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ScienceDirect

Diamond & Related Materials 17 (2008) 1143–1149

DIAMOND AND RELATED MATERIALS

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Diamond nanoseeding on silicon: Stability under H_2 MPCVD exposures and early stages of growth

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Abstract

Detonation nanodiamond dispersed on silicon surfaces underwent different H_2 MPCVD exposures. The induced changes at the surface have been characterized *in situ* by XPS and XEELS. Then, a short CH_4/H_2 growth step was applied. This sequential study revealed an excellent stability of detonation nanodiamond. The sp^3 etching rate is insufficient to remove nanodiamond even under intense H_2 plasma. The H_2 exposure could be successfully used to remove C–C sp^2 carbon without altering sp^3 seeds. Moreover, the formation of silicon carbide observed after the hydrogen treatment is thought to be helpful to enhance the adhesion of nanodiamond particles on the substrate.

Keywords: Nanoparticles; Chemical vapor deposition; Etching; Surface characterization

1. Introduction

Nanocrystalline diamond films are very promising for Nano/Micro-ElectroMechanical Systems (NEMS, MEMS), tribological coatings, electrochemical electrodes and heat spreaders [1]. However, most of these applications require a low surface roughness. To achieve very high nucleation density at the early stages of growth, several treatments of the substrate surface have been carried out such as scratching [2], biasing [3] or ultrasonic seeding with micrometric diamond powder [4]. More recently, seeding using detonation nanodiamond has been reported [5]. Diamond crystallites produced by the detonation process exhibit very small grain size between 5 and 10 nm [6,7]. However, aggregation occurs during the cooling cycle of the detonation shock wave [8]. A subsequent leads to separation of particles to so called ultradispersed diamond (UDD) which can be further chemically purified and use in suspension in a liquid media [9,10].

On the other hand, very few studies dealing with the UDD stability on seeded surfaces are yet available. Indeed, their adhesion to the substrate is an important issue for applications. Other essential questions are related to their chemical and thermal stabilities under Microwave Plasma Chemical Vapour Deposition (MPCVD) environment. The main objective of this study is to investigate the chemical stability of the detonation nanodiamond powder dispersed on silicon surfaces under MPCVD exposures. The present study has been achieved using an *in situ* approach with a MPCVD reactor connected to an Ultra-High Vacuum (UHV) system where chemical surface analysis was performed by X-ray Photoemission Spectroscopy (XPS) and X-ray Electron Energy Loss Spectroscopy (XEELS).

2. Experimental

“Diamond Nano-Powder” as supplied by Gansu Lingyun Nano-Material Co., Lanzhou has been used. The experimental procedure used for the dispersion and the seeding has been previously reported [10]. Briefly, detonation powder has been milled using zirconia beads at high power to break it down to its

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doi:10.1016/j.diamond.2008.01.008

core. Then, the result was cleaned in severe acids and dried. The resulting powder was re-dispersed in water using an ultrasonic horn at 400 W (50% duty cycle) with a water cooled flow cell. Silicon wafers previously cleaned were immersed in the aqueous colloid in an ultrasonic bath for 30 min. Substrates were then rinsed in pure deionised water [10].

Samples were analysed by XPS using an Al Kα anode with a monochromator. The binding energy scale was calibrated versus the Au 4f 7/2 peak located at 84.0 eV [11]. The Inelastic Mean Free Paths (IMFP) of photoelectrons calculated into Si, SiO_2, graphite and diamond matrix have been previously estimated to 2.8 nm [12], 3.3 nm [13], 2.1 nm [14] and 1.9 nm [14], respectively. A tilted geometry was chosen to provide a higher sensitivity to the surface. Curve fitting procedure was performed to extract the components in the C 1s spectra using Voigt functions with a Lorentzian half width of 0.2 eV. The Gaussian width was adjusted according to reference samples analysed in the same experimental conditions. The XPS ratios P_x/C_{total} corresponding to the integrated intensity of each peak P_x over the total area of the C 1s spectrum have been calculated and reported in the Tables 2, 4 and 5. A complementary analysis has been performed using XEELS at the carbon core level. XEELS provides useful data for the identification of the carbon binding states.

