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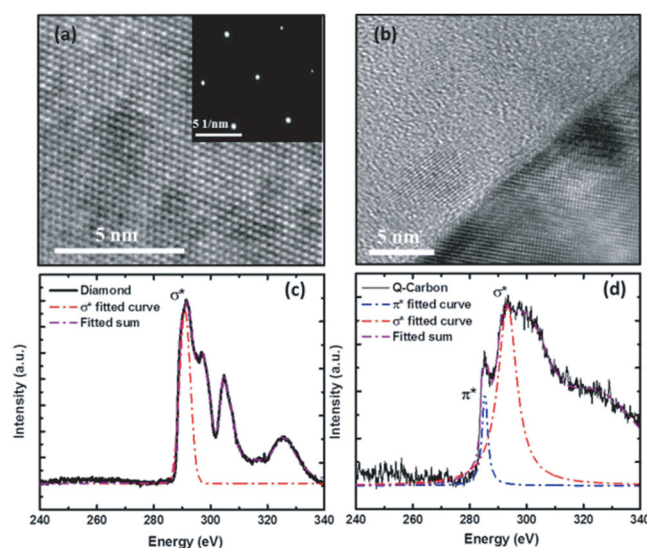
Q-carbon discovery and formation of single-crystal diamond nano- and microneedles and thin films

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We report the formation of single-crystal diamond nanoneedles, microneedles and thin films on sapphire (0001). By using nanosecond excimer laser pulses, we convert amorphous carbon into a new state of Q-carbon by rapid melting and quenching. The Q-carbon consists of amorphous mostly sp^3 bonded carbon and rest 10–15% sp^2 , from which diamonds are nucleated. These nanodiamond nuclei in Q-carbon provide a seed for growth of diamond. These nanoneedles and microneedles are found to be single crystals often oriented along $\langle 110 \rangle$ directions. The (111) single-crystal diamond film are formed, when sapphire (0001) provides a seed for diamond growth from super undercooled liquid.



Keywords: Q-carbon, Carbon to Diamond Conversion, Diamond Microneedles, Raman Spectroscopy

Introduction Formation of diamond nanoneedles and microneedles is scientifically challenging with tremendous impact on field emission-based devices and biomedical applications, including drug delivery. The diamond nanoneedles and microneedles will lead to minimally invasive transdermal medical devices used for various applications, including drug delivery, fluid sampling, micro-dialysis and electrochemical sensing.

These devices are associated with less pain and tissue damage as compared with conventional hypodermic needle-based devices.[1] In this context as well as other applications related to field emission and display devices, the formation of diamond microneedles has been an interesting challenge. It has been found that nanoneedles with diameter 800 nm and less can breach the cell membranes without causing irreversible damage

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of the membrane provided insertion duration is less than a few tens of minutes.[2]

Previous attempts on the formation of microneedles have focused on reactive ion etching of nanocrystalline diamond thin films, where the length is limited by deposited thickness of diamond and diameters of microneedles are limited to larger sizes by reactive ion etching.[3] The resulting microneedles have a nanocrystalline structure with a significant concentration of defects, which can provide traps and recombination centers. In another approach, the dependence of diamond growth rates during chemical vapor deposition (CVD) of diamond thin films has been used to get single-crystal microneedle of limited sizes.[4] By controlling the CVD parameters, enhanced growth either along the $\langle 111 \rangle$ direction or along the $\langle 100 \rangle$ direction can be achieved and microneedles, albeit limited sizes and aspect ratios, can be formed. Besides the limitations on size and aspect ratio, the CVD requires high temperatures with overall low throughput, as the process occurs in solid state.[4] On the other hand, in our liquid-phase-mediated growth, the growth rates are very high with high aspect ratio, leading to the formation of nanoneedles as well as microneedles. The preferred growth orientation under a rapid liquid-phase growth is found to be $\langle 110 \rangle$.[5]

Here, we report the formation of single-crystal diamond nanoneedles and microneedles by a novel method, where these needles are formed through direct conversion of carbon into diamond at ambient temperature and atmospheric pressure in air without any need for catalyst or hydrogen to stabilize sp^3 bonding for the formation of the diamond phase.[6] We show that amorphous carbon films on sapphire and glass substrates can be melted in a highly undercooled state around 4,000 K, some 1,000 K below the graphite–diamond–liquid triple point (at 5,000 K and 12 GPa of pressure).[7] By using high-power nanosecond laser pulses, the amorphous carbon layers are rapidly melted and quenched into a new state of carbon (referred to as Q-carbon). By controlling nucleation and growth, we are able to generate a variety of microstructures, including nanodots, nanoneedles, microdiamonds, microneedles and large-area single-crystal diamond thin films on epitaxial templates, such as sapphire. The focus of this paper is on the nanoneedles and microneedles, which nucleate from the Q-carbon and grow rapidly under liquid-phase-mediated explosive recrystallization to several microns, where the growth direction is $\langle 110 \rangle$. The $\langle 111 \rangle$ diamond single-crystal thin films are formed, when (0001) sapphire (via planar matching) or (001) Cu (via lattice matching) provides a template for epitaxial growth. We present detailed structural characterization and bonding characteristics of nanoneedles and microneedles, and discuss the mechanism of single-crystal growth orientation.

