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Vacuum 81 (2007) 1412–1415
VACUUM
SURFACE ENGINEERING, SURFACE INSTRUMENTATION & VACUUM TECHNOLOGY
www.elsevier.com/locate/vacuum

DC substrate bias effects on the physical properties of hydrogenated amorphous carbon films grown by plasma-assisted chemical vapour deposition

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Abstract

Hydrogenated amorphous carbon (a-C:H) films have been grown from argon/methane gas mixtures by electron cyclotron resonance chemical vapour deposition (ECR-CVD) on silicon substrates. The effects of the application of a DC substrate bias on the structural, morphological and mechanical properties of the films have been explored by multiple analysis techniques such as infrared and micro-Raman spectroscopy, atomic force microscopy, nanoindentation and pin-on-disk wear testing. In general, within the range of applied substrate bias (i.e. from −300 up to +100 V) we have observed a strong correlation between all measured properties of the a-C:H films and the ion energy. This work shows that the properties can differ greatly and indicates a threshold energy in the order of 90 eV. For the production of hard, low-friction coatings energies above this value are required.

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Keywords: Amorphous carbon; Bias; PACVD; Smoothness; Hydrogen; Tribology

1. Introduction

Hard amorphous carbon (a-C) films exhibit a variety of useful properties such as a high wear resistance, low-friction coefficient, chemical inertness, surface smoothness and biocompatibility. In particular, the surface smoothness becomes a crucial property for developing protective coatings for magnetic storage devices and low-friction coatings. Therefore, over the last years special attention has been paid to the production of ultrasmooth a-C films. In addition, in magnetic storage technology, a slightly hydrogen-rich surface is desired because of the lubricant work [1]. Since the optimum hydrogen content of the carbon layers does not necessarily coincide with their maximum hardness [2], the development of ultrasmooth *and* hard hydrogenated amorphous carbon (a-C:H) films becomes essential. In earlier works on ion-assisted deposition of a-C:H films, it has been demonstrated that the ion energy plays a crucial role in the formation of a-C:H films with desirable properties [3–5]. The addition of argon to a methane ECR plasma results in increased hydrocarbon ion concentrations and dangling bond densities at the depositing surface [6]. Therefore, in this work a-C:H films have been deposited with a fixed methane-to-argon gas flux at varying external bias and their corresponding film properties have been studied.

2. Experimental

a-C:H films have been grown by an ECR-CVD reactor operating with a 2.45 GHz microwave plasma source at 205–210 W input power. Gas mixtures of methane/argon (15/35 sccm) are applied keeping the operating pressure at 1.1×10^{-2} Torr. A DC bias varying from −300 to +100 V is applied to the p-type (1 0 0) silicon substrates ($1 \times 1\,\text{cm}^2$) while no intentional heating is employed. The substrate temperatures were measured by a thermocouple attached to the substrate holder. A maximum substrate temperature as low as 120 °C was found for 1-h deposition at the

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0042-207X/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.vacuum.2007.04.021

maximum applied substrate bias (i.e. −300 V), so any substrate temperature effect on the a-C:H film properties has been excluded. It should be noted that the use of a DC bias might result in an effective bias which is lower than the applied DC bias in the case of growing insulating a-C:H films. However, independent IR spectroscopy analysis does not show any changes in structure for layers up to 2–3 μm. Due to the much thinner films considered here, shielding of the applied DC voltage can be discarded, as was also confirmed in previous work [7].

Infrared (IR) and micro-Raman spectra were taken with a 270-50 Hitachi IR spectrophotometer and a Renishaw 2000 system with 514.5 nm Ar laser light, respectively. Atomic force microscopy (AFM) characterization [5] was performed with Nanoscope IIIa (Veeco) equipment operating in tapping mode with silicon cantilevers. Nanoindentation tests were performed with a Nanotest (Micro-Materials, Ltd.) at loads up to 3 mN with a Berkovich diamond indenter at atmospheric conditions. Pin-on-disk wear tests were performed on MicroTest equipment using 3 mm sized WC-Co balls applying loads of 3 N and linear velocities of 0.01 m/s at atmospheric conditions.

