



Characterization of temperature-induced changes in amorphous hydrogenated carbon thin films

Christian Hopf^{a,*}, Thierry Angot^b, Etienne Aréou^b, Thomas Dürbeck^a, Wolfgang Jacob^a, Céline Martin^b, Cédric Pardanaud^b, Pascale Roubin^b, Thomas Schwarz-Selinger^a

^a Max-Planck-Institut für Plasmaphysik, EURATOM Association, Boltzmannstr. 2, 85748 Garching, Germany

^b Aix-Marseille Université, CNRS, PIIM UMR 7345, 13397 Marseille cedex 20, France

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ABSTRACT

Hard hydrogenated amorphous carbon thin films were heated in vacuum to different temperatures and held at these for at least 30 min. Afterwards, the cooled-down samples were analyzed by various techniques. Strict and reproducible correlations were found between all the determined parameters and the annealing temperature. Single-wavelength ellipsometry shows that the real part of the refractive index of the films at 633 nm wavelength decreases with temperature while the extinction coefficient increases. It also shows swelling of the films with a thickness increase of about 50% for films heated to ≈ 1000 K. The associated decrease of mass density is proportional to the decrease in refractive index. Ion beam analysis shows that hydrogen is released from the films during heating with only about 5% of the initial H remaining after annealing at 1300 K while no significant loss of carbon can be detected. The losses of hydrogen during heating are monitored by temperature programmed desorption and they are in good agreement with the ion-beam-analysis results. Raman spectroscopy delivers evidence of aromatization of the films under heat treatment. Indication of first structural changes is found already at 600 K while the quickest changes of the refractive index, thickness, and hydrogen content with temperature occur around 850 K.

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1. Introduction

Carbon-based thin films are used for a wide range of applications such as wear-resistant and anti-corrosive protective coatings [1,2]. Hydrogenated amorphous carbon thin films (hard a-C:H) are a subclass of such coatings [3]. The properties of a-C:H depend critically on the hydrogen content. Films with a high hydrogen content of typically up to $H/(H + C) \sim 0.5$ are soft and polymer-like while a-C:H with a low hydrogen content of around $H/(H + C) \sim 0.3$ are hard, wear resistant, and have a low coefficient of friction [4]. The applications of hard a-C:H are, however, restricted by its limited thermal stability. Above about 700 K the films lose hydrogen, become more graphitic, hardness decreases and wear increases [5,6].

On the other hand, heat treatment of a-C:H (and other amorphous carbon) films after deposition has also beneficial effects. For instance, annealing was found to reduce compressive stress in the films [5,7,8] limiting the maximum thickness above which the films delaminate from the substrate. Rapid thermal annealing of a-C:H coatings on silica optical fibers was shown to improve their protective qualities in harsh environments [9]. And heating by short laser pulses is a possibility for locally changing the electronic properties of a-C:H [10] and a-C [11] films.

In magnetic confinement nuclear fusion carbon was for a long time the preferred choice for the first-wall material due to its favorable

radiative properties [12]. A disadvantage that leads to its replacement in the designs of new fusion devices is, however, the high erosion yield that would seriously limit the lifetime of plasma-facing components. Furthermore, the eroded carbon is redeposited along with hydrogen from the plasma in locations with no or little erosion, producing layers that can have a high hydrogen content like soft a-C:H [13,14] or can structurally resemble hard a-C:H [15,16] and can contain substantial amounts of other elements [17]. In an all-carbon machine operating with a D/T mixture this redeposition can be a dominant mechanism of the retention of radioactive tritium [18]. However, the amount of hydrogen isotopes stored in these layers strongly depends on the temperature they experience during plasma operation. At higher temperatures the layers are modified and lose hydrogen, leading to a decreased hydrogen isotope retention [13,19].

