Chemically vapor deposited diamond-tipped one-dimensional nanostructures and nanodiamond–silica–nanotube composites

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ABSTRACT

Composite thin films of nanodiamond and silica nanotubes were synthesized by means of microwave plasma assisted chemical vapor deposition (MPCVD) on silica nanotube matrix that was seeded with nanodiamond particles. SEM, Raman spectroscopy, and EDX were used to analyze the composite. Wet chemical etching was applied to selectively remove exposed silica from the composites for further revealing the nanostructure of the composites. Nanodiamond grew around silica nanotubes and filled the space left between silica nanotubes to form a continuous film. When appropriately selected sizes of nanodiamond particles were used as diamond seeds, silica nanotubes capped with CVD-grown diamond crystals were also obtained. Potential applications and implication of composites of nanodiamond and 1-D nanostructures will be discussed.

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1. Introduction

Diamond's outstanding physical and chemical properties when combined with one-dimensional nanostructures may lead to hybrid nanodevices with excellent and unique functions and performance. For example, the widely used atomic force microprobe (AFM) will have much improved durability and precision when diamond AFM probes are used. When a wear resistant super-hard diamond tip is supported by a non-diamond nanorod or nanotube, the hybrid device provides scientists even broader options of probe functions and capabilities. Unique optical, electronic, chemical, and biological properties of diamond coupled with the excellent wear resistance and hardness and a wide variety of supporting nanorods or nanotubes are, therefore, highly desirable and may open up new dimensions for nanodevices based on 1-D nanostructures.

Chemical vapor deposition of diamond from carbon containing gases and compounds in the presence of atomic hydrogen has been making consistent progresses in the past twenty-some years [1–3]. Various energy sources including hot metal surfaces, electrical discharges, combustion flames, and laser excitation have been applied to assist in the chemical vapor deposition (CVD) of diamond on diamond seeds or nuclei [4,5]. Atomic hydrogen of various amounts in different CVD environments was found critical to preferentially depositing diamond phase of carbon. By enhancing the bombardment of substrates by hydrocarbon ions via a negative bias to the substrate with respect to a plasma, diamond nuclei can also be created without needing pre-synthesized diamond seeds. On the other hand, pre-synthesized diamond seeds can be placed onto selected surfaces on which further diamond growth is to be carried out. These diamond seeds can be micro-nanodiamond debris created by abrasive polishing or ultra-sonic agitation induced impact by diamond particles on substrates. Diamond particles of nanometers or tens of nanometers in sizes that are usually synthesized by means of explosive techniques followed by purification processes are also often applied by various means to adhere to substrate surfaces and serve as diamond seeds for further CVD growth of diamond. In this work, microwave plasma assisted chemical vapor deposition (MPCVD) is applied to grow diamond on diamond seeds of nanometers to tens of nanometers in sizes that are selectively adhered to the opening ends of silica nanotubes to form one-dimensional nanostructures with diamond tips.

2. Experimental details

Silica nanotubes ranging from tens of nanometers up to 140 nm in diameter and several micro-meters in length were synthesized in-house by one of the co-authors, C. S. Yeh, and used for fabricating diamond–silica nanotube composites with diamond-tipped one-dimensional nanostructures. Detailed process for synthesizing the

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silica nanotubes will appear elsewhere. Silica nanotubes of 2 mg by weight were mixed with 1 mL of distilled water. The solution was ultra-sonicated to keep silica nanotubes in a uniform suspension. Solutions that contained diamond nanoparticles of an average of 10 nm and 30 nm in size, respectively, in methanol were mixed with the silica nanotube containing solution. The mixed solutions were then ultra-sonicated for 30 min before being applied onto various substrates such as silicon, silicon dioxide at a substrate temperature of 90 °C.

Chemical vapor deposition processes for both nanocrystalline and polycrystalline diamond were applied to grow diamond on top of the diamond seeds. When the nanodiamond process was employed, a gas mixture of 1% CH_4+2% H_2+97% Ar was used while the microwave power was kept at 800 W with the gas pressure kept at 150 Torr during the growth process [6]. For the crystalline diamond deposition process, a gas mixture of 1.5% CH_4 diluted in 98.5% H_2 was used while the microwave power was kept at 1100 W with the gas pressure kept at 45 Torr throughout the whole process [7]. The growth temperature for the nanodiamond process was measured with a dual-color optical pyrometer to be approximately 600 °C, while the substrate tempera-ture for polycrystalline diamond growth was set at approximately 700 °C.