3. Results and discussion

Under the applied deposition conditions, the obtained a-C:H films are homogeneous in film thickness and composition over the entire silicon substrate. In Fig. 1, the a-C:H film thickness as a function of the applied DC bias is displayed for a fixed deposition time of 1 h. In the range of bias values going from +100 V towards −150 V, the thickness increases, while for bias values more negative than −200 V, a slightly lower thickness is observed. A maximum thickness of about 1130 nm is obtained for substrate biases of −200 and −150 V. The difference in film thickness as a function of the applied bias can be related to the operating film growth and (sub-)surface processes initiated by the incoming hydrocarbon and argon ions. At highly positive substrate biases, only radicals, neutrals and electrons will reach the growing film surface. Hence, a-C:H film growth is determined by the physisorption, chemisorption and incorporation of the hydrocarbon growth precursors only. For more negative substrate bias, the impinging positive ions will increase the sticking of the radical growth precursors through the creation of dangling bonds. This will ultimately lead to enhanced film growth. However, at ion energies larger than the threshold energy required for physical sputtering [8,9], the sputtering of bounded carbon atoms will negatively influence the overall growth rate and results in an optimum growth rate at about −200 V.

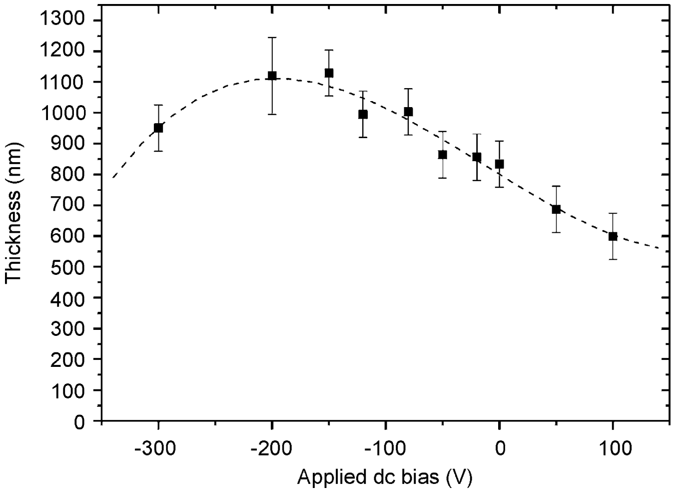

Fig. 1. a-C:H film thickness after 1 h of deposition as a function of the applied DC bias. A third order polynomial fit is added as a guide to the eye.

AFM scan profiles (3 μm) of a-C:H films deposited for 1 h under different bias conditions are displayed in Fig. 2. For all films grown in the range of +100 to −80 V applied bias, the surface is relatively rough (root mean square roughness, σ, in the 4.5–6 nm range) and is cauliflower-like. In contrast, for large negative biases the film surface becomes very smooth (σ~0.1–0.2 nm). Thus, a levelling of the surface morphology has taken place due to the relative high energy of the incoming ions [5,10]. The transition from cauliflower-like to smooth surfaces is quite sharp and is observed at about −90 V applied bias. Note that this transition coincides with the threshold energy of about 80–90 eV for physical sputtering of a-C:H films by argon ions [8,9].

IR absorption spectra of the a-C:H films deposited at varying substrate bias are shown in Fig. 3. The films grown in the range of +100 V to about −100 V applied bias display contributions of the (a)symmetric stretching of sp^3-bonded $-CH_2$ and $-CH_3$ groups for the strong absorption band around 2900 cm^{-1}. The three individual contributions can be identified as the (1) symmetric

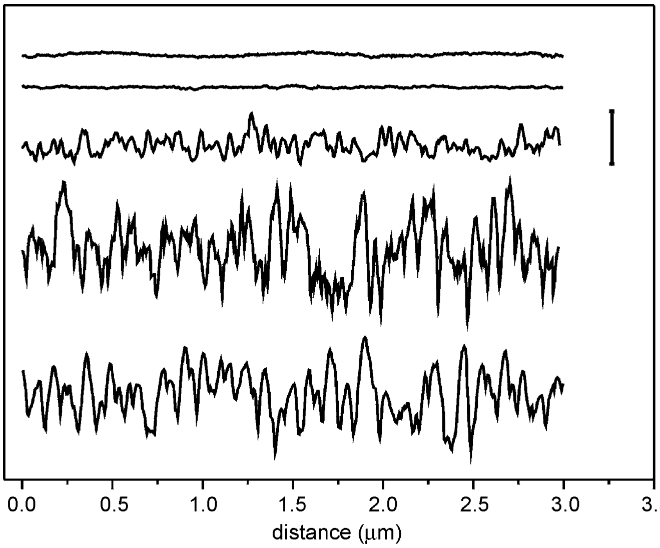

Fig. 2. Surface profiles of the a-C:H films deposited for 1 h at (going from bottom to top of figure) +100, 0, −90, −175 and −250 V applied bias, respectively. The vertical scale bar indicates 10 nm.

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