Experimental The amorphous diamond-like carbon films were deposited on sapphire (c -plane) and glass substrates by using KrF laser (pulse duration = 25 ns, wavelength = 248 nm, energy density = 3.0 J cm^{-2}) to a thickness of 50–500 nm. These films were characterized by transmission electron microscopy (TEM) and Raman and found to be amorphous containing Raman signature on sapphire (DLC broad peak = $1,580 \text{ cm}^{-1}$) with estimated sp^3 fraction up to 50%. The Raman spectra for films on glass substrates contained D ($1,349 \text{ cm}^{-1}$) and G ($1,580 \text{ cm}^{-1}$) peaks with considerably less sp^3 around 20–25%. The WITec confocal Raman microscope system alpha300 M was used for micro Raman with highest sensitivity for 532 and 355 nm excitation wavelengths. These films were irradiated in air with ArF laser pulses (pulse duration = 20 ns, wavelength = 193 nm, energy density = $0.3\text{--}0.6 \text{ J cm}^{-2}$). After the laser annealing (LA) treatment, these films were characterized by high-resolution scanning electron microscopy, electron backscattered diffraction (EBSD) with characteristic diamond Kikuchi patterns, high-resolution transmission electron microscopy, x-ray diffraction and Raman spectroscopy. The EBSD measurements provide a very powerful technique to study the structure (diamond vs. any other phase) and the details of relative orientations through Kikuchi patterns of nanoneedles and microneedles with respect to the substrate. High-resolution SEM and EBSD measurements were carried out using FEI Verios 460 L SEM and FEI Quanta 3D FEG FIB-SEM for phase identification and determination of grain orientation. Aberration-corrected STEM-FEI Titan 80-300 and JEOL-2010 STEM/TEM were used for electron energy loss spectroscopy (EELS) with a resolution of 0.15 eV and high-resolution TEM (point-to-point TEM resolution 0.18 nm; STEM-Z resolution 0.08 nm with information limit of 0.06 nm).

Results and Discussion

Formation of Q-carbon. We show that a direct conversion of carbon into diamond can occur in air at ambient temperatures and pressures without any need for catalysts and hydrogen to stabilize sp^3 diamond bonding.[6] According to the equilibrium (P vs. T in Figure 1) phase diagram,[7] graphite, diamond, liquid and vapor are thermodynamically stable forms of carbon. At low pressures, graphite converts into vapor above around 4,000 K. According to the phase diagram, diamond synthesis from liquid carbon will require even higher temperatures and pressures as the graphite–diamond–liquid carbon triple point occurs at 5,000 K/12 GPa, where $1 \text{ GPa} = 9,869 \text{ Atm}$. In the thermodynamically stable forms of carbon, graphite, diamond, liquid and vapor, we introduce

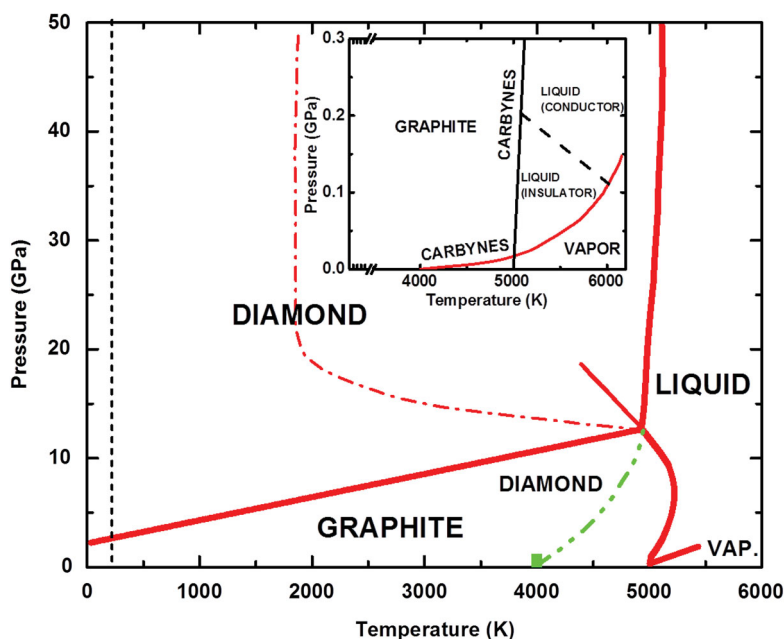


Figure 1. (Colour online) Carbon phase diagram (P vs. T) following Bundy et al. [7] which has amorphous diamond-like carbon melting at 4,000 K at ambient pressures (as shown by dotted green line).

amorphous metastable carbon with some sp^3 content and super undercooled state of liquid carbon (Figure 1). [7] This can be accomplished by nanosecond laser melting of diamond-like carbon, where undercooled state is at about 4,000 K, some 1,000 K below the melting point of graphite.