When the concentration of nanodiamond seeds that were applied to the substrate surface was high, a diamond–silica composite film was synthesized. When the concentration of nanodiamond seeds was low, individual silica nanotubes with their openings capped with diamond crystals were fabricated. After diamond deposition, samples were subjected to wet chemical etching using hydrofluoric acid solutions to etch away exposed silica nanotubes. The diamond–silica composite film became a free-standing porous diamond film with a network of one-dimensional channels which were previously occu-pied by silica nanotubes. Optimized process for synthesizing porous diamond films and their properties will be reported elsewhere. In this paper, the focus is placed on the fabrication of one-dimensional nanostructures with diamond tips and the characterization of the structures.

3. Results and discussion

Shown in Fig. 1 is a diamond crystal that was grown at one of the opening ends of a silica nanotube. Diamond nanoparticles of 10 nm suspending in methanol was used to place diamond seeds at the opening of silica nanotubes. Standard polycrystalline diamond growth conditions stated previously were applied to grow diamond onto the diamond seed. A well-faceted diamond crystal can be seen to cap one end of the nanotube to form a diamond-tipped nanotube. Nanodia-mond particles tended to adhere more easily at the openings of the
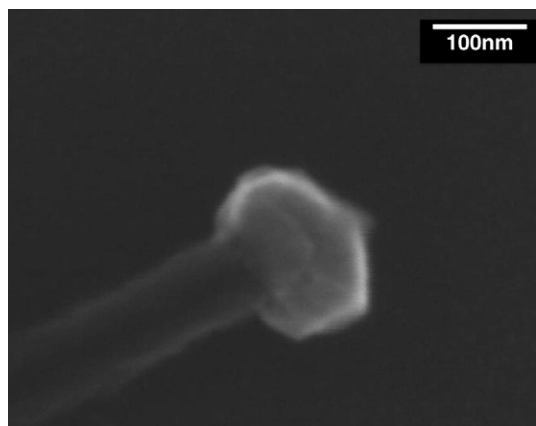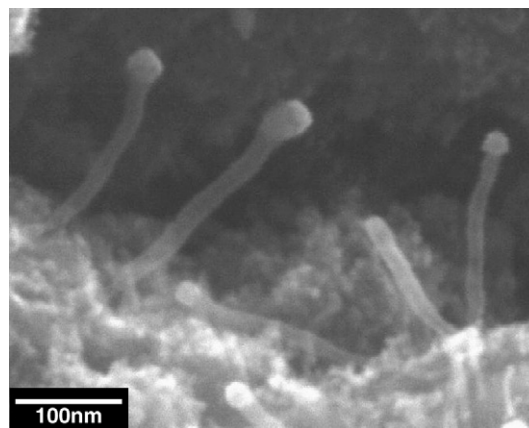

Fig. 2. One-dimensional nanostructures formed by growing nanodiamond on diamond-seeded silica nanotubes.

silica nanotubes than on the sidewalls likely due to mechanical lock-in effect of diamond nanoparticles by the silica nanotube openings. The small radius of curvature of the sidewall of the silica nanotube makes the effective contact area between a chemically inert diamond nanoparticle small. The curved sidewalls, therefore, allowed poor adhesion with diamond nanoparticles, especially those with well-faceted surfaces of larger sizes. The microwave plasma CVD growth increased the size of the diamond seeds and caused the tube openings to be capped. Diamond growth under the conditions intended for the growth of nanodiamond as stated previously also resulted in similar results as shown in Fig. 2.

For the solution containing nanodiamond particles with an average of 10 nm in size, the distribution of diamond sizes was broad and contained both larger diamond clusters as well as smaller diamond nanoparticles. Diamond nanoparticles which were smaller than the radius of curvature of the silica nanotubes and those without well-faceted surfaces could more possibly adhere to the side walls of the silica nanotubes. Diamond crystals grown on sidewalls of silica nanotubes were also observed. Some smaller diamond nanoparticles could even enter the interior of the silica nanotubes. More detailed characterization of the growth process in confined space and the synthesized carbon phases inside silica nanotubes will be reported in a separate paper.

