Porous diamond foam with nanometric diamond grains using Bias Enhanced Nucleation on iridium

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ABSTRACT

Porous diamond foam exhibiting a three-dimensional structure was synthesized by applying prolonged Bias Enhanced Nucleation on iridium buffer layers. The Raman spectrum of this material recorded at 325 nm looks very close to the signature obtained for detonation nanodiamonds. HRTEM investigations well confirm the presence of diamond crystals with nanometric size between 2 and 6 nm. All these diamond nanocrystals form a three-dimensional structure very different from ultrananocrystalline diamond (UNCD) generally embedded in a graphitic matrix. According to its high specific surface area, such a 3D material may have promising applications for sensors.

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1. Introduction

The synthesis of porous materials constitutes an important current challenge for the development of energy and health applications. Indeed, due to their high surface area, these materials are suitable for gas storage and supercapacitors [1,2] or for encapsulation of drugs [3]. Porous diamond films would combine a high surface area with bulk and surface properties of diamond like a functional surface by grafting, a biocompatibility and an electrochemical activity for boron doped diamond [4]. Several previous attempts were reported to fabricate diamond materials with enhanced specific surface area. For example, Masuda et al. used a porous alumina mask to fabricate a diamond matrix by oxygen etching [5]. Another approach combines a graphitization of a boron doped diamond film with an oxygen etching leading to a porous diamond material [6]. CVD conditions were tuned to grow polycrystalline diamond films on silicon with different grain size and various surface morphologies were induced by air annealing [7]. The seeding of templates with nanodiamonds was also used as a powerful technique to obtain diamond foam. SiO$_2$ spheres were seeded with detonation nanodiamonds and a boron doped diamond coating was overgrown

[8,9]. After removal of SiO$_2$ core by HF etching, diamond foam was used as an electrode. The growth of boron doped diamond porous membranes usable for peptides detection was also achieved by seeding of fiberglass filters [10]. An alternative way to obtain diamond membranes is the chemical etching of nanocrystalline diamond/3C-SiC composites [11]. Recently, Hébert et al. reported that properties of electrodes combining carbon nanotubes and boron doped diamond are governed by their high aspect ratio [12].

The present manuscript focuses on the synthesis of a diamond porous material composed of nanometric crystals using prolonged Bias Enhanced Nucleation (BEN) on iridium buffer layers. Up to now, BEN is effectively the most powerful procedure to induce diamond heteroepitaxy on substrates of different natures [13]. According to its specific surface reactivity to CVD environment, iridium is currently the best heterosubstrate to obtain highly oriented diamond films. Using specific BEN conditions, a porous diamond foam can also be grown originating from islands at iridium surface. The crystalline structure as well as the chemistry of this carbon material was investigated using high resolution transmission electron microscopy (HRTEM) and Raman spectroscopy.

2. Experimental

Iridium buffer layers were epitaxially grown on SrTiO$_3$ (001) substrates using an evaporation cell [14]. Their polar and azimuthal misorientations measured by X-ray diffraction are 0.22° and 0.26°,

respectively. BEN process includes three different steps: step 1 — a surface cleaning under pure hydrogen plasma with a microwave (MW) power/pressure couple of 400 W/20 mbar during 10 min, step 2 — a stabilization of the substrate temperature by adding 4% of methane in hydrogen plasma before the BEN step during 10 min. Concerning the step 3, the substrate holder was electrically insulated from the metallic walls of the reactor, which were maintained at ground potential; thus, it was possible to apply a negative voltage to the substrate holder during plasma exposition using the same conditions than those of the second step (4% of methane in hydrogen, MW power/pressure of 400 W/20 mbar). The iridium surface underwent a BEN step at −307 V corresponding to a bias current of 17 mA and a temperature of 660 °C. Details about BEN conditions - step 3 - such as how to apply the bias voltage and measure the bias current on Ir/SrTiO$_3$ were reported elsewhere [14]. No further CVD growth step was applied.

After BEN, samples were characterized by Raman spectroscopy for two excitation wavelengths (λ = 325 nm and 514 nm) using both a Renishaw RM1000 and A Horiba Jobin Yvon T64000 spectrometers. More details of the set-up are described in [15]. The surface topography was then observed by field emission scanning electron microscopy (FE-SEM) performed with a Zeiss Supra 40 microscope. By using an in-lens detector, a high lateral resolution of approximately 3 nm was obtained. HRTEM observations were carried out using a FEI Tecnai F20 field emission gun microscope operating at 200 kV and equipped with a Gatan Imaging Filter. Images were taken near the Scherzer focalization (63 nm) using a (1k × 1k) CCD camera. Local area fast Fourier transform diffractograms, equivalent to electron diffraction patterns, were exploited in order to determine structural and crystallographic characteristics of the observed nanocrystals.