After MPCVD exposures, the samples were characterized *ex situ* by Field Emission Gun Scanning Electron Microscopy (Hitachi S-4500 FEG-SEM) providing a high brightness and a lateral resolution close to 10 nm for our samples. The surface coverage S and the density of seeds N_D were extracted from FEG-SEM pictures. Images have been recorded with acceleration voltages of 2 kV or 30 kV.

Seeded silicon underwent pure hydrogen MPCVD exposures followed by an identical short growth step (CH_4 0.6%/H_2 99.4%). The experimental parameters relative to the MPCVD exposures are given in the Table 1. During the exposure, the sample temperature has been measured using a pyrometer. For the hydrogen plasma, the influences of exposure time and substrate temperature have been studied. Indeed, these parameters are strongly involved in the etching of carbon species at the surface. Two different sample temperatures were used. At each temperature, two exposure times were considered.

3. Results

3.1. Silicon surface seeded with detonation diamond powder

The silicon surface seeded with detonation diamond powder was studied by XPS. The C 1s core level exhibited a broad shape (Fig. 1a). Four main components were observed at 285 eV, 285.8 eV, 286.5 eV and 287.3 eV assigned to C–C sp^2 [15,16], C–C sp^3 [15,16], C–OH [17] and C–O–C bonds [18], respectively (Table 2). Three weaker contributions are also detected at 284.5 eV, 288.2 eV and 289.2 eV. The two last components are corresponding to C═O and OH–C═O bonds [18,19]. The carbon binding state associated with the peak located at 284.5 eV could be assigned to oxycarbides [20,21].

Table 1
MPCVD conditions

	Pressure (hPa)	MW power (W)	T (K)	t (min)
H_2 plasma	30	550	993	5/15
	47	850	1213	15/45
Growth step H_2/CH_4 0.6%	30	550	993	5

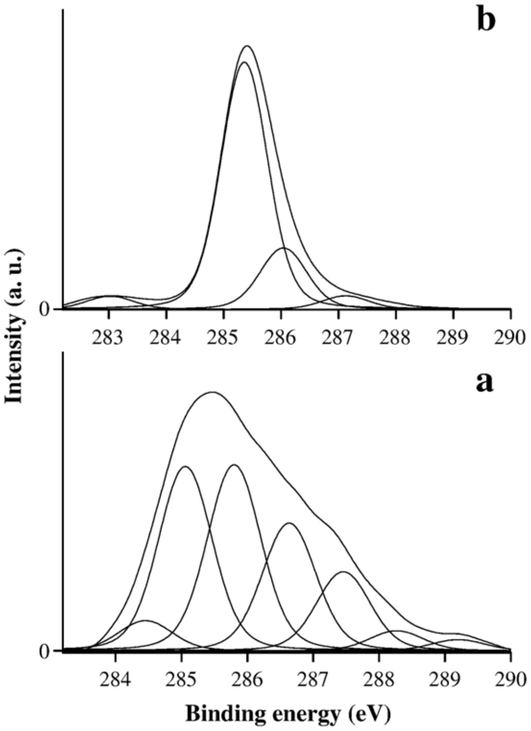

Fig. 1. 1XPS C 1s core level of nanoseeded silicon surface a) initial surface; b) after the short growth step.

Diamond particles produced by the detonation process exhibited a defective shell as previously reported using HRTEM [7]. The shell thickness was recently estimated down to 1 nm from Small Angle X-ray Scattering (SAXS) modelling [22]. The core particle size is very small, 4.5 ± 0.5 nm by powder X-ray diffraction [6] and HRTEM [7]. According to the Inelastic Mean Free Paths given in the experimental part, the defective shell is significantly probed by XPS. This is in agreement with the intense XPS ratio of C–C sp^2 bonds (28% of the total carbon area). Moreover, the presence of hydroxyls, carbonyls and carboxyls bonds at the surface of detonation nanodiamonds were resulting from the cleaning in acids as previously reported [9]. The C–O–C signature by FTIR has even been associated with the aggregation of nanodiamond detonation powder occurring during the dispersion process [23,24]. The XEELS spectrum recorded at the C 1s core level (Fig. 2a) confirmed the presence of C–C sp^3 bonds with the clear signature of surface and bulk diamond plasmons at 24.4 eV and 34.7 eV, respectively [25].

A part of the silicon surface remained uncovered leading to the observation of Si peaks in the XPS spectra. At the Si 2p core level, components corresponding to oxidized silicon were observed (not shown). The ratio of the total integrated area of C 1s