Another solution containing a more uniformly distributed and suspended diamond nanoparticles of 30 nm in size was also prepared. A similar process was applied to place diamond seeds onto silica nanotubes. As expected, silica nanotubes capped with diamond were fabricated easily with little growth of diamond on sidewalls of silica nanotubes. As shown in Fig. 2, multiple diamond capped silica nanotubes were seen close to each other without diamond growth on side walls of silica nanotubes. This applies to growth conditions for both nanodiamond and crystalline diamonds. The SEM photo shown in Fig. 2 was taken from a specimen grown under nanocrystalline diamond growth conditions. As it can be seen from the diamond at the ends of silica nanotubes, these diamonds are less faceted than what is shown in Fig. 1.

As stated in the standard processes for fabricating one-dimen-sional nanostructures with diamond tips, the solution that was applied to a substrate contained both diamond-seeded silica nano-tubes as well as diamond nanoparticles in suspension. When the concentration of diamond nanoparticles is adequately high, a continuous diamond film was grown to cover the silica nanotubes and the surface of the substrate. Most silica nanotubes are embedded inside the diamond film. In areas where the concentration of suspending diamond nanoparticles was low, only silica nanotubes with diamond tips could be seen as shown in Fig. 2.
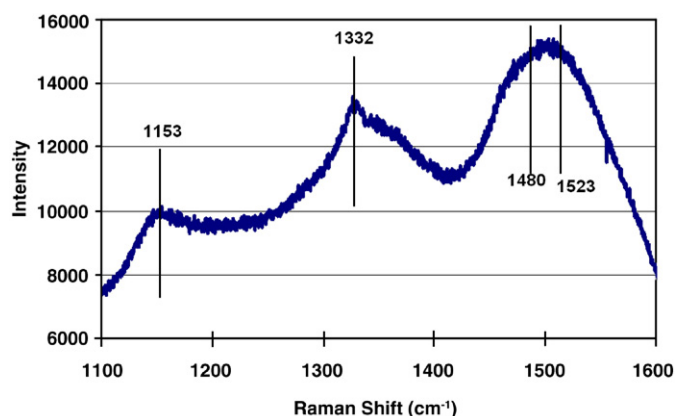

Fig. 1. A silica nanotube with a diamond crystal capping one of the tube openings.

Fig. 3. Raman spectrum taken from the samples shown in Fig. 2, which was grown under standard nanodiamond deposition conditions.

Fig. 5. Photoluminescence spectra of the samples before (top) and after (bottom) being subjected to HF wet chemical etching.

Raman spectra were taken to analyze the synthesized nanodiamond–silica composite. One of the spectra for nanodiamond deposition is shown in Fig. 3. The peak located at 1331 cm^{-1} is a signature of diamond crystal. The broad band around 1500 cm^{-1} that accompanies the 1150 cm^{-1} peak and often appears as the shoulder of the G mode is believed to be caused by disordered sp^3 carbon or trans-polyacetylene [8–12]. The diamond peak appears sharper when the deposition time increases.

Nanodiamond–silica composite samples were chemically etched using hydrofluoric acid solution in order to dissolve exposed silica nanotubes. After the etching process, diamond capped nanotubes shown in Fig. 2 were no longer found. Instead, needle-like nanostructures could be seen in areas where the concentration of nanodiamond seeds was low as shown in Fig. 4. Holes could also be clearly seen scattering around the surface of the nanodiamond–silica composite film indicating that embedded silica nanotubes were etched away by the hydrofluoric acid solution. Energy dispersive X-ray (EDX) analysis was applied to analyze the diamond–silica composite film before and after etching by hydrofluoric acid. The percentage of silicon content by weight in the diamond film decreased from typically more than 18% before etching to less than 10% after. The percentage of carbon content by weight increased from originally less than 68% to 90%. Apparently, many silica nanotubes originally detectable by EDX have been etched away as expected. Some unexposed silica nanotubes were protected by the chemically inert diamond and remained intact from the wet chemical etching process.