3. Results and discussion

Field emission scanning electron microscopy (FE-SEM) revealed a very different surface morphology compared to the one leading to heteroepitaxy or UNCD films. Fig. 1 shows a time lapse of the 3D structure developing during the BEN time by using three different samples. It originates from islands at iridium surface and forms a large covering of the substrate at longer time. Furrows resulting from a roughening of the iridium surface during BEN could be observed as dark lines on the SEM picture. Their height was estimated to be about 2 nm from AFM measurements [14]. Any crystals shape is observable using the in lens detector of FE-SEM knowing that the lateral resolution is close to 3 nm (see Fig. 2 after 60 min of BEN step). According to the cross-section provided on Fig. 3c, the growth rate is estimated to 4 μm/h. This cross-section well exhibits a very different microstructure compared to nanocrystalline diamond (NCD) film grown using the same CVD reactor (Fig. 3d). The CVD conditions for this NCD film correspond to 10% of methane in hydrogen and a MW power/pressure of 1000 W/35 mbar. The porous character of the diamond material can be more or less evidenced by indentation experiments. In fact, micro-indentation leads to an irreversible micrometric deformation of the film without any crack formation (Fig. 3a) which is

some probable evidence of the presence of voids. The same indentation procedure applied to NCD film does not induce any residual deformation; we only observed metal deposition (dark traces) on the contact area (Fig. 3b). These two materials have totally different mechanical behaviors under micro-indentation because of their structures: NCD film is composed of nanodiamond crystals without void whereas the structure obtained by prolonged bias on iridium induces a film composed of nanodiamond crystals with the presence of voids and 3D structure.

To further characterize this material, Raman spectroscopy was first carried out. The corresponding spectra are given in Fig. 4. Using the 514 nm excitation, spectra are dominated by a clear signature of disordered graphite, see the two maxima that correspond to the well-known "D" and "G" lines peaking at about 1350 and 1600 cm^{-1} respectively. As sometimes observed in nanocrystalline CVD films, apparent maxima at about 1160 and 1480 cm^{-1} can also be distinguished. They are usually assigned to *trans*-polyacetylene fragments at the grain surfaces or within the grain boundaries [16]. This is an indirect indication that the foam contains hydrogen. A careful examination of the signal further suggests the presence of a component at about 1330 cm^{-1}. Tuning the excitation wavelength at 325 nm, this signal is now clearly observed, meaning that this material clearly contains diamond, along with some graphitic material. The diamond Raman mode is slightly downshifted to 1330 cm^{-1} with respect to bulk diamond (1332 cm^{-1}). Moreover, its shape appears slightly asymmetric. A similar downshift and asymmetry can be observed by Raman on detonation nanodiamonds with size much smaller than 10 nm under the same detection conditions [15]. This was previously assigned to confinement effects [15,17,18]. Thus, Raman spectroscopy suggests that this material is rather similar to detonation nanodiamond in terms of crystal size. However, the main difference between the present material and purified detonation nanodiamond is the higher relative amount of graphitic and non-diamond material [15]. To get a more complete description of the porous diamond foam, HRTEM was used. Here, the analyzed sample is simply a fragment of porous diamond foam removed from the substrate and placed on a TEM grid.

Those HRTEM investigations clearly confirmed that this diamond material is composed of nanometric crystals with size included between 2 and 6 nm (Fig. 5a), which exhibit interplanar distances of 0.207 nm corresponding to diamond {111} planes (Fig. 5b). FFT treatment of HRTEM images also reveals the presence of sp^2 carbon with interplanar distances of 0.33 nm as shells surrounding diamond nanocrystals (Fig. 5c) which nicely confirmed the Raman observations (disordered graphite with a small in plane coherence length). Moreover, HRTEM observations suggest that diamond crystals are coalesced forming a continuous 3D nanocrystalline structure (see in particular the plan view of the fragment of porous diamond foam shown in Fig. 6). There are lots of cavities inside the material defined by the specific shape of porous diamond foam. Indeed, the expansion of film during the prolonged Bias Enhanced Nucleation grows randomly in all directions and forms
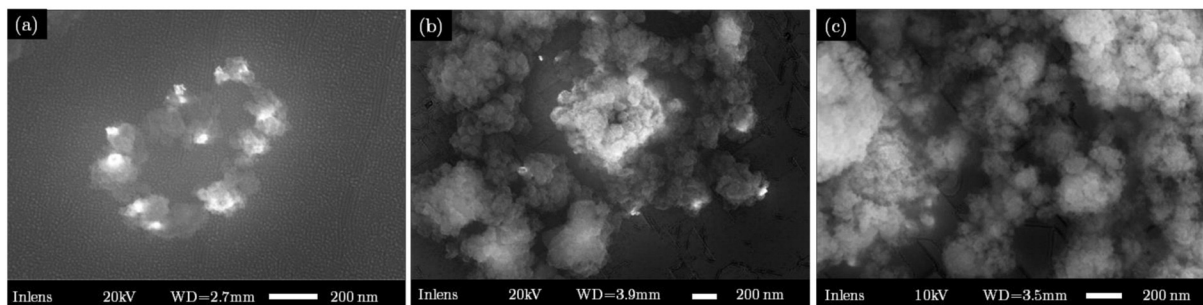

Fig. 1. FE-SEM pictures of diamond foam at the surface of Ir/SrTiO$_3$ samples after: a) 10, b) 20 and c) 40 min of BEN step.