The temperatures profiles were calculated by SLIM computer simulation code developed by Singh and Narayan. [8] By quenching this super undercooled state, we are able to form Q-carbon, nanodiamond, microdiamond and single-crystal thin films by controlling the nucleation and growth times. The new state of carbon (Q-carbon) has a very high fraction of sp^3 bonded carbon and the rest sp^2 , and is expected to possess novel physical, chemical, mechanical and catalytic properties. There is a considerable reduction in volume, when as-deposited amorphous carbon is melted in the undercooled state and quenched as Q-carbon. The Q-carbon exhibits unique properties, including ferromagnetism at and above room temperature. The formation of cubic diamond phase can occur if a sufficient time is allowed for homogeneous nucleation or substrates which are lattice or plane matched with the cubic diamond are provided during nucleation. [9,10]

During nanosecond pulsed laser heating, the super undercooled carbon is formed near the film–substrate interface, and upon quenching this super undercooled state turns into a new phase of carbon (Q-carbon). The Q-carbon layer can break into a cellular (filamentary) structure upon quenching. The formation of a cellular structure results from interfacial instability at the solid–liquid interface, driven by either by solute segregation or

strain. [11] The Q-carbon can be converted into diamond, which provides a direct path for the conversion of carbon into diamond.

Figure 2(a) shows the formation of Q-carbon, which exhibits many unique properties, such as enhanced field emission (negative surface potential), robust ferromagnetism and very high hardness. We also see enhanced contrast under secondary electron imaging and direct conversion of Q-carbon into diamond. Figure 2(b) shows the formation of nanodiamonds (2–8 nm diameter) which are faceted at the smallest size. The Q-carbon can be converted into nano and microneedles, as shown in Figure 2(c), the details of which are the primary goal of this paper. Figure 3 shows a schematic for the formation of diamond nanoneedles and diamond microneedles from the new phase of carbon (Q-carbon) which is created near the substrate and carbon film interface. During nanosecond pulsed laser irradiation (ArF 193 nm laser, pulse duration 20 ns and energy density 0.5 J cm^{-2}), amorphous carbon melts near the film–substrate interface in a super undercooled state. The diamond nanoneedles and microneedles are formed from liquid carbon by rapid recrystallization from the liquid phase into diamond.

This Q-carbon phase has been characterized by high-resolution TEM to determine structural characteristics and microstructural features. These results are shown in Figure 4(b), where Q-carbon contains an amorphous structure with some nanodiamonds embedded into it after quenching. The number density of nanodiamonds is found to be a strong function of time allowing for nucleation and growth during quenching. The high

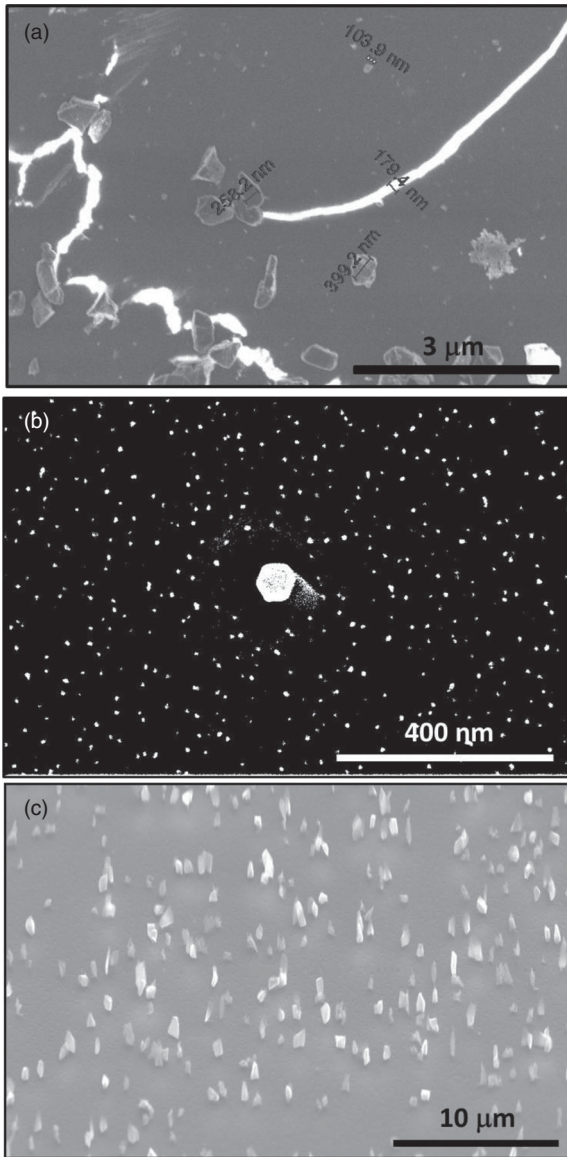


Figure 2. (a) Formation of Q-carbon with enhanced contrast and nucleation of diamond from the Q-carbon; (b) formation of nanodiamond 2–8 nm diameter and (c) the formation of nanoneedles and microneedles.

resolution transmission electron microscopy (HRTEM) from single-crystal microdiamond is shown in Figure 4(a), with $\langle 110 \rangle$ columns as confirmed by imaging and inset diffraction. To investigate the details of bonding characteristics, EELS studies were carried out using aberration-corrected STEM-FEI Titan 80-300 with an energy resolution of 0.15 eV. The characteristic EELS spectrum from the Q-carbon is shown in Figure 4(d), which has a sloping edge at 285 eV with a broad peak at 292 eV. From the Voigt profile fit of the EELS spectrum, the sp^3 was estimated to be about 80% and rest sp^2 , which is consistent with Raman results from the Q-carbon, and is also shown in the Figure 4(d). The peak positions for σ^* and π^* edges are fixed at 292

and 285 eV, respectively. All the other fitted peaks are not shown to avoid confusion. The EELS results from microdiamond are shown in Figure 4(c) with characteristic sp^3 (σ^*) bonding. The spectrum contains a sharp edge at 288 eV with a peak at 292 eV, corresponding to sp^3 (σ^*) bonding, which is a signature EELS spectrum for diamond.

