and it plays a critical role in the following evolution of protein adsorption processes [4]. On the other hand the knowledge of surface behaviour of amorphous carbon films is not only of interest in terms of biocompatibility but also for the use of amorphous carbon films in areas like sensor applications [5]. Several methods are known to study protein adsorption on amorphous carbon materials. Logothetidis et al. [6] used ellipsometry to determine the thickness of the adsorbed protein layer. Ma et al. [7] used photometric indirect methods to measure the adsorbed amount of HSA and fibrinogen. These authors correlated surface free energies and root-mean-square roughness (Rq) values to the biocompatibility of amorphous carbon film surfaces and found higher HSA adsorption rates at higher Rq and hydrogen contents of the studied films. Roy et al. [8] used enzyme linked immunosorbent assay to determine the protein adsorption on silicon doped amorphous carbon films. Furthermore, Randeniya et al. [9] incorporated silicon and silicon oxide into amorphous carbon films and measured their haemocompatibility. Ong et al. [10] studied the haemocompatibility of silicon incorporated DLC films and found that increasing silicon content reduces platelet adhesion. Similar findings were published by Okpalugo et al. who studied platelet adhesion on silicon incorporated DLC [11].

Protein adsorption itself was measured on a wide range of materials with different methods to obtain not just the adsorbed amount but also structural information of the proteins at interfaces [12]. The quartz crystal microbalance (QCM-D), which is based on the piezoelectric effect of quartz can be used as nanogramme sensitive balance and thus allows a direct measurement of adsorbed polymers [13] or proteins [14]. QCM-D allows to study adsorption processes on a wide range of different surfaces by coating quartz crystal sensors with the considered material. The instrument enables a dynamic real-time measurement of the protein adsorption process which can give

* Corresponding author. Tel.: +43 316 380 5413; fax: +43 316 380 9850.
*E-mail address:* rupert.kargl@uni-graz.at (R. Kargl).

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additional information about the structure of the adsorbed layer [15]. QCM has already been used to measure the deposition rate [16] and water [17] or protein adsorption [18] on DLC coatings. The aim of this work was to investigate the deposition and structural details of hydrogenated amorphous carbon films (a-C:H) and silicon doped hydrogenated amorphous carbon films (a-C:H:Si) on QCM-D crystals. We have chosen to coat standard silicon oxide coated quartz crystals with two structural classes of amorphous carbon films. These films were investigated with regard to their surface properties such as surface morphology and structural/elemental composition. We studied the films with contact angle (CA) measurements, atomic force microscopy (AFM), Raman spectroscopy, elastic recoil detection analysis (ERDA) and Rutherford backscattering spectroscopy (RBS). Subsequently, the applicability of these carbon coated QCM-D sensor surfaces for protein adsorption studies has been shown by measuring the adsorption of HSA. This study should be seen as basis and prerequisite for further investigations on the biocompatibility of DLC coatings using the QCM-D method.

## 2. Experimental details

### 2.1. Film deposition

#### 2.1.1. Substrate pretreatment

All substrates were plasma cleaned prior to deposition of the films. An ALS 340 linear ion beam source from Veeco (CO, USA) was operated at a discharge voltage of 2 kV with argon (Ar) (nominal purity: >99.999%) at a flow rate of 20 ml $min^{-1}$. The process pressure was $1 \cdot 10^{-3}$ hPa.

#### 2.1.2. Deposition of hydrogenated amorphous carbon films

For the deposition of hydrogenated amorphous carbon films (a-C:H), a magnetron cathode from AJA (MA, USA) equipped with a graphite target (nominal purity >99.95%) was used. The magnetron cathode was powered with a pulsed power supply from Advanced Energy (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 target. Acetylene ($C_2H_2$) (nominal purity>99.96%) was introduced in the coating chamber together with Ar (nominal purity>99.999%) resulting in $C_2H_2$ concentrations between 0 and 30% at a total gas flow of 30 ml $min^{-1}$. The deposition pressure was ~$5 \cdot 10^{-3}$ hPa.

#### 2.1.3. Deposition of silicon doped hydrogenated amorphous carbon films

For the deposition of silicon doped hydrogenated amorphous carbon films (a-C:H:Si) a magnetron cathode from AJA equipped with a silicon target was powered with a Dressler RF power supply set to 13.56 MHz (Dressler, Germany). The power density on the target was set to 6.7 W $cm^{-2}$. $C_2H_2$ and Ar were used as process gases. The total flow was 50 ml $min^{-1}$, whereas the $C_2H_2$ concentration in the process gas was varied from 4 to 10%. Deposition pressure was ~$2 \cdot 10^{-3}$ hPa.

