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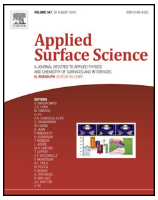

Surface morphology and grain analysis of successively industrially grown amorphous hydrogenated carbon films (a-C:H) on silicon

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ABSTRACT

Silicon (1 0 0) has been gradually covered by amorphous hydrogenated carbon (a-C:H) films via an industrial process. Two types of these diamond-like carbon (DLC) coatings, one more flexible (f-DLC) and one more robust (r-DLC), have been investigated. Both types have been grown by a radio frequency plasma-enhanced chemical vapor deposition (RF-PECVD) technique with acetylene plasma. Surface morphologies have been studied in detail by atomic force microscopy (AFM) and Raman spectroscopy has been used to investigate the DLC structure. Both types appeared to have very similar morphology and sp^2 carbon arrangement. The average height and area for single grains have been analyzed for all depositions. A random distribution of grain heights was found for both types. The individual grain structures between the f- and r-type revealed differences: the shape for the f-DLC grains is steeper than for the r-DLC grains. By correlating the average grain heights to the average grain areas for all depositions a limited region is identified, suggesting a certain regularity during the DLC deposition mechanisms that confines both values. A growth of the sp^2 carbon entities for high r-DLC depositions is revealed and connected to a structural rearrangement of carbon atom hybridizations and hydrogen content in the DLC structure.

1. Introduction

During the last few decades, the interest in amorphous hydrogenated carbon (a-C:H) films has constantly increased [1,2]. Particularly hydrogenated diamond-like carbon (DLC) films are of great interest because of their wide range of applications such as: biocompatible coatings, protecting materials for probes, tubes and lenses, coatings of magnetic hard disk drives, etc. [1,2]. DLC is a metastable form of amorphous carbon forming a great variety of crystalline and disordered structures due to the ability of C-atoms to exist in three hybridization states: sp^1, sp^2 and sp^3, permitting the incorporation of hydrogen atoms in this structure [1–3]. The deposition of DLC films for laboratory purpose is usually realized with the techniques of chemical vapor deposition (CVD) from different feed gases such as CH_4, C_2H_2, C_2H_4 and C_2H_6 [1,3–5]. In such deposition mechanisms ions and radicals play a critical role [6,7]. One important growth mechanism of DLC films is the subplantation model that involves the subplantation of incident plasma species [8–10]. Ions and radicals of sufficient energy penetrate the surface of the growing film, enter a subsurface interstitial site and increase the local density. The local bonding will then reform around the interstitial position and any excess of energy rapidly dissipates in a thermal spike during which the excess density relaxes by thermally activated diffusion [11–13]. Von Keudell et al. proved that DLC films have three characteristic depths [7]. The first is the surface, and its properties are dominated by reactions of hydrocarbon and hydrogen species. The second is in a region 2 nm deep and it is controlled by reactions of atomic hydrogen. The third is in a region deeper than 2 nm and it depends upon the reactions of hydrogen ions that, different from the other species, can penetrate deepest into the film due to their small size [1,7]. Robertson proposed a cluster model and its modification predicting that sp^2 sites are arranged in plane π-bonded clusters embedded in a sp^3-bonded matrix, where the sp^2 clusters are limited to single sixfold rings and short chains of sp^2 sites [14,15].

The properties of the carbon films are strongly affected by the precursor gas used for the deposition and depend on the ratio between sp^3 and sp^2 hybridization of the carbon atoms and the amount of present hydrogen [1]. Films with a constant hydrogen content and a high value of sp^3/sp^2 ratio have properties similar

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to those of diamond, such as superior hardness, chemical inertness and high electrical resistance [1]. Films with a lower value of sp^3/sp^2 ratio instead have properties closer to graphite, such as softness and good electrical conductivity [1]. The hydrogen content mainly affects the film density and hardness, the surface roughness [16–20] and the intrinsic stress of the film [21–25]. The reduction of the hydrogen content leads to a decrease of the density and hardness of the film, producing high structural disorder [17,18]. With increasing hydrogen concentration instead the density of the grains on the surface becomes higher. This smoothens the surface morphology and decreases the roughness on the film surface [20]. Films with the highest hydrogen content are furthermore less stressed; the intrinsic stress decreases with the increasing of the sp^3 ratio in C—H bonds, suggesting that the network in the film is segmented by the termination with hydrogen atoms, so that the intrinsic stress can be released [21,22].

Despite the efforts made to understand how the film's properties depend on the experimental deposition settings [1], at the authors' knowledge there are not many studies that deeply investigate the surface morphology and the growing mechanisms involved with the film growth. Markwitz et al. observed an atomic interlocking between a-C:H coating and silicon. These coatings were fabricated using butane as a precursor carbon source with a direct ion beam deposition technique under high vacuum at low temperature [26]. Maheswaran et al. have shown that the DLC films grow on silicon (1 0 0) substrates following an island growth model (Volmer-Weber growth mode) [27]. In their experiment the DLC films were synthesized using RF-PECVD and methane as a precursor gas. They demonstrated that the DLC films nucleate in the surface defects as islands and the growth of the islands occurs not only as adatoms but also by coalescence among the neighboring islands.