In the following, we present results from Raman spectroscopy of Q-carbon and diamond microneedles. The as-deposited carbon films contained characteristic D ($1,349\text{ cm}^{-1}$) and G ($1,580\text{ cm}^{-1}$) peaks, as shown by the green curve in Figure 5. Figure 5 also shows Raman results (red curve) from Q-carbon on the sapphire substrate with a diamond peak at $1,333\text{ cm}^{-1}$ with a broad peak around $1,350\text{ cm}^{-1}$ and a small peak at $1,140\text{ cm}^{-1}$, associated with strained sp^2 carbon at the interface. By fitting this Raman spectrum ($1,140$, $1,333$ and $1,580\text{ cm}^{-1}$), we obtain 76–81% sp^3 and rest sp^2 fraction. By using confocal 532 nm excitation wavelength, we can get rid of sapphire (substrate) Raman peaks, which appear with 633 nm wavelength of the Raman laser. A slight up shift of the primary Raman peak is related to quench in strains, and a bump at $1,140\text{ cm}^{-1}$ in the Q-carbon spectrum is characteristic of sp^2 bonded carbon at the interfaces in nanodiamond. The Raman results from a microdiamond (black curve) on the sapphire substrate are shown after a single laser pulse of ArF laser (energy density (0.6 J cm^{-2})). A sharp diamond peak at $1,331.54\text{ cm}^{-1}$ and a small G peak of residual unconverted amorphous graphite are observed. The Raman shift ($\Delta\omega$) is related to $\Delta\omega$ (in cm^{-1}) = $2.2 \pm 0.10\text{ cm}^{-1}\text{ GPa}^{-1}$ along the $[111]$ direction, $\Delta\omega$ (in cm^{-1}) = $0.73 \pm 0.20\text{ cm}^{-1}\text{ GPa}^{-1}$ along the $[100]$ direction, and $\Delta\omega$ (in cm^{-1}) = $3.2 \pm 0.23\text{ cm}^{-1}\text{ GPa}^{-1}$ for the hydrostatic component.[12] The biaxial stress in thin films can be described as a combination of two-thirds hydrostatic and one-third uniaxial stress. The biaxial stress can be estimated using $\sigma = 2\mu(1 + \nu)/(1 - \nu) \cdot \Delta\alpha \cdot \Delta T$, where μ is shear modulus, ν is Poisson's ratio, $\Delta\alpha$ is the change in thermal coefficient of expansion and ΔT is the change in temperature.

Formation of Nanoneedles and Microneedles.

The formation of nanoneedles (80 nm diameter) and microneedles (100–500 nm) in diameter and length as long as 3,000 nm is shown in Figure 6. These nanoneedles and microneedles can be made longer and hollow by manipulating the laser variables. The inset shows EBSD, also known as backscatter Kikuchi diffraction (BKD), for diamond structure determination and phase identification. The EBSD studies were carried out using the field-emission scanning electron microscope. This is a powerful technique to determine the crystal structure of nano- and microdiamonds (with resolution of 10 nm) and their relative orientations with respect to the substrate. In

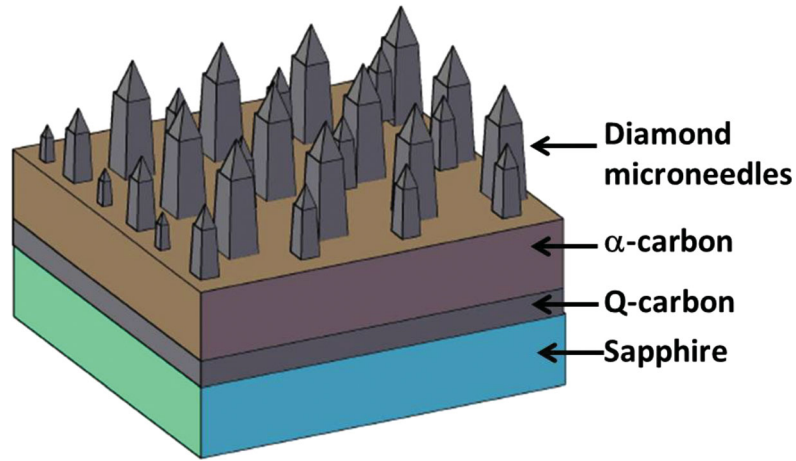


Figure 3. (Colour online) Schematic showing the formation of nanoneedles and microneedles from a carbon film on sapphire or glass substrates. The α -carbon is the remaining amorphous carbon.