Several studies in the literature have investigated the thermal stability and the temperature-induced modifications of various types of a-C:H films. With temperature programmed desorption (TPD) (also referred to as thermal desorption spectroscopy (TDS) or thermal effusion spectroscopy (TES)) it was found that the temperature at which thermal decomposition starts as well as the released species strongly depend on the initial composition of the film [20–24]. The onset of decomposition of hard a-C:H with $H/(H + C) \sim 0.3$ is at about 700 K while for soft a-C:H with a hydrogen content around 0.5 it starts already at 100 K lower temperature. Furthermore, while the hard films release hydrogen, minor amounts of methane and negligible amounts of higher hydrocarbons, the soft films release significant amounts of larger hydrocarbon

* Corresponding author. Tel./fax: +49 89 32 99 26 17.

E-mail address: christian.hopf@ipp.mpg.de (C. Hopf).

molecules up to $C_4H(D)_x$ or $C_5H(D)_y$ ($x \leq 10, y \leq 12$) [23–25]. Using a-C:H/a-C:D bi-layers it was demonstrated that the released hydrogen and methane molecules are formed in the bulk and diffuse to the surface as molecules [20].

Besides these TPD studies the structural changes of a-C:H under heat treatment have been probed by various techniques. The basic observations can be summarized as follows: The optical gap E_{04} was found to decrease for both hard and soft a-C:H [26–28]. Fourier transform infrared spectroscopy (FTIR) indicated a transformation of sp^3 carbon into sp^2 carbon and a loss of hydrogen for both hard and soft films [5,27,28], in accord with an aromatization (sometimes also referred to as ‘graphitization’) observed in Raman spectroscopy by an increase of the D peak intensity and a shift of the G peak position to higher wave numbers [6]. The loss of hydrogen was also confirmed by ion beam analysis [6,29]. The electrical resistivity was shown to decrease [30]. Other parameters studied were the film thickness that was found to either decrease [26] or increase [23,28] and the refractive index at fixed wavelength [5,28] that was reported to increase due to annealing in contradiction to our data presented in this paper.

The aim of the present study is to investigate the temperature-induced changes in a wide temperature range of up to 1300 K with a comprehensive set of analysis techniques using as far as possible initially identical a-C:H and a-C:D films. The optical properties are probed with single-wavelength ellipsometry at 633 nm. Changes of the thickness due to heating are quantified by ellipsometry and/or profilometry. Structural changes of the carbon network are monitored using Raman spectroscopy. The remaining hydrogen content is determined with ion beam analysis and the released hydrogen is monitored using temperature-programmed desorption. The results are discussed and compared to the data reported in the literature.

2. Experimental

2.1. Sample preparation and heating (sets A, B, C and D)

Several sets of hard a-C:H films were deposited on silicon wafers, heated *in vacuo* with a base pressure below 10^{-4} Pa in different devices, and analyzed by various techniques after cooling down.

One set, denoted as set A, was primarily intended to measure temperature-dependent erosion rates (not reported in this paper) of the films when exposed to a flux of atomic hydrogen. The films of this set were deposited onto a silicon wafer on the driven electrode of a capacitively coupled 13.56 MHz rf discharge in a device named KesCaBo, described previously in [31]. Methane with a gas flow of 7.2 sccm was used as working gas and the discharge pressure was 2 Pa. The rf power was set such that a self bias of -300 V was achieved. Under these conditions the resulting films were hard a-C:H with a refractive index of $n - i\kappa = 2.15 - i0.10$ at 633 nm. It is known from earlier [32,33] as well as recent quantitative analysis that films deposited with the quoted deposition parameters have a hydrogen concentration of $H/(H + C) \approx 0.3$ and a carbon density of $\approx 8.5 \times 10^{22} \text{ cm}^{-3}$. Furthermore, it is known that their refractive index is well correlated with the films' properties and can hence serve as a simple characteristic number [32]. The thickness of the films after deposition was approximately 200 nm. The coated wafer was then cut into pieces of approximately $1 \times 1 \text{ cm}^2$. For the erosion experiments these small a-C:H coated Si samples were fixed on an electrically heated substrate holder by thin metal strips which shielded parts of the film from exposure to hydrogen, thus preventing erosion in these places. The films were heated to the desired temperature of up to ≈ 1000 K and held at that temperature for at least 30 min to be sure that the sample was in thermal equilibrium. The samples were then exposed to atomic hydrogen at that temperature for as long as was required to achieve substantial, but not complete, erosion of the films during H exposure. Afterwards, the films were cooled down and later scanned across the erosion crater with a

single-wavelength *ex-situ* ellipsometer working at 633 nm to derive the optical properties and the film thickness profile.

