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Near-surface mechanical properties and surface morphology of hydrogenated amorphous carbon thin films

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Abstract

The study of the near-surface nanomechanical properties of thin films is a very ambitious task and can be accomplished by advanced surface sensitive techniques. Depth-sensing nanoindentation (NI) is a widely used technique for the nanomechanical characterization of thin films, but it has the inherent limitation of the substrate influence to the measured hardness (H) and elastic modulus (E). Thus, sophisticated modeling is required to determine H and E at the surface. On the other hand, surface acoustic methods seem more promising for such a study. Among them, atomic force acoustic microscopy (AFAM) is a scanning probe microscopy technique based on the resonant vibration of the AFM cantilever. In this work, we study the near-surface nanomechanical properties and the surface morphology of soft hydrogenated amorphous carbon (a-C:H) thin films. We use NI, employing the continuous stiffness measurements technique, and AFAM for the imaging of the variations of the surface mechanical properties and the accurate determination of the elastic modulus. We analyze NI data using empirical models in order to estimate near-surface E and H and the results are compared to those obtained by AFAM. From depth-sensing NI, it was found that the a-C:H thin films present "pop-in" events, which are eliminated by changing the deposition conditions e.g. increasing the negative bias voltage to the substrate (V_b). Near-surface H and E of the a-C:H thin films measured with nanoindentation were found to initially increase with increasing $|V_b|$. Further increase of $|V_b|$ has no effect on the E and H values. Finally, by comparing the results from AFAM and NI, we conclude that the obtained values for E by NI are lower for all the a-C:H thin films.

Keywords: Hydrogenated amorphous carbon; Surface morphology; Nanoindentation; Atomic force acoustic microscopy

1. Introduction

In recent years, several techniques have been developed to study the nanomechanical properties of thin films. Among them, nanoindentation (NI) is a widely used technique for the measurement of the elastic modulus (E) and the hardness (H), either on a single loading–unloading cycle (CI) [1] or during dynamic loading (continuous stiffness measurements, CSM) [2]. In the case of thin and ultra thin films, a limitation to the measurement of the nanomechanical properties with this technique arises from the small thickness of the films and as a consequence the measured values of H and E are affected by the mechanical response of the substrate. The main advantage of CSM technique, compared to CI, is that it provides the H and E values continuously versus the penetration (contact) depth of the indenter. Thus, the appropriate models, which take into account the substrate effect, can be applied, in order to estimate the real hardness (H_f) and elastic modulus (E_f) values of the surface of the thin films.

In addition, surface acoustic methods seem more promising for the measurement of the nanomechanical properties of the surface. Several scanning techniques were used for the detection of the surface mechanical response to the acoustic waves. Among them near-field techniques, like atomic force microscopy (AFM), provide better lateral resolution compared to optical scanning techniques, which are restricted by Abbe's principle. In this study we employ atomic force acoustic microscopy (AFAM) [3], a non-destructive technique for the imaging of the variations of the nanomechanical properties of the surface and the quantitative determination of the near-surface elastic modulus. AFAM is based on the vibration at the resonant frequency of an AFM cantilever, which is in continuous contact with the surface of the film, when an external ultrasonic signal is applied to the sample.

Hydrogenated amorphous carbon (a-C:H) thin films are candidate materials for many cutting edge technological applications, such as protective coatings for optical systems, barrier

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coatings on flexible polymeric substrates for packaging and heamocompatible thin films for biomedical applications [4–7]. Thus the surface properties, like the morphology and the mechanical properties, are very important for the performance of the final system. In this work, we study the surface morphology and the near-surface nanomechanical properties of a-C:H thin films. The near-surface E_f and H_f values of the samples were estimated, after extracting the substrate effect, from nanoindentation CSM measurements. The surface topography as well as the imaging of the variation of the surface nanomechanical properties was studied using atomic force microscopy and AFAM, respectively. Finally, the E_f values from nanoindentation were compared to those obtained from AFAM measurements.

2. Experimental

Hydrogenated amorphous carbon thin films were deposited on Si (001) substrates, by rf reactive magnetron sputtering of a 99.999% pure graphite target at high vacuum ($P<10^{-5}$ Pa) conditions. First, the substrates were chemically cleaned and then dry-etched with very low energy Ar^+ ion bombardment before the deposition process. Argon, at 2 Pa partial pressure, and hydrogen, 10% of the total pressure, were used as the carrier and the reactive gas, respectively. The deposition of the a-C:H thin films was realized either without (floating) or with negative bias (V_b) voltage, ranging from −20 V to −100 V, applied to the substrate.