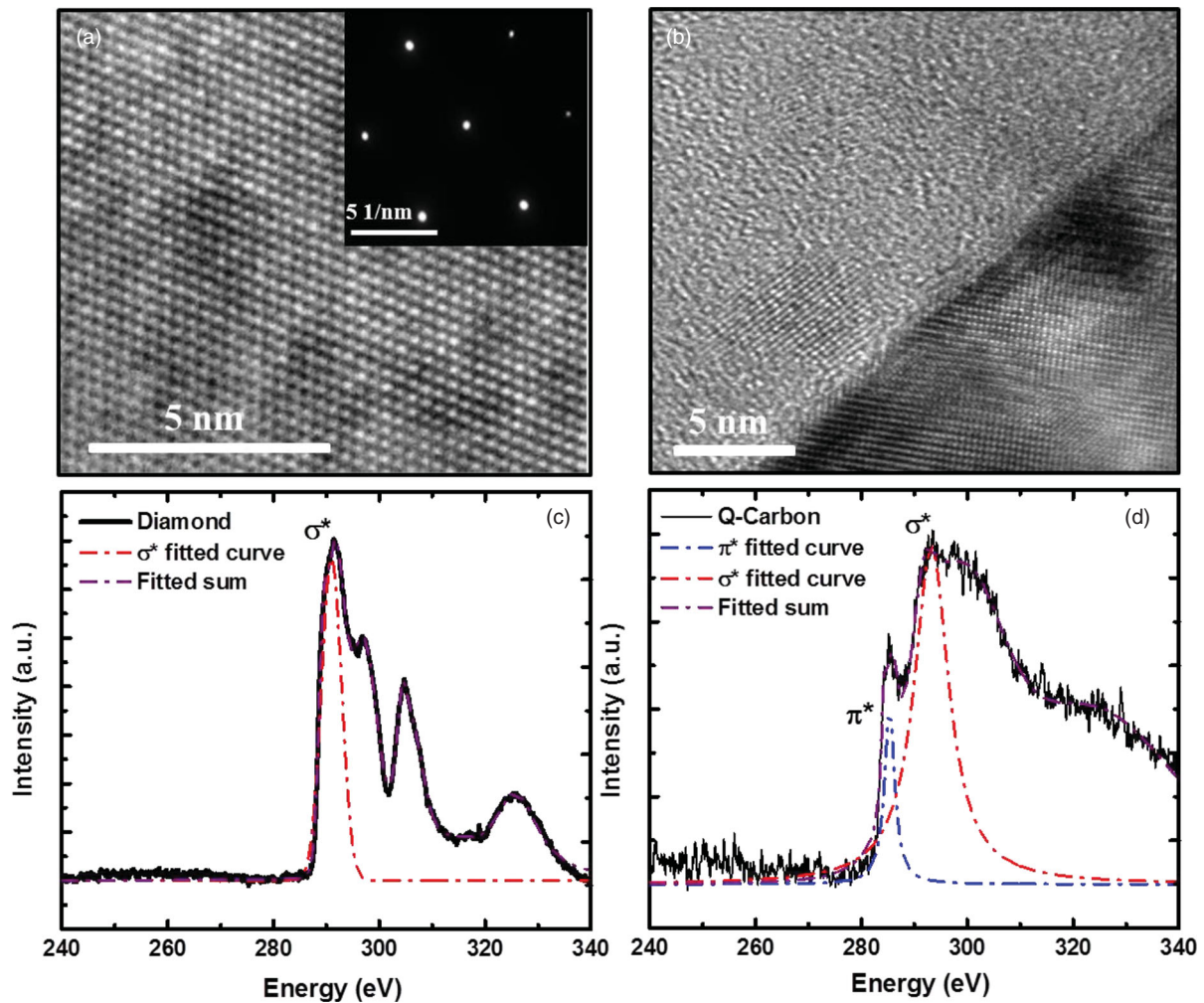


Figure 4. (Colour online) High-resolution TEM and EELS from diamond and Q-carbon from cross-section TEM sample with diamond on sapphire using FEI Titan: (a) the $\langle 110 \rangle$ HRTEM image showing individual columns of atoms with a resolution of 0.18 nm with inset $\langle 110 \rangle$ electron diffraction pattern from diamond; (b) HRTEM from Q-carbon showing amorphous structures and some nanodiamonds; (c) EELS spectrum from microdiamond (energy resolution 0.15 eV) showing a sharp edge at 288 eV with a peak at 292 eV and (d) EELS spectrum from Q-carbon has a sloping edge at 285 eV with a broad peak at 292 eV. From the Voigt profile fit of the EELS spectrum of Q-carbon, the sp^3 was estimated to be about 80% and rest sp^2 .

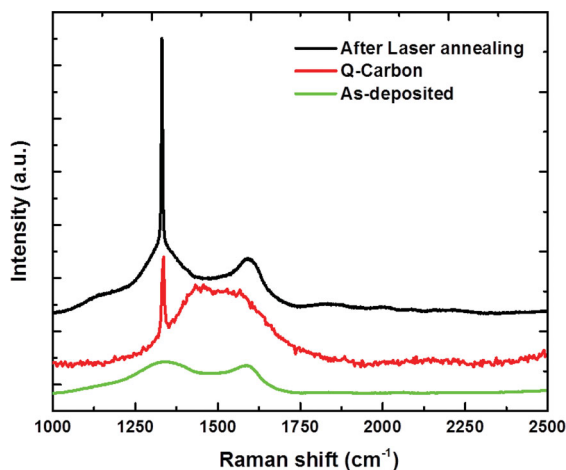


Figure 5. (Colour online) Raman spectroscopy of diamond (after LA), Q-carbon and as-deposited DLC on sapphire employing 532 nm laser.

the EBSD a stationary electron beam strikes a tilted crystalline sample and the diffracted electrons form a pattern on a fluorescent screen. This pattern is characteristic of the crystal structure and orientation of the sample region from which it was generated. The microneedles grow up to two to three microns in length. These microneedles grow out of the Q-carbon formed near the sapphire interface through the carbon over layers which must be

