



Single-crystal diamond microneedles shaped at growth stage

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ARTICLE INFO

Article history:

Received 26 March 2013

Received in revised form 18 July 2013

Accepted 3 September 2013

Available online 13 September 2013

Keywords:

Chemical vapor deposition

Thermal oxidation

Polycrystalline diamond

CVD simulation

ABSTRACT

Single-crystal diamond microneedles were extracted from (001) textured polycrystalline films. The films were produced using a plasma enhanced chemical vapor deposition (CVD) from a CH₄/H₂ gas mixture activated by a direct current discharge. The as-grown textured polycrystalline CVD films consist of pyramid-shaped micrometer size diamond crystallites embedded into a nanodiamond ballas-like material. The less ordered fraction of the CVD film material was removed selectively using thermal oxidation. A dependence of the diamond needle shape on the CVD and the oxidation process parameters was revealed via a computer simulation and experimental studies. Ability for mass production of the diamond microneedles of different shapes was demonstrated. The needles are suitable for various applications from microcutting tools to quantum information processing.

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1. Introduction

Diamonds obtained by chemical vapor deposition (CVD) attract great attention due to numerous potential applications exploiting their outstanding mechanical, optical and electronic properties [1–3]. These properties and realization of the potential applied abilities of a CVD diamond depend also on phase composition, structural properties, surface morphology and geometry of the crystallites composing the CVD films. Well-developed CVD techniques allow formation of the films with predetermined, in some range, orientation of the diamond crystallites. From the most general point of view, the crystallographic orientation of the diamond crystallites in a film is determined by the ratio of their growth rates along the different crystallographic directions. This ratio may be controlled by the CVD process parameters (a substrate temperature, carbon-containing gas concentration and others) [4]. In particular, a ratio of the growth rates along the <001> and <111> crystallographic directions (V_{001} and V_{111} , correspondingly), expressed by a parameter $\alpha = 3^{1/2} V_{001}/V_{111}$, is usually used to characterize the CVD processes [5,6]. For the parameter α close to 1 the preferential growth of the diamond crystallites along the <111> direction is achieved, so that the basic shape of the diamond crystallite is a cube. For the values of α about 3 the fastest growth is along the <100> direction, changing the basic shape of the diamond crystallite to an octahedron. By varying the growth process parameters one is able to change α , and, thus, to change the morphology of the CVD films. Together with the van der Drift model, assuming a competition in the growth of the diamond crystallites

depending on their orientation [7], such an approach may enlighten the growth process and provide new advanced functional materials.

In experimental studies the films' and individual crystallites' morphology observations using microscopy techniques (optical, electron, scanning probes, etc.) are usually combined with Raman spectroscopy and other methods to reveal structural characteristics and properties of the materials. In particular, the Raman spectra of a crystalline diamond have a sharp peak at about 1332 cm⁻¹ while graphitic inclusions can be indicated by the presence of peaks at 1350 cm⁻¹ and 1580 cm⁻¹ [8]. If the size of the diamond crystallites is getting smaller than several nanometers, the presence of a nanodiamond in the film is traced by the Raman peaks at 1140 cm⁻¹ and 1470 cm⁻¹ [9]. All these bands are present in the Raman spectrum of the films, consisting of a mixture of nano- and micro-sized diamonds and a graphitic material, in different proportions depending on a relative amount of the corresponding materials and their location (at outer surface of the film or on its interface with substrate; in between individual grains or inside the crystallites; etc.). The relative amount of these fractions in the CVD film may be evaluated efficiently with use of thermogravimetry analysis (TGA), for instance [10].

The complexity of the interrelations between the experimentally determined characteristics and the growth parameters requires an involvement of an additional modeling and numerical simulations to provide further understanding of the diamond film formation and optimization of the CVD process for obtaining of desirable shapes of the diamond crystallites. In this paper we combine the experimental investigations and the computer simulations to reveal a consistent pattern of the (001) textured polycrystalline diamond film growth for a particular CVD process. These studies open a way to develop a practical method for obtaining the films consisting of the diamond crystallites with predetermined shapes and provide their mass production.

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2. Experimental

The (001) textured diamond films were produced on standard grade Si (001) wafers using a plasma enhanced chemical vapor deposition (PECVD) system described elsewhere [11]. The substrates of a 25×25 mm size made from the (001) polished Si wafers with a thickness of $460 \mu\text{m}$ were used. Immediately before the CVD processing the silicon substrates were treated by an ultrasonication in a suspension of a micrometer-sized diamond powder in order to increase the density of the nucleation sites. The diamond deposition occurs during carbon condensation from a hydrogen–methane gas mixture activated by a direct current (DC) discharge. The growth parameters that provide a stable DC discharge plasma and formation of the polycrystalline (001) textured diamond films were found empirically (the substrate temperature of about 900°C , total gas pressure of 9.5 kPa , gas mixture composition $\text{CH}_4:\text{H}_2 = 5:95$, discharge voltage of about 700 V , and discharge current density of about 1 A/cm^2) [11].

The duration of the CVD processes has been chosen in a range of 2 to 100 h depending on the desirable film thickness (and the diamond crystallite length) taking into account an approximate growth rate of about $1 \mu\text{m}$ per hour. The as-grown CVD films were thermally oxidized to remove selectively the smallest diamond crystallites, nanodiamond fraction, disordered carbon and graphitic inclusions. The selective removal of the carbonaceous materials occurs as a result of their gasification. The thermal oxidation of the diamond films was performed in a furnace at 650°C in air under a normal atmospheric pressure for 2 h. The oxidation temperature was chosen using the previously reported experiments [10].