Another set of samples, set B, was specifically intended for a study of temperature-induced changes of a-C:H films. In this case, the films were directly deposited to a thickness of approximately 200 nm in the device PlaQ (for details of the setup see [34]) that also provides a heatable substrate holder and an *in situ* ellipsometer. Thus, the experimental steps deposition, heat treatment, and the subsequent erosion – necessary to determine the optical properties and thickness after the heat treatment by ellipsometry – could all be performed one after the other without breaking the vacuum and without moving the sample. The films were deposited in a methane ECR plasma at 0.5 Pa with an additional rf bias of -300 V applied to the substrate. The properties of the films thus obtained are very similar to those of set A as indicated by their similar refractive index of $n - i\kappa = 2.09 - i0.07$, measured during the deposition run. The films were then heated to and held at the desired temperature for about 1 h. During heating the sample was continuously monitored with ellipsometry. An initial quick shift of the ellipsometric angles was observed (see Fig. 1) that slowed down and almost came to a halt before the end of the heating period at all temperatures. At the end of the heating phase the heater was switched off with no active cooling. For the highest heating temperature the sample cooled to below 600 K in less than 10 min. After cooling down to $T < 330$ K the samples were exposed to an oxygen plasma which erodes the films from the top without modification of their optical properties [35]. Ellipsometry data obtained during this erosion run provide the refractive index and the thickness of the films after heating. The maximum heating temperature of set B was ≈ 870 K.

A further set of samples, set C, was deposited in the same device and at identical parameters as set A. The thickness of the films was also similar with ≈ 220 nm. The whole coated wafer was again cut into several smaller pieces. Groups of these pieces at a time were then transferred in air to a UHV temperature programmed desorption setup (TESS [25]) where they were heated *in vacuo* inside a glass tube in a tube furnace. At the start of the heat treatment the preheated furnace was moved from its remote parking position to the heating position, where the samples in the quartz tube are in the middle of the furnace's tube. Thermal equilibrium is reached in about 5 min. The sample was then held at the desired target temperature for another 30 min and subsequently cooled down by moving the furnace back to its parking position at a sufficient distance to the

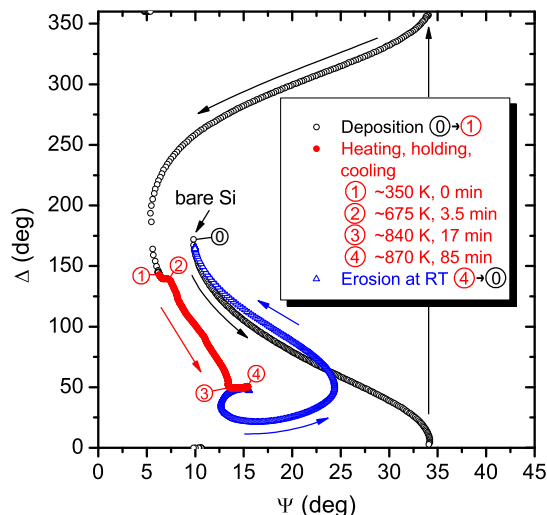


Fig. 1. Ellipsometry raw data, expressed by the ellipsometric angles Ψ and Δ , of a complete deposition–heating–erosion cycle. The film was deposited on the substrate at room temperature (black open circles), then heated to, held at, and cooled down from 870 K (red solid circles), and finally eroded in an oxygen plasma at room temperature (blue open triangles).

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