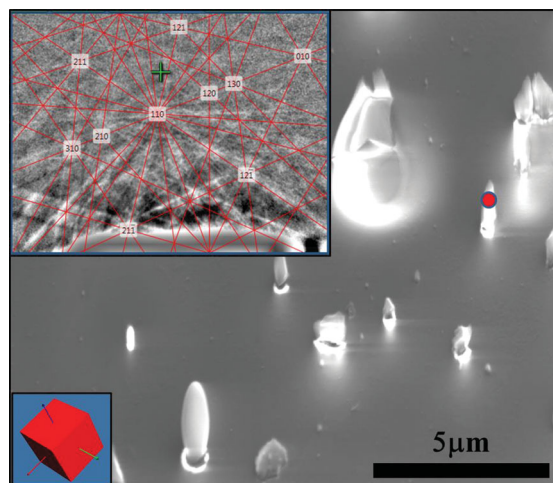


Figure 6. (Colour online) EBSD patterns microdiamonds growing out the Q-carbon near the sapphire interface: the (110) EBSD Kikuchi pattern from the encircled nanodiamond (red); and relative orientation of the diamond microcrystallite.

molten during the growth of these needles. The formation of such long microneedles requires crystal growth velocities of the order of $5\text{--}10\text{ ms}^{-1}$, and, therefore, it can occur only in the liquid phase, where diffusivity is of the order of $10^{-4}\text{ cm}^2\text{ s}^{-1}$.

Figure 7 illustrates the formation of nanodiamond (Figure 7(a)) and different shapes of nanoneedles and

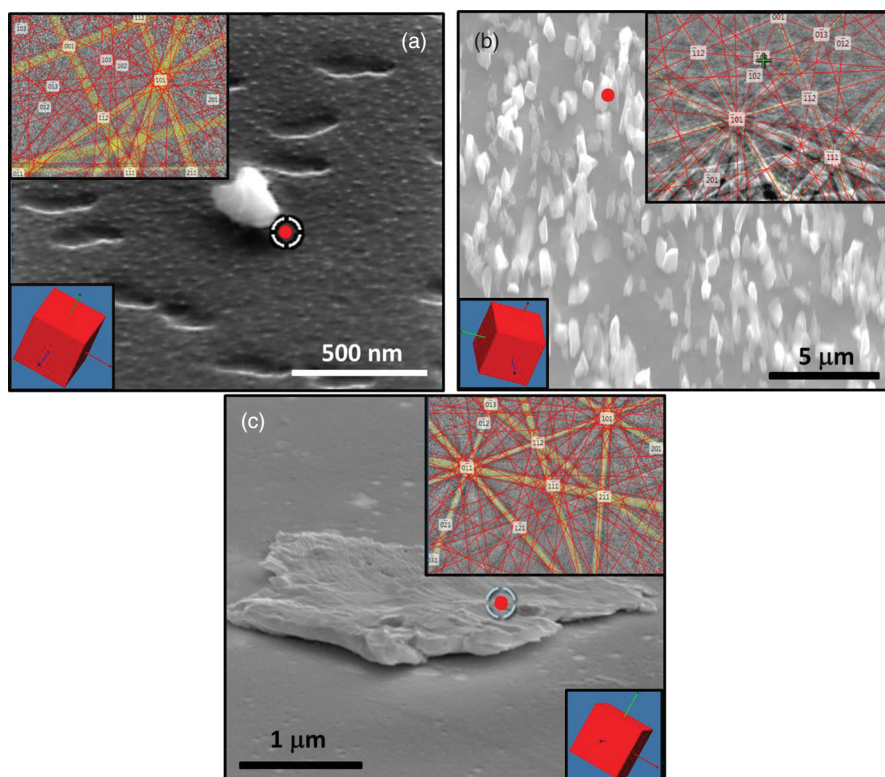


Figure 7. (Colour online) Formation of (a) nanodiamonds and (b) microneedles on sapphire. The inset EBSD pattern of the red dot indicates the detail of the (110) diamond crystal structure. (c) Shows area diamond (111) single-single-crystal thin film which has grown epitaxially with the (0001) sapphire substrate.

