The growth of nano-scale diamond tips on diamond/Si

Ya Ko Chih\textsuperscript{a}, Jennchang Hwang\textsuperscript{a,}\textsuperscript{*}, Yu Lun Chueh\textsuperscript{a}, Li Jen Chou\textsuperscript{a}, An Pin Lee\textsuperscript{b}, Chwung Shan Kou\textsuperscript{b}

\textsuperscript{a}Department of Materials Science and Engineering, National Tsing-Hua University, Hsin-Chu City, Taiwan, ROC
\textsuperscript{b}Department of Physics, National Tsing-Hua University, Hsin-Chu City, Taiwan, ROC

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Abstract

We report the discovery of vertically aligned nano-scale diamond tips grown on the rugged polycrystalline diamond/Si substrates in a planar microwave plasma enhanced chemical vapor deposition system. The diamond nanotips exhibit three different morphologies (C-, cone-, and rod-like-shape) that can be monitored by varying substrate temperature and bias voltage. Experimental results indicate that the rod-like nanotips exhibit the best diamond quality, C-shape nanotips the second best, and the cone-shape nanotips the worst.

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1. Introduction

The drive to fabricate nano-scale materials in forms of nanotubes or nanotips has been stimulated by the discovery of carbon nanotube (CNT) in the past years [1]. Zine oxide (ZnO) [2], carbon [3], silicon [4], and indium gallium nitride (InGaN) [5] nanotips have been successfully fabricated by using various chemical vapor deposition techniques. Diamond is a special material with high mechanical hardness, thermal conductivity, electron and hole mobilities, and chemical stability [6–9], which make more attractive the fabrication of diamond nanotips or nanotubes in the mechanical, thermal, and electrical applications. However, the growth of diamond nanotips has been considered difficult based on two possible reasons. First, the synthesis of diamond by plasma enhanced chemical vapor deposition (PECVD) is a high-temperature (~900°C) process, at which temperature the synthesized diamond is always in the form of a film, rather than of nanotips. Second, a structure of nanotips can be successfully grown on various substrates, such as silicon, copper, and...
graphite, at low temperature (~200–400°C) [10–12]. However, these nanotips consist of a great amount of sp² bonds, which should be treated as amorphous carbon nanotips rather than diamond ones. It is thus of interest to find out a way to inhibit the formation of sp² bonds such that the growth of diamond nanotips is enabled at a low-temperature process.

We attempt to search for an appropriate substrate which favors the formation of sp³ bonds, rather than sp² bonds, during growth of nanotips. Polycrystalline diamond is the reasonable choice because the probability of forming sp³ bonds on the diamond surface is higher than other crystal surfaces. In this case, the inhibition of the formation of sp² bonds becomes possible at a low temperature process. In this article, we will demonstrate the growth of diamond nanotips on polycrystalline diamond surfaces at a low temperature. The growth of diamond nanotips is very sensitive to substrate temperature and bias voltage. Experimental results indicate that three different shapes of diamond nanotips (C-shape, cone-shape, and rod-like-shape) can be fine-tuned by varying the substrate temperature and bias voltage.

2. Experimental procedure

Diamond nanotips were grown on polycrystalline diamond/silicon (D/Si) substrates in a 2.54 GHz planar microwave plasma enhanced chemical vapor deposition (MPECVD) system. The polycrystalline D/Si substrate is about 540 µm thick and 5 × 5 mm² in size. The characteristics of the planar-MPECVD system can be found in the previous published paper [13]. In a typical experiment, planar-MPECVD chamber was pumped down to a base pressure of 4 × 10⁻² Torr, and a mixture of 30% CH₄ and 70% H₂ was fed into the chamber to ignite the CH₄/H₂ mixed plasma at 3000 W and at a total pressure of 0.17 Torr. Nano-scale diamond tips were grown on the polycrystalline D/Si substrates at different substrate temperatures (125, 200, and 350°C) and different bias voltages (−50, −150, and −250 V) for 2 h. No metal catalysts are required for the growth at such low temperatures. A field emission scanning electron microscope (FESEM) image was obtained by flashing ultra-thin Au onto nano-scale diamond tips because the tips are not conductors. Raman spectroscopy was used for the chemical analysis of nano-scale diamond tips. The morphology and structure of an individual diamond nanotip were characterized by using a transmission electron microscope (TEM, JEM-3000F) operated at 300 kV.

3. Results and discussion

Vertically aligned diamond nanotips of ~50 ± 20 nm in diameter and ~600 ± 200 nm in length (Figs. 1(a) and (b)) were grown on the rugged polycrystalline diamond/silicon substrates at 125°C and a bias voltage of −250 V. The aspect ratio of diamond nanotips is about 12:1 in average. Each diamond nanotip exhibits C-shape at its top and the tip density is about 1.5 × 10¹⁰ cm⁻² as shown in the top-view SEM micrograph (Fig. 1(a)). The C-shape is considered to be a metastable shape since it does not have the smallest surface area of a tip structure. When the substrate temperature is raised to 200°C, the C-shape disappears and becomes a rod-like shape as shown in Fig. 1(c). The diameter of a rod-like shape diamond nanotip is ~60 ± 20 nm, slightly larger than that of a C-shaped one. The lengths of diamond nanotips are about the same (Fig. 1(d)). When the substrate temperature is increased to 350°C, diamond nanotips exhibit larger diameters and they bind together to form a film with lots of nano-scale pinholes, as shown in Figs. 1(e) and (f). This indicates that a tip structure is easier to form at a low-temperature process.