Unlike diamond capped nanotubes shown in Figs. 1 and 2, needle-like nanostructures formed after wet chemical etching did not appear
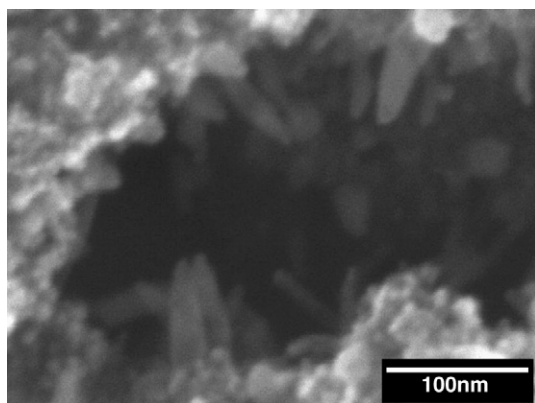

Fig. 4. Needle-shaped nanostructures formed after wet chemical etching by hydrofluoric acid in grown areas with low concentration of excessive nanodiamond seeds besides diamond-seeded silica nanotubes.
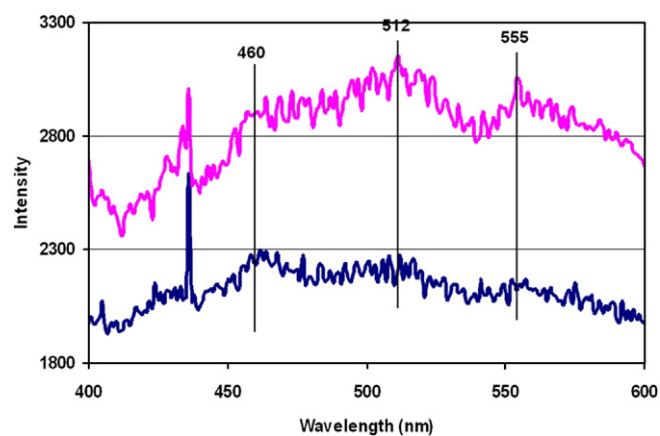
like previously described nanotubes with diamond tips but instead are sharp needles with base diameter of about 20–30 nm that are consistent with the diameter of a number of silica nanotubes. Since silica should be etched away by hydrofluoric acid, what was left over as seen in Fig. 4 is most likely diamond, non-diamond carbon phase, or silicon carbide originally grown inside silica nanotubes. Although the EDX used has a focus spot of 5–10 nm in diameter, background noise caused by the electron scattering after it hits the specimen could have an as high as 100% reading for the content of carbon. The signal coming from Si has been eclipsed. Detailed study of CVD growth in confined space within nanotubes is being undertaken.

Room-temperature photoluminescence (PL) spectra were taken using excitation of 325 nm light from a He–Cd laser. The collecting time was 3000 ms. Because of non-uniform silica nanotube distribution, the intensities taken from the measurements are not as high as those reported by other groups. The background photoluminescence was taken into considerations in order to minimize its effects. The top PL spectrum shows the emissions from the as-grown specimen (top curve in Fig. 6). Four characteristic emission peaks and bands are present, i.e., 426 nm, 460 nm, 512 nm, and 555 nm. The luminescence peak around 2.23 eV (555 nm) is from the self-trapped excitons. It is likely caused by the structural defects suggesting that the self-trapped exciton is confined to a SiO$_4$ tetrahedron [13,14]. The peak at the wavelength of 512 nm, corresponding to 2.42 eV, could be attributed to defect centers associated with oxygen deficiencies in the silica nanotubes [15,16]. The band at 2.70 eV (460 nm) is ascribed to the neutral oxygen vacancy (≡Si–Si≡) [13,16–18] and the band at 2.91 eV (426 nm) is due to some intrinsic diamagnetic defect centers, such as a two-fold coordinated silicon lone-pair center (O–Si–O) [13,14,16,19,20]. In this study, these bands caused by various defects of silica nanotubes were used to determine the presence of the silica nanotubes. After wet chemical etching using hydrofluoric acid solution, the intensities of these three peaks were reduced but not completely minimized (bottom curve in Fig. 5). Some embedded silica nanotubes that could not be etched away by hydrofluoric acid solution still contribute to some extent to the light emission detected by PL.

4. Conclusions

Fabrication of one-dimensional nanostructures with diamond tips has been successfully achieved. Diamond nanoparticles adhere to openings of silica nanotubes by means of mechanical locking and encapsulate the openings after chemical vapor deposition of diamond. The selective seeding technique can be applied to nanotubes of materials other than silica. By etching away silica in the diamond–silica composite films using hydrofluoric acid solution, porous

diamond nanostructures with one-dimensional nanochannels could be obtained. One-dimensional nanostructures with diamond tips, porous diamond films, diamond with nanochannels, and needle-shaped carbon-based nanostructures are among many possible nanostructures observed from the reported process according to SEM examination. Further studies of diamond growth in confined space inside nanotubes of silica and composites employing other materials are being undertaken.

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