The as-deposited and oxidized films were characterized by Raman spectroscopy using a Jobin Yvon Ramanor U1000 instrument, equipped by a microscope, with excitation at the 514.5 nm line of an argon-ion laser. Morphology peculiarities of the produced samples were examined by scanning electron microscopy (SEM) imaging using a LEO 1550 (Zeiss) microscope.

A simplified model of the diamond film formation was developed using a basic assumption that a deposition of carbon atoms occurs layer by layer. Taking into account different atomic densities for the different crystallography facets it corresponds to non-equal deposition rates along the different crystallography directions. In the numerical simulations only two dimensional (2D) problems for diamond growth in direction perpendicular to substrate surface were considered. The model assumes that the amount and the role of a disordered carbon and graphitic inclusions are negligible. Additionally, the growth model was developed to simulate only (001) textured film formation and, thus, considers growth in a plane perpendicular to the $\langle 110 \rangle$ direction. The modeling was performed using Wolfram Mathematica 8 software (see more details in the Supplementary Data).

3. Results and discussion

3.1. Diamond needles production by oxidation of (001) textured films

The polycrystalline (001) textured diamond films of different quality, including those, that contain only micrometer-scaled crystallites of about equal size, were obtained in our previous studies [12]. However the films formed of a mixture of diamond crystallites of different dimensions, ballas-like nanodiamond fractions and some negligible amounts of graphitic and amorphous carbon were the most interesting for the present investigations. A typical morphology of such kind of the textured diamond films produced by the CVD is presented on a SEM image shown in Fig. 1. The films consist of micrometer-sized crystallites with well-formed (001) facets of near equal lateral dimension. The rectangular facets of these ‘large size’ crystallites on the surface of the film are surrounded by a material exhibiting much less ordering with a morphology characteristics, which cannot be resolved with SEM imaging. A Raman spectrum of the film (Fig. 2, curve 1) shows the presence of a

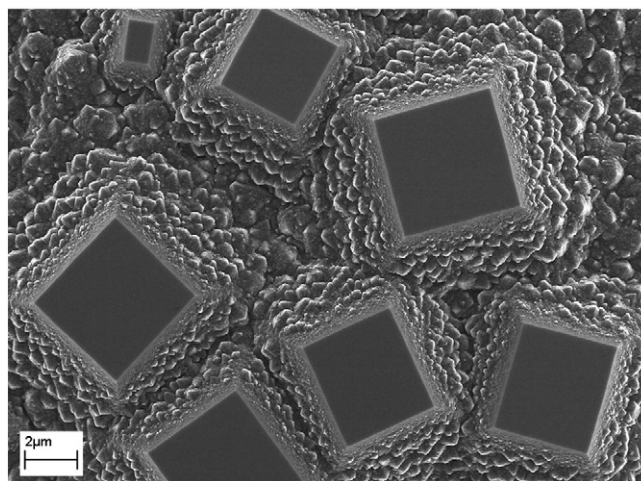


Fig. 1. Typical SEM image of the (001) textured PECVD diamond film.

“diamond” line at 1332 cm^{-1} , crystalline graphite lines at 1580 cm^{-1} (well ordered) and 1350 cm^{-1} (disordered) and weak “nanodiamond” lines at 1140 cm^{-1} and 1470 cm^{-1} .

The low-ordered (submicron- and nano-sized) diamond and amorphous materials were removed selectively by an exposure of the as-grown CVD films in a furnace at a temperature of about 650°C in air [10]. As one can see in Fig. 2 (curve 2) a remaining part of the material in the oxidized CVD film produces only a narrow “diamond” peak in the Raman spectrum. The SEM images for the oxidized film material represented in Fig. 3 demonstrate clearly that these oxidized films consist mainly of individual needle-like crystallites with a quite perfect pyramidal geometry. The pyramid-shaped needles retain their original position with the vertices orientated to the substrate. However the needles may be tilted easily (and even detached from the substrate) by mechanical manipulations. The dimensions of the diamond pyramids are in range of a few to hundreds of micrometers depending on the duration of the CVD process. For example, the sample shown in Fig. 3 contains the crystallites with a length of about $20 \mu\text{m}$ and rectangular base of about $2 \times 2 \mu\text{m}$. Some of the needles presented in the bottom image of Fig. 3 were tilted by touching the film surface with tweezers.

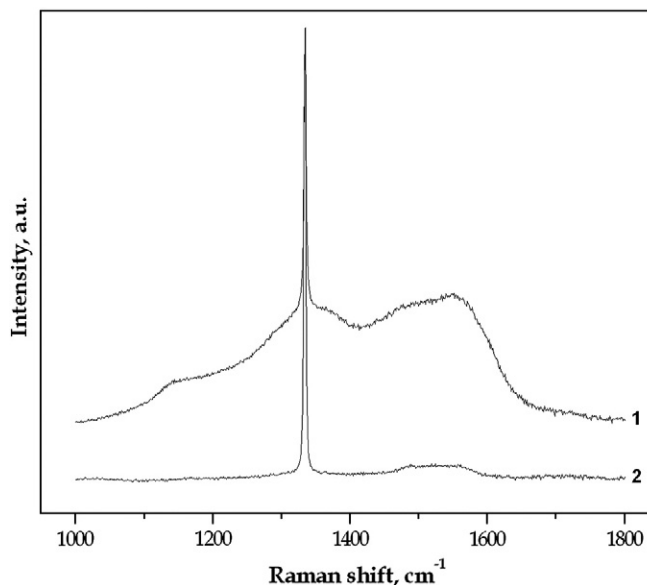


Fig. 2. Raman spectra of the (001) textured CVD diamond film: curve 1 – as-deposited film, curve 2 – film oxidized at 650°C .

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