In the present study two different types of amorphous hydrogenated carbon (a-C:H) films on silicon (1 0 0) are investigated. One type of the present a-C:H forms a more flexible coating (f-DLC) while the other type a more robust one (r-DLC). The DLC coatings were produced by RF-PECVD technique using acetylene gas as a carbon source [28]. Since both commercially available coatings show different features on the large scale, the surface morphologies of the DLC films were studied by atomic force microscopy (AFM) and the DLC grains found on the surfaces were analyzed in detail for both DLC types. Raman spectroscopy was used to characterize the chemical structure of the present DLC.

2. Experimental details

2.1. Sample preparation and coating

Silicon (1 0 0) wafers of 100 mm diameter were obtained in the best commercially available quality (Silicon Materials, Kaufering, Germany). The samples were separated by laser procedure into samples of 1 cm^2 squares (WGD WAFER & GLASSUBSTRATE DICING GmbH & Co. Kg, Linsengericht, Germany) and used as delivered. Silicon samples were mounted on a homemade aluminum sample holder with quarters of a carbon pad (Plano G3347, Plano GmbH, Wetzlar, Germany). The two DLC types were deposited on the samples with various thicknesses: six for the f-type and eight for the r-type. The coating process was done using radio frequency plasma-enhanced chemical vapor deposition (RF-PECVD). A detailed description of the RF-driven (13.6 MHz) commercially available plasma source (model COPRA DN 400, CCR GmbH, Troisdorf, Germany) is given in references [29,30] and the process of coating is described in detail in references [28,31–33]. The entire coating process consists of two steps. First the samples are cleaned by exposing them to oxygen plasma at about 1 Pa and 200 W of RF irradiation to obtain a suitable surface for coating. This cleaning process is not the same for the two types of DLC because of the differently oriented sample holder [28]. In the second step the samples are exposed to acetylene plasma at 0.65 Pa and 107 W at room temperature. Throughout the coating process all samples are situated at a distance of 275 mm in front of the plasma source in a high vacuum chamber. In the direct deposition method for r-type more ionic species impinge the substrate surface. This method results in a higher degree of cross-linked sp^3 carbon centers in the coating because of more subplantation processes [30]. In the indirect deposition for f-type mainly radical species are present and diffuse on the substrate surface because the sample's face is presented opposite to the plasma without being in line of sight with the plasma source [31]. Different thicknesses were produced by varying the length of the deposition time, dependent on a deposition rate of 2 nm/min for the f-type and of 10 nm/min for the r-type. Some of the silicon wafers were half covered by aluminum foil and the thickness of the deposited carbon film was checked with a profilometer (Veeco Instruments Inc., Dektak3 surface profile measurement system, Plainview, NY, USA).

2.2. Recording of AFM images

The specific sample surface morphologies of raw and coated silicon material with various layer thicknesses were analyzed by atomic force microscopy (AFM, Omicron NanoTechnology GmbH, Taunusstein, Germany). The method used in AFM measurements was contact mode with standard silicon nitride PNP-TR cantilevers (NanoAndMore GmbH, Wetzlar, Germany) in ambient air and room temperature. The detected area was always set to 5 μm × 5 μm. The tips were regularly calibrated by a cellulose acetate replica (Pelco, calibration specimen for atomic force microscopy, 607-AFM) of a 2,160 lines/mm waffle pattern diffraction grating to avoid tip sample convolution and tip blend. All the measurements shown here were done at least at three different positions, spread over the entire sample. By repetition of the AFM images, it was ensured that the images were taken properly, as done in all former studies [28,34]. In the present study, all the images show the normal force signals (F_N) in a 2.5 μm × 2.5 μm representative area.

2.3. Image analysis

All images were analyzed using commercial Scanning Probe Image Processor software (SPIP version 4.6.1, Image Metrology A/S, Hørsholm, Denmark). First, the images were plane corrected using an LMS fit of degree 3. A median filter was used to reduce the worst horizontal noise. To reduce the low frequency noise, a convolution smooth mean filter and a convolution smooth low pass filter were used. Finally, the long waves were removed and values outside the color boundaries filtered out. All the parameters of the filters were chosen in order to obtain the best picture quality and the most accurate representation of the surface for the analysis. The grains on the surface were then analyzed using the threshold method and the height and area of the grains were evaluated. To obtain the average height and area of the grains, the threshold level was set at the top layer of the DLC deposition in order to consider the height and area of the grains for their entire shape. To determine the number of grains with respect to the height, the grains were individually examined starting with the highest threshold level suitable for their detection. The number of grains at this threshold was recorded, and then the threshold was decreased by 1 nm steps. At each individual step the number of grains was recorded until the bottom level at 1 nm. The complete analysis was made for the entire 5 μm × 5 μm square image and for all recorded images. Typical examples from single images are given in Fig. 7 below. The grains were analyzed in detail for all the recorded images at least with two profile lines,