Oriented single-crystal diamond cones and their arrays

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One of the major problems in material science has been the difficulty in modification of the most endurable material, diamond, due to its extreme hardness and chemical inertness. Here, we report the development of a conical structure of diamond by performing bias-assisted reactive ion etching in hydrogen plasma. The diamond cones produced by this method are uniformly distributed over large areas on silicon substrates. Each cone was identified to be a single crystal with an apical angle as small as 28° and a very sharp tip (tip radii ~2 nm). Their [001] axes are perpendicular to the substrate surface and parallel to each other. Such striking structures of individual single-crystal diamond cones and their arrays, in addition to their scientific value, may lead to a breakthrough in the design of high-performance mechanical and electronic devices. [DOI: 10.1063/1.1568546]

The potential application of materials depends not only on their intrinsic physical and chemical properties, but also on their surface geometries in which they appear. The special geometrical configurations of many materials, for example, with conical structure, may provide the properties that cannot be observed in either their bulk or their film forms.[1,2] Conical arrays have been suggested in designs of many instruments, such as controlled thermonuclear fusion devices,[3–5] absorbers in solar cells,[6,7] and cold cathodes in field-emission devices.[8] Such applications, however, require materials enduring harsh operation conditions. Diamond, with its "record properties," including the highest hardness, the highest thermal conductivity, outstanding chemical inertness, wide bandgap semiconducting property, and negative electron affinity (NEA)[9] prepared in conical forms can serve in similar applications and ensure some unique applications in mechanics, chemistry, and electronics. Indeed, much effort has been devoted to develop diamond in tip formats, and the preliminary work has already shown some advantages in practical applications. For instance, sharp silicon probes coated with chemical vapor deposition (CVD) polycrystalline diamond films[10,11] and polycrystalline diamond pyramids made by a molding technique[12] have been used in scanning probe microscopes (SPM) and have shown a significantly higher dynamic range than any probes known to date. It was also demonstrated that coating silicon tips with diamond could dramatically improve the emission parameters, including the emission threshold, maximum emission current density, current stability, and reproducibility.[13] However, such polycrystalline diamond tips had rough surfaces, and were either fragile in their surface coating forms or had large apical angles in their bulk (pyramid) form, which limited the device performance especially in the case of probes used in SPM instruments.

We have developed an interesting structure made of single-crystal diamond cones characteristic with very high aspect ratio, nanotip radius, and high uniformity over large areas. The experiments were performed in a commercial ASTeX® microwave plasma CVD reactor equipped with a 1.5-kW microwave generator. The fabrication process of diamond single-crystal cones is based on two fundamental steps: (i) deposition of diamond films serving as input materials for (ii) subsequent bias-assisted reactive ion etching (RIE) in a hydrogen plasma that is responsible for emerging the conical structure. In accord with our previous work,[14] pyramidal-shaped [001]-textured diamond films were first deposited on (001) silicon wafers 3 in. in diameter using bias-enhanced nucleation and maintaining the alpha growth parameters[15] close to 3. An *in-situ* bias-assisted reactive ion etching process was then applied in a subsequent step for the cone formation. Hydrogen was fed only into the microwave reactor at a gas flow rate of 200 sccm to maintain the reactant pressure at 40 Torr. The input microwave power was 1500 W and the substrate temperature was 850 °C. A negative substrate bias of −400 V was applied to the substrates throughout the etching process, inducing a bias current of 140 mA. The etching of the textured diamond films under such conditions took 40 min.

The crystallographic orientation of the diamond films synthesized in step (i) plays a decisive role for the formation and crystalline nature of the diamond cones produced in step (ii). The [001]-textured pyramidal-shaped diamond films, as shown by the scanning electron microscopic (SEM) image in Fig. 1(a), yielded an array of the sharpest tips with a uniform apical angle. The majority of diamond grains had their [001]-axes perpendicular to the substrate surface and most of them had their [110] axes parallel to each other. After etching, the samples were observed by SEM in both plain and cross-sectional views. It was found that the pyramidal diamond grains have been converted to conical tips entirely, and each cone has a smooth surface, as illustrated in Fig. 1(b). The tips are highly uniform in both size and apical angle. Raman spectra collected from the array of these tips indicate their diamond nature. The low-magnification transmission electron microscopic (TEM) image of a typical diamond tip, in

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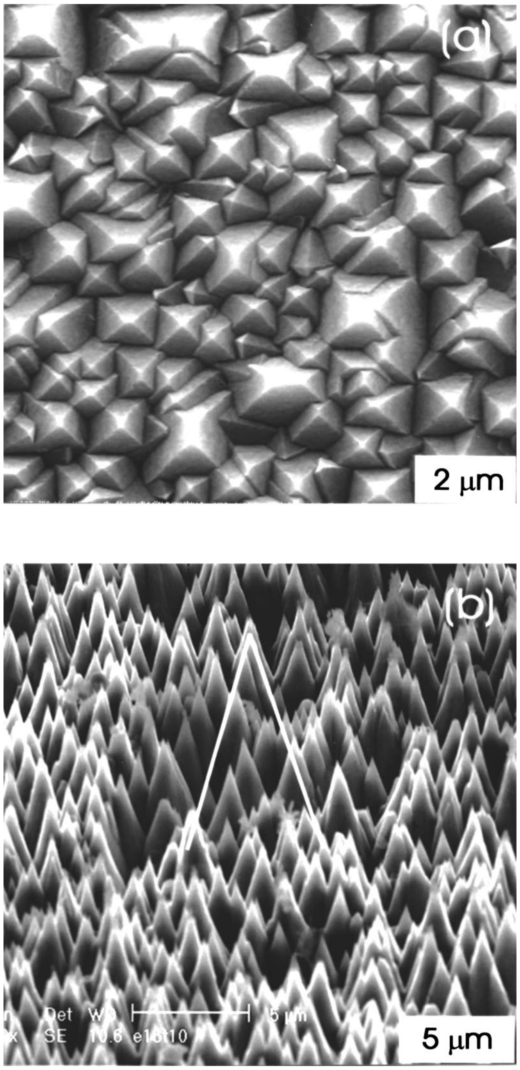