The diamond qualities of nanotips grown at different substrate temperatures can be extracted from their Raman spectra in Fig. 2. The nanotips grown at 125°C exhibit a strong diamond characteristic peak at 1334 cm⁻¹ and a very weak graphite background centered at 1580 cm⁻¹ (G band). Davis [14] reported that the co-existence of sp² or graphite bonding in diamond would shift the Raman frequency to a frequency higher than 1332 cm⁻¹. The 1334 cm⁻¹ position is thus an
Fig. 1. FESEM at a magnification of 50,000 showing the diamond nanotips grown at; (a) 125°C, plane view; (b) 125°C, side view; (c) 200°C, plane view; (d) 200°C, side view; (e) 350°C, plane view; (f) 350°C, side view.

indication of the existence of very small amount of sp² or graphite bonding. However, the ratio of Raman cross-section for graphite to diamond has been reported to be about 50:1 per unit volume [15]. The nanotips in Figs. 1(a) and (b) are thus reasonably treated as diamond nanotips. The very weak G band indicates the existence of a very small amount of sp² or graphite bonding. The G band results from the stretching vibration of any pair of sp² sites, whether in C–C chains or in aromatic rings [16]. Usually, a broad D band centered at 1350 cm⁻¹ coexists with the G band for amorphous carbon films grown in a MPECVD system. D band is the breathing mode of sp² sites only in aromatic rings. The disappearance of D bands in Fig. 2 suggests that all the sp² sites in diamond nanotips are in chains, not in rings.
When substrate temperature is raised from 125 to 200 °C, the diamond characteristic peak shifts from 1334 to 1332 cm\(^{-1}\) and its full-width at half-maximum (FWHM) reduced from 10.1 to 6.6 cm\(^{-1}\). The peak area ratio \(I_{\text{diamond}}/I_{\text{G}}\) also increases from 0.93 to 1.23. Nanotips grown at 200 °C have better diamond quality than that grown at 125 °C. When substrate temperature increases further to 350 °C, the coalescence of nanotips is clearly observed which leads to the formation of a film-like structure as shown in Fig. 1(e). The diamond film exhibits a weak and broad diamond peak at 1332 cm\(^{-1}\) and the peak area ratio of \(I_{\text{diamond}}/I_{\text{G}}\) reduces to 0.51. This indicates that the diamond film in Figs. 1(e) and (f) has the worse diamond quality.

Raman spectra are insufficient to prove that the nanotips are made of diamond because the Raman signal may have contributions directly from the polycrystalline diamond substrate due to the open structure of nanotips. The qualities of diamond nanotips are further justified by the TEM micrograph and the electron diffraction (ED) patterns of a selected diamond nanotip grown at 200 °C (the best growth condition). Fig. 3(a) shows the TEM micrograph of a diamond nanotip of about 50 nm in diameter scratched from the as-grown diamond nanotips. The crystal structures along the nanotip in Fig. 3(a) are, respectively, characterized and shown in Figs. 3(b)–(d). At the top part of the nanotip, a discrete ED pattern is clearly observed and identified to be a single crystalline diamond structure looking along [\(\bar{1}12\)] zone axis [17]. At the center part, the same discrete ED pattern still appears but with a much weaker brightness, suggesting that the diamond quality becomes worse. Note that one additional bright spot labeled “A” is also located next to (1 1 1), which is identified to be a \{1 1 1\} type diffracted spot and may result from another diamond grain. At the bottom part, a similar ED pattern appears with a very vague poly ring structure. The first poly ring overlaps with the \{1 1 1\} type diffracted spots, which seems to be diffracted from nano-diamond grains inside the bottom of the nanotip. The second poly ring is very vague and seems not to overlap the \{2 2 0\} type diffracted spots. This probably results from the sp\(^2\) sites in diamond nanotips.
Bias voltage is very crucial in the growth of diamond nanotips on the rugged polycrystalline diamond surfaces. When bias voltage reduces from $-250$ to $-150$ V, the C-shape diamond nanotips no longer exist. All the diamond nanotips are vertically aligned and in cone-shape, as shown in Fig. 4(a). And their Raman spectrum (Fig. 4(b)) exhibits diamond characteristic peak at $1333\, \text{cm}^{-1}$ and a weak and broad graphite background centered at $1580\, \text{cm}^{-1}$. The $I_{\text{diamond}}/I_{\text{(G)}}$ ratio is determined to be 0.59, smaller than 0.93 taken at $-250$ V bias voltage. The FWHM of the diamond peak is $11.0\, \text{cm}^{-1}$, larger than $10.1$ taken at $-250$ V bias voltage. All these indicate that the C-shape diamond nanotips have better diamond quality than cone-shaped ones. When bias voltage reduces further to $-50$ V, the cone-shape diamond nanotips remain stable, as shown in Fig. 4(c). However, their nucleation density tremendously reduces and nanotips no longer uniformly cover the rugged polycrystalline diamond surface. No Raman spectrum from the nanotips in Fig. 4(c) can be detected.

4. Conclusions

In summary, diamond nanotips have been successfully grown on the rugged polycrystalline diamond/Si substrates in a planar-PECVD system. The morphologies of diamond nanotips strongly depend on substrate temperature and bias voltage. When substrate temperature increases from 125 to 200 $^\circ$C, diamond nanotips changes from C-shape to rod-like shape. The rod-like diamond nanotips have better diamond quality than the C-shaped ones. The change in morphologies may be attributed to the reduction of surface energy. When the bias voltage is reduced from $-250$ to $-150$ V, diamond nanotips change from C-shape to cone-shape. The cone-shape diamond nanotips have worse diamond quality than the C-shaped ones.

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References