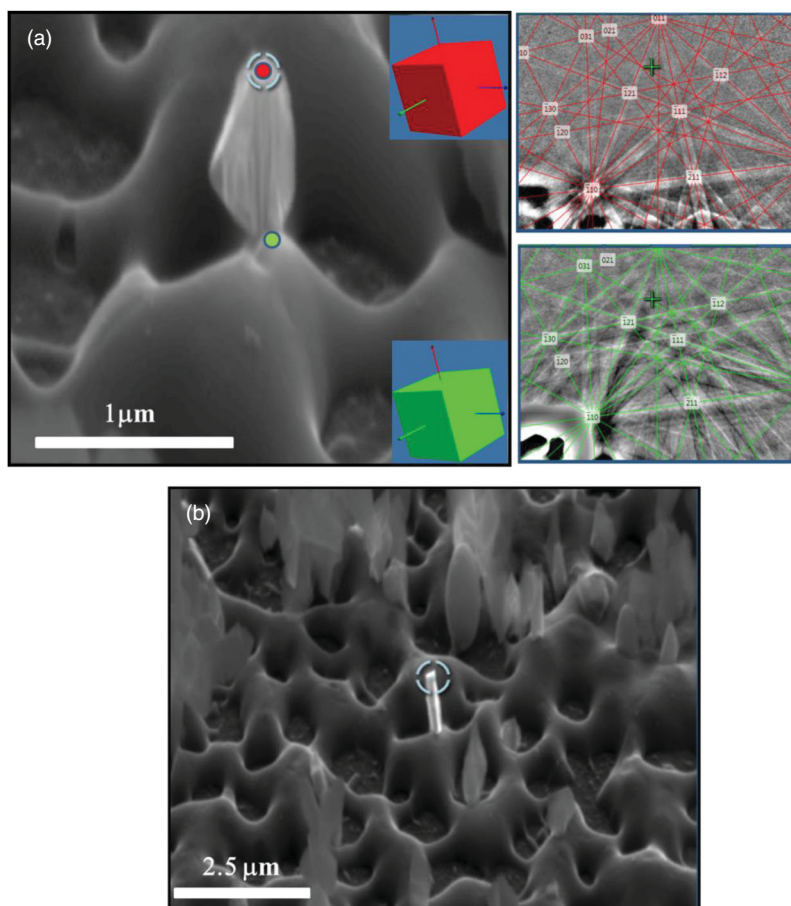


Figure 8. (Colour online) Diamond grown on copper substrate, (a) a comparative EBSD patterns (red: diamond and green: copper) from the underlying copper template and diamond microneedles establish the epitaxial nature of the formed structures and (b) shows the formation of a diamond-faceted pillar surrounded by {100} and {110} planes.

microneedles (Figure 7(b)), which have grown without any catalyst, and the presence of hydrogen which is needed during CVD to stabilize the diamond sp^3 bonding.

Each figure has an inset EBSD pattern from areas indicated, showing details of $\langle 110 \rangle$ diamond nanoneedles and microneedles. Figure 7(c) shows a large-area single-crystal $\langle 111 \rangle$ diamond thin film which has grown epitaxially with the (0001) sapphire substrate with a following epitaxial relationships: $\langle 111 \rangle$ dia // $\langle 0001 \rangle$ sapphire out of the plane, and in plane $\langle 110 \rangle$ dia // $\langle -2110 \rangle$ sapphire. According to the domain epitaxy paradigm 19 {110} half planes match with 20 (-2110) planes of sapphire to accommodate the planar lattice misfit.[13] These results are consistent with HRTEM, as shown earlier in Figure 4(a).

By using a copper template,[9,10] which is lattice matched with diamond without any alloying effects, we are able to grow epitaxial microneedles, as shown in Figure 8(a). A comparative EBSD patterns from the underlying copper template and diamond microneedles establish the epitaxial nature of these structures.

Figure 8(b) shows the formation of a faceted pillar which is surrounded by {100} and {110} planes.

The residual amorphous carbon can be etched away by oxygen plasma, and we can study the details of formation nanoneedles and microneedles. Figure 9(a) illustrates that nanoscale perturbation sets in the Q-carbon liquid, which was quenched in this case. Figure 9(b) and 9(c) shows the formation of nanoneedles and microneedles from the Q-carbon phase. The Raman studies from these etched samples show very clean spectra without any presence of residual amorphous peaks, as shown in Figure 10.

Mechanism of Nanoneedle and Microneedle Formation.

The formation of nanoneedles microneedles with diameter 80–500 nm and length 2,000–3,000 nm is shown in Figure 6. From laser–solid interactions and heat flow calculations,[8] we estimate melt lifetime around 250 ns. The formation of such long microneedles will require growth velocities of the order of 5–10 ms^{-1} . We propose that the formation of microneedles