The nanomechanical properties of the thin films were measured using nanoindentation and AFAM. A Nano Indenter XP commercial apparatus was used for nanoindentation experiments. The nanoindenter is placed in an acoustically isolated enclosure, over an antivibration table and is equipped with the appropriate electronics for the CSM measurements [2]. Several indents (8–10), with 30 μm spacing and loading rate 0.05 mN/s, were made at every sample for statistical purposes. Thus, the presented H and E are the mean values. A Berkovich type diamond tip, with 50-nm nominal radius, was used as the indenter.

The near-surface elastic modulus of the a-C:H thin films was also investigated by AFAM, which is a technique based on the scanning probe microscopy (SPM) principles. The main difference with the classical SPM is that the AFAM configuration includes a piezoelectric transducer, with 2.5 MHz central frequency, which is placed below and in contact with the sample. The transducer emits longitudinal acoustic waves which cause out-of-plane vibrations of the sample surface. By setting the SPM probe (cantilever) in contact with the sample surface, we can acquire the so-called acoustic images, which represent the vibration amplitude of the cantilever. The latter vibrates in contact with the sample surface at a fixed frequency, close to the resonance one. The acoustic images of every sample were acquired simultaneously with the topographic ones, in order to study in terms of surface morphology and nanomechanical properties of the exact same surface areas of the samples. We also acquire the cantilever vibration spectra to estimate E_f [8]. Measurements were performed with a SOLVER P47H Scanning Probe Microscope (NT-MDT, NTI Instruments) in ambient environment, at room temperature. Standard silicon cantilevers with nominal spring constant $k_c=1$ N/m, 10 nm nominal radius and typical resonance frequency 20 kHz was used for AFM and AFAM measurements.

3. Results and discussion

The thickness of the studied a-C:H thin films was measured using spectroscopic ellipsometry (SE) in the 1.5–6.5 eV energy region [9]. The thickness of all the biased a-C:H thin films is ~150 nm and the unbiased one is ~200 nm. The surface morphology of the a-C:H thin films was studied by AFM in contact mode. In Fig. 1, the RMS roughness of the surface is shown. The presented results were originated from a 5×5 μm^2 scanning area. The RMS roughness (Ra) of the samples was found to decrease with increasing $|V_b|$ from 2.7 to less than 0.3 nm. The high Ra values of the unbiased a-C:H thin films are attributed to the island growth mode. Similar results have been reported for the unbiased non-hydrogenated a-C thin film [10]. The observed reduction with increasing $|V_b|$ is attributed to the re-sputtering process of the species at the surface occurred during the growth of the thin film [10].

Concerning the microstructural characteristics of a-C:H thin films, spectroscopic ellipsometry analysis revealed that the volume fraction of sp^3-hybridized carbon bonds increased from 40% to 45% with increasing $|V_b|$ [11]. In addition, X-ray Reflectivity (XRR) measurements revealed that the density of the samples increases from 1.1 g/cm^3 ($V_b>0$) to 1.5 g/cm^3 ($V_b=-100$) [12]. Thus, the a-C:H thin films were expected to be soft ($H<8$ GPa) [4]. The presented nanoindentation results below agree with the above assumption.

In Fig. 2(a,b), typical loading–unloading curves from CSM nanoindentation experiments are shown. In the case of the thin films grown without and with $V_b=-20$ V applied to the substrate, a pop-in behavior was observed [13]. The pop-in is comprised by a step, which appears in the loading curve as the displacement of the indenter increases, while the load remains constant. The pop-in event indicates that fracture was induced to these samples by the diamond nanoindenter and it is

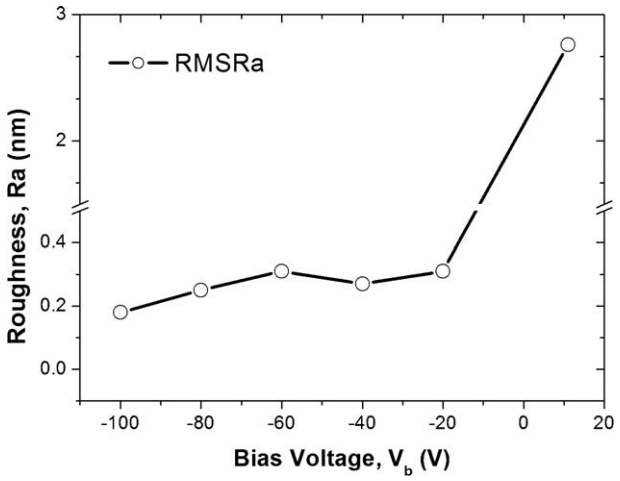

Fig. 1. Evolution of RMS roughness, measured using AFM, vs. bias voltage V_b.