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Initial stages in the growth of carbon films produced in an $Ar-CH_4-H_2$ microwave discharge: Composition and surface layers morphology

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X-ray photoelectron spectroscopy and atomic force microscopy are employed in the characterization of the first stages in the growth of carbon layers on a (001) Si substrate which is not scratched with diamond powder before placing it in an Ar-2%CH₄-H₂ plasma discharge. Results show that the first layers could be formed in SiC grains where the carbon diamond particles nucleate. The high nucleation density of $1.10^9-5.10^9$ nuclei. cm⁻² and the low aggregates density lead to a smooth surface. © 1996 American Institute of Physics. [S0003-6951(96)03812-8]

Carbon or diamond layers deposited using reactive low pressure plasma are now extensively used in a wide range of technological areas because of their attractive physical and chemical properties. Diamond has a high thermal conductivity, the best hardness known so far and a wide band optical transparency. Moreover, it is quite a good electrical insulator.

However, a great number of industrial applications requires a better control of the interfacial structure which is strongly correlated to the nucleation, epitaxial growth, defect formation, and adhesion on the substrate.^{1,2}

X-ray photoelectron spectroscopy (XPS) is useful in the characterization of the surface composition and the hybridization of surface elements. Atomic force microscopy (AFM) is a good tool for atomic scale measurements of surface morphology because of its high lateral (0.01 nm) and its high vertical (1 nm) resolution. Moreover, samples do not need any preparation before analysis.

The aim of this letter is to investigate the initial stages of carbon layers growth on (001) Si wafers in an $Ar-CH_4-H_2$ microwave plasma.

The experimental setup is shown in Fig. 1. A microwave discharge is produced within a fused silica tube (external diameter = 19 mm and internal diameter = 16 mm). The power supply is a SAIREM GMp 12 kE operating between 0 and 1200 W. Active species are generated in the plasma and are carried out into the stainless-steel reactor containing the sample holder which is located far from the discharge center. Before each experiment, a pressure of 10^{-5} Pa is maintained by means of a turbomolecular pump (Balzer TPU 180H). During deposition, the total pressure in the vessel is kept constant using an Alcatel roots blower pump (70–700 m³ h⁻¹) which maintains a gas drift velocity of about 5–100 m s⁻¹. The substrate temperature is controlled using a thermocouple calibrated with a two color pyrometer (IRCON mirage).

The carbon films are deposited with a 2% CH₄ in Ar–H₂ gas mixture at a P(H₂)/P(Ar) partial pressure ratio of 2 in order to maximize CH_{x<3} concentrations and H atom density, respectively. The choice of these parameters is the result of a study described in detail in Ref. 3. At a suitable pressure of 0.13 kPa, achieved using a total flow rate of 2000 sccm, the plasma is expanded out of the discharge center. This reactor geometry allows us to select the impinging carbon species from CH_{x<3} to C₂H_y by moving the substrate

along the axis of the reactor from positions close to the center of the discharge (6 cm) to positions far in the postdischarge (20 cm). As the layers consist almost entirely of C sp^3 bonding when the substrate is close to the center of the discharge,³ the depositions were performed at 6 cm of the discharge center. Under these conditions, the density of CH_{x<3} remains low resulting in a low growth rate of the carbon films which allows us to investigate the first stages of carbon films growth. The microwave power is equal to 900 W. The substrate holder is heated at 800 °C. The experiments are performed during 1, 2, and 3 h. Before each deposition, the Si substrate is cleaned in acetone but is not scratched with diamond powder.

XPS studies are performed with a Leybold Heraeus LHS 12 (CNRS, Université of Nantes) using a nonmonochromatic Mg $K\alpha$ radiation hv=1253.6 eV) and a spectrometer pass energy of 50 eV.

AFM measurements are conducted with a Digital Instruments Nanoscope II operating in constant force mode. A very small tip attached to a cantilever spring $(1=200 \ \mu m)$ with a force constant of 0.12 N m⁻¹ touches the sample surface and the attractive and/or repulsive forces bend the cantilever spring.⁴ The deflection of the cantilever is optically detected:⁵ a laser beam is specularly reflected from the cantilever surface and the direction of the reflected light beam is sensed with a position sensitive (two elements) photodetectors.^{4,5}

Three piezoelectric ceramics x, y, and z move the tip in



FIG. 1. Schematic of the experimental setup.