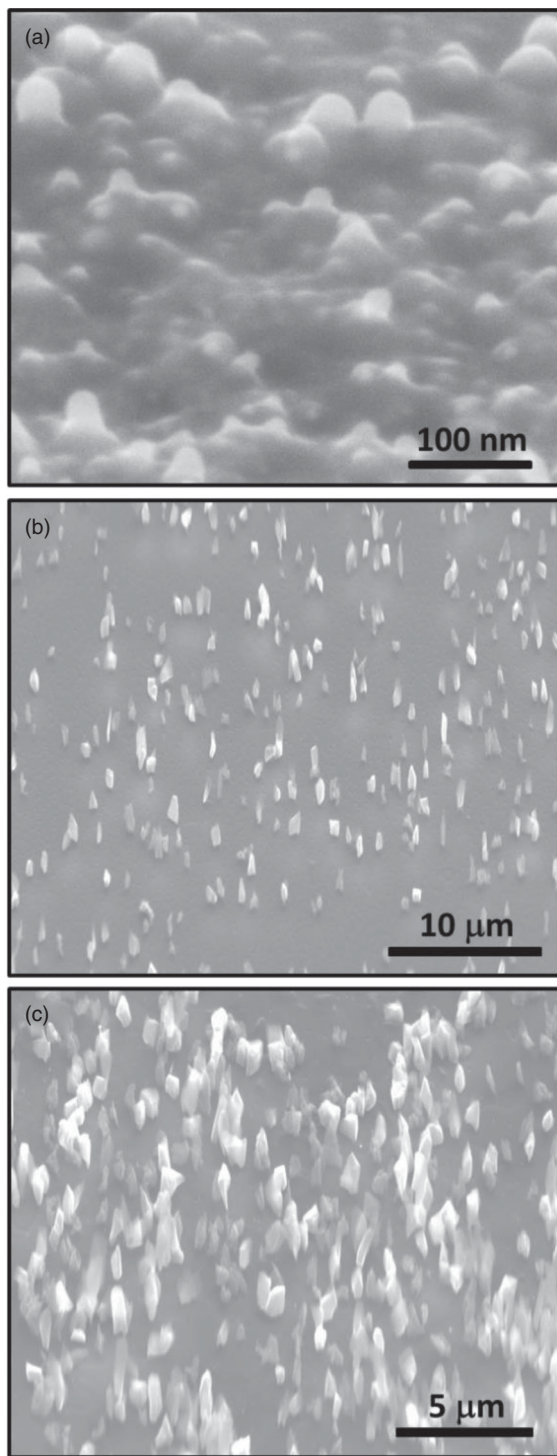


Figure 9. SEM micrographs of (a) nanodiamonds and (b) and (c) microdiamonds formed from Q-carbon after etching process.

occurs by rapid explosive recrystallization, where nanodiamonds nucleate from the Q-carbon and grow rapidly by liquid-mediated explosive recrystallization [5] with liquid-phase diffusivities of the order of $10^{-4} \text{ cm}^2 \text{ s}^{-1}$.

When carbon melts around 4,000 K in a highly undercooled state near the carbon film/sapphire interface,

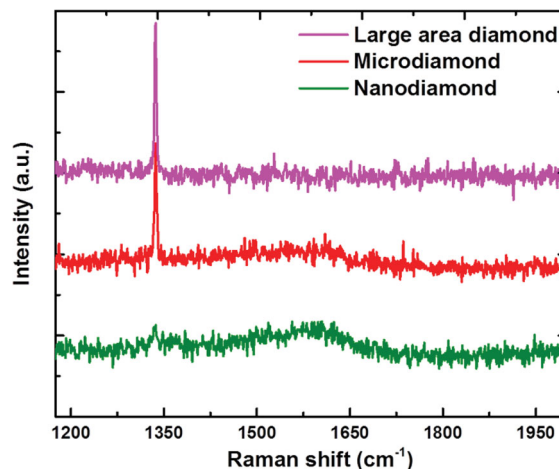


Figure 10. (Colour online) Raman spectroscopy of nanodiamond, microdiamond and large-area thin films using 633 nm laser excitation wavelength.

there is a reduction in volume or shrinkage. Since the carbon in the molten state is metallic; therefore, carbon atoms assume a closed packed structure, which can be quenched into the Q-carbon. This shrinkage and internal melting result in the formation of bubbles which burst out and diamond microneedles and nanoneedles grow out of these areas, depending on the size of the bubble. The length of a nanoneedle or a microneedle can be determined by growth velocity in the liquid phase, which is given by $v = K_s T_m / ((D\tau)^{0.5} \rho L)$, K_s is thermal conductivity of sapphire ($5.65 \text{ W m}^{-1} \text{ K}^{-1}$), T_m is the melting point of carbon (4,000 K), D is the thermal diffusivity ($1.0 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$), ρ is mass density of liquid carbon (3.5 g cm^{-3}) and L is latent heat of carbon ($8,000 \text{ J g}^{-1}$). Substituting these values, a rough estimate of the growth velocity is obtained to be $2\text{--}3 \text{ ms}^{-1}$, giving the length of microneedle about a micron.[8] The undercooling values for amorphous diamond-like carbon are considerably higher than those achieved during melting of crystalline carbon such as highly oriented pyrolytic graphite samples, which did not yield diamond. Since heating and quenching rates are a strong function of laser and substrate variables, the formation of Q-carbon is a strong function of laser substrate variables. For example, thermal conductivity of the substrate plays a critical role in the formation of Q-carbon.[14–18]

In summary, the formation of Q-carbon is achieved, when amorphous carbon films are heated to about 4,000 K and melted and quenched rapidly. This super undercooled state of carbon is about 1,000 K below the melting point of carbon, as shown in the modified phase diagram of carbon. We have achieved synthesis and processing of nanodiamonds, microdiamonds and microneedles at ambient pressure and atmospheric pressure in air. Single-crystal thin films are formed, when underlying (0001) sapphire or (001) copper can

provide a template for diamond epitaxy by plane or lattice matching. The irradiation with ArF Excimer laser pulses (wavelength 193 nm or photon energy of 6 eV and pulse duration of 20 ns) leads to confinement of laser energy and selective melting of diamond-like carbon films. This nanosecond pulsed laser melting of amorphous carbon can lead to a highly undercooled state which can be quenched into a new state of Q-carbon from which nanodiamonds, microdiamonds and microneedles are formed. These structures from practical and inexpensive sapphire and glass substrates can be conveniently harvested and substrates recycled. We can scale-up the formation of nanoneedles and microneedles as the single nanosecond laser pulse yields to significant quantities of these structures because of rapid processing in the liquid phase. We have made extensive Kelvin Probe Force Microscopy measurements to show reduced surface potential and enhanced field emission associated with Q-carbon, nanoneedles and microneedles.[6] The carbon deposition and LA steps can be integrated easily in a single-chamber environmentally friendly processing. These diamond nanoneedles and microneedles can be easily harvested as they are embedded into amorphous carbon, which can be easily etched using oxygen plasma in the same chamber.

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