All studied films were deposited by rotation of the substrate carrousel through the sputtering plasma at a target to substrate distance of 100 mm. The film thickness was kept constant at 100 nm for the samples used in the HSA adsorption studies. For all depositions the chamber was evacuated to a base pressure of $\leq 3 \cdot 10^{-5}$ hPa. In order to exclude thermal damage of the QCM-D sensors, depositions were carried out at a maximum substrate temperature of 40 °C.

### 2.2. Film characterisation

#### 2.2.1. Film thickness and surface morphology

The film thickness was determined using a stylus profilometer from Veeco (CO, USA). AFM images of the films were obtained with Veeco AFM (CO, USA) in air at ambient condition. The scan area was $5 \times 5\ \mu m^2$. Images were taken in tapping mode.

#### 2.2.2. Film elemental composition

The amount of hydrogen in a-C:H:Si films which were deposited on silicon wafers was determined by ERDA with a 2 MV tandetron accelerator using a beam of 4.2 MeV $^7Li$ ions [19]. The beam was collimated by a $1 \times 2\ mm^2$ rectangular shaped slit placed in front of the entrance of the experimental chamber which was equipped with two detectors. The RBS detector for silicon determination was placed at a scattering angle of $\theta = 150°$ and the ERDA detector at the recoil angle of $\varphi = 30°$. The incident beam angle and the exit angle as measured from the normal to the sample surface were both 75°. An 11 μm thick aluminium absorber foil was inserted in front of the ERDA detector to block the scattered $^7Li$ ions. The measured RBS and ERDA spectra were analysed using SIMNRA code [20]. In a-C:H:Si films the amounts of hydrogen were calculated from SIMNRA code fits using a polyimide film as a hydrogen reference [19]. Silicon amounts in the films were determined with SIMNRA code fits from RBS spectra of a-C:H:Si films. Carbon amounts were calculated by subtraction of the sum of silicon and hydrogen atomic percent, assuming that silicon, hydrogen and carbon in the films equal 100 at.%.

X-ray photoelectron spectroscopy (XPS) was performed by using an Omicron Multiprobe system (Germany) with a monochrome AlKα (1486.6 eV) X-ray beam. The Si 2p signal at 100.5 eV was used for Si–C determination, whereas the oxygen amount was determined from the O 1s signal at 533 eV. Oxygen on the outermost surface of a-C:H:Si films was determined with XPS on untreated samples. For the determination of oxygen in the a-C:H:Si films, sputtering with $Ar^+$ ions of 2 keV energy and subsequent XPS measurements were performed.

#### 2.2.3. Film structure

A Raman spectrometer from HORIBA, Jobin Yvon S.A.S. (France) was used to characterise the carbon hybridisation in a-C:H and a-C:H:Si films. The instrument was operated at an excitation wavelength of 532 nm. An Olympus 100× objective was used to focus the laser beam on the samples. The power of the laser on the film surfaces 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 silicon band position of 520 $cm^{-1}$ was used as drift standard. A resolution of 2 $cm^{-1}$ could be achieved with the spectrometer. All amorphous carbons show their dominating Raman features in the spectral range of 800 to 2000 $cm^{-1}$: the so-called D-band, which is present at ~1360 $cm^{-1}$ and the G-band present at ~1560 $cm^{-1}$ [21]. The G-band has its origin in the bond-stretching of all pairs of $sp^2$ atoms in rings and chains and the D-band originates from the breathing modes of distorted carbon rings. These two bands were fitted by Gaussian functions. The spectral observations were interpreted according to the following rules [21]: the intensity ratio $I_D/I_G$ is a measure of the size of the $sp^2$ phase organised in rings. The intensity ratio $I_D/I_G$ is low in case that the $sp^2$ phase is organised in chains, whereas a higher intensity ratio of $I_D/I_G$ is an indication of an increase of the $sp^2$ phase in aromatic rings. The full width at half maximum of the G-band (FWHM (G)) is a key parameter of monitoring structural disorder in amorphous carbon films. Structural disorder arises from the bond angle and bond length distortions in the amorphous carbon network. The FWHM (G) is small when $sp^2$ clusters are more defect-free and ordered. A higher FWHM (G) is thus indicative for an increase in disorder that is linked to an increase in $Csp^3 - Csp^3$ bonding content. A typical signature of a-C:H samples measured by visible Raman spectroscopy is the increasing photoluminescence background for increasing hydrogen content. This effect is caused by the saturation of non-radiative recombination centres. The ratio between the slope, m, of the fitted linear background and the intensity of the G-band, $m/I_G$, can be empirically used as a measure of the bound hydrogen in the investigated films. The hydrogen content of a-C:H films was investigated using this method. The detailed calculation of the hydrogen content in at.% with this method can be found elsewhere [22].