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FIG. 2. XPS spectra of Si 2p and C 1s core levels of as-deposited C layers in an Ar–CH $_4$ –H $_2$ plasma at various times; (a) before C deposition, (b) 1 h, (c) 2 h, and (d) 3 h.

the scanning area (x, y) of up to 12 μ m×12 μ m. In the constant force mode, the net force between the tip and the sample is used as the feedback parameter in the *z* feedback circuit which controls the displacement of the sample in the *z* direction normal to the surface. The height profile is obtained after each (x, y) scan.

The atomic force images are not filtered nor processed. They are just fit by subtracting a "polynomial plane" which consists of a surface whose cross section is a second order polynomial in one axis and an horizontal line in the other axis.

XPS spectra of Si 2p and C 1s recorded in function of deposition time are reported in Fig. 2. Before deposition, the Si wafer is oxidized: the Si 2p core level signal corresponding to Si and SiO₂ are found at 99.2 and 103.6 eV, respectively. These values are in good agreement with the binding energies in Ref. 6. A chemical shift of 1 eV towards lower binding energy for SiO₂ is reported in Ref. 7.

An Ar–H₂–CH₄ plasma exposure leads to a strong decrease of the peak intensity at 99.2 eV. Furthermore, the peak corresponding to the silicon oxide disappear. The SiC signal appears at 101 eV after 1 h of deposition. The SiC binding energy is consistent with Ref. 8 but is sightly higher by about 0.8 eV than that of SiC indicated in Refs. 6 and 7. This binding energy shift towards higher energy could be caused by electrostatic charging effects. These results indicate that a thin SiC layer of about 10 nm has formed at the carbon diamond/Si interface.

The C 1*s* core level spectra consist of two peaks after 1 h of deposition. The signal at 283 eV, typical of carbidic carbon⁹ is also slightly shifted towards higher binding energies and corresponds to the formation of a SiC compound. The peak at 285 eV is probably due to a spectra convolution of the C 1*s* XPS signal at 285.5 eV indicated on the spectrum (a) and another one at lower binding energy. The peak at 285.5 eV is assigned to remaining adsorbed hydrocarbons. The peak at lower binding energy is correlated to subsequent



FIG. 3. AFM images of an as-deposited C film exposed to an Ar-CH₄-H₂ plasma during 1 h. (a) 5 μ m×5 μ m scan, (b) 1 μ m×1 μ m scan, and (c) 250 nm×250 nm scan.

carbon diamond layer growth.^{6,7,10} Its intensity increases with increasing time deposition.

The morphology of the carbon film deposited in 1 h is shown in Fig. 3. The nucleation density is very large because it ranges between 1.10^9 and 5.10^9 nuclei cm⁻². The carbon film consists of small and rather round grains very close to

each other. The largest grains are ~ 200 nm wide and 40 nm high. According to Figs. 3(b) and 3(c), one grain located above the first layers seems to be slightly faceted.

The surface structure is consistent with previous AFM studies of MPCVD diamond films containing a large amount of carbon phase which are deposited with 2% of CH₄ in $H_2^{11,12}$ and with an AFM structure of the early stage nucleation of diamond.¹³ AFM images of MPCVD carbon films show many aggregates of particles of 30–40 nm in size.¹⁴

According to Refs. 11, 12, 14, and 15, there is no significant difference between the layer morphology of MPCVD carbon diamond and silicon carbide. Since XPS data indicate a large amount of SiC, we suggest that the layers consist of mainly SiC grains where the carbon diamond particles nucleate. This is corroborated by EDS studies that investigate the interface between silicon substrate and diamond film.¹⁶ The diamond crystals are attached to the substrate by strong Si–C bonds which are localized at the center of each particle.

In summary, we have shown that XPS and AFM may be together fruitfully employed in the analysis of the composition and morphology of the first layers built on a Si substrate during carbon deposition in an $Ar-CH_4-H_2$ microwave plasma. The high nucleation density achieved without any surface pretreatment and the quite small amount of aggregates leads to a smooth surface.

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