FIG. 1. SEM images of (a) an [001]-oriented pyramidal-shaped diamond film prepared for the fabrication of (b) a single-crystal diamond cone array. Image (b) was collected from a sample tilted in an angle of 45° towards the SEM detector. Note that nearly all diamond cones are uniform in both size and aspect ratio.

Fig. 2, and corresponding transmission electron diffraction pattern, as an inset in Fig. 2, demonstrate the tip sharpness (28°) and its single-crystal character. An overall observation of the bright-field image in Fig. 2 shows crystal defects. The crystal defects, mainly microtwins and stacking faults (black lines within the tip grains), are two-dimensional defects lying on the {111} lattice planes. These crystals with the evident defects have their [011] axes parallel to the electron beam and perpendicular to the image plane. The defect orientation of about 54.8° to the substrate surface (as shown in the figure) indicates that the axes of the single-crystal cones are parallel with the [001] crystal direction (normal to the substrate surface), like the original pyramidal diamond grains subjected to etching. A thin surface layer, in Fig. 2, with a uniform thickness of 7 nm, is amorphous carbon formed by ion bombardment during the etching procedure, and can be removed by reactive plasma etching in hydrogen if desired.

CVD diamond films grow in a columnar structure forming textured crystal orientation with grain boundaries as described by the Volmer–Weber growth model. Unlike crystal

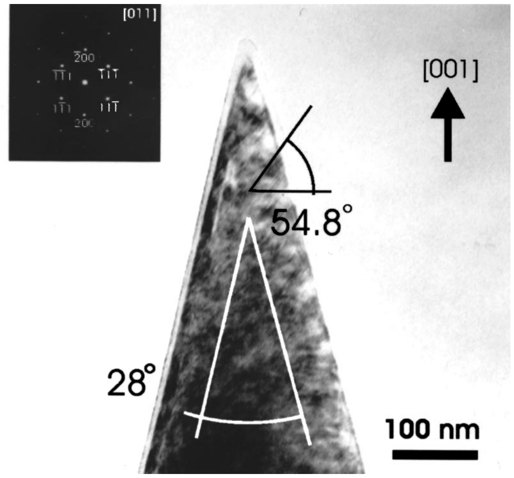

FIG. 2. Low-magnification TEM image of a single diamond cone elucidating its sharpness and orientation. The corresponding transmission electron diffraction inserted indicates its single-crystal nature.

bulk, the columnar (grain) boundaries confine sp^2-atomic configuration or defective sp^3 atomic bonding, which are believed to be essential for the formation of diamond cones. In the bias-assisted RIE process [step (ii)], the hydrogen ions induced in the microwave plasma are accelerated by the electrical field across the plasma sheath to the biased substrate and produce an ion flux (ion bombardment) in parallel to the normal of sample surface. The ion bombardment contributes to the localized conversion of diamond to graphitic or amorphous phases (as evidenced by the amorphous carbon coverage of diamond cones in Fig. 2), which further promotes chemical etching with plasma activated atomic hydrogen. Detailed study the NEA of polycrystalline diamond shows that the higher electron intensities are emitted from defective sites or graphitic/amorphous phases confined in grain boundaries.[13] The unevenly distributed electron emission then induces inhomogeneous distribution of positive space charge, plasma sheath, and electric field. As a result, the ion bombardment is regionally increased, and thus both physical (ion bombardment) and chemical (activated atomic hydrogen) preferential etching is enhanced in the grain boundary zones. The original pyramidal [001] textured structure is then continuously sharpened by gradually removing diamond material with preference to the peripheral regions of crystallites via the localized increase in current density to yield, finally, arrays of single-crystal diamond cones.

The apical tip radius shown in the high-resolution TEM image (Fig. 3) is measured as small as 2 nm, which represents approximately 10 carbon atoms only along the tip radius. Inheriting the intrinsic properties of diamond, the single-crystal diamond cones/cone arrays with the highest aspect ratio and the smallest tip radii ever reported, may have great advantages for the applications in high-resolution SPMs as recording probes, nanoindenters, nanomachining, and electron field-emission devices.

In summary, we have developed a diamond nanostructure consisting of arrays of sharp single-crystal diamond cones. The cones are uniform in both apical angle and cone size. Their [001] axes are perpendicular to the substrate surface and parallel to each other. The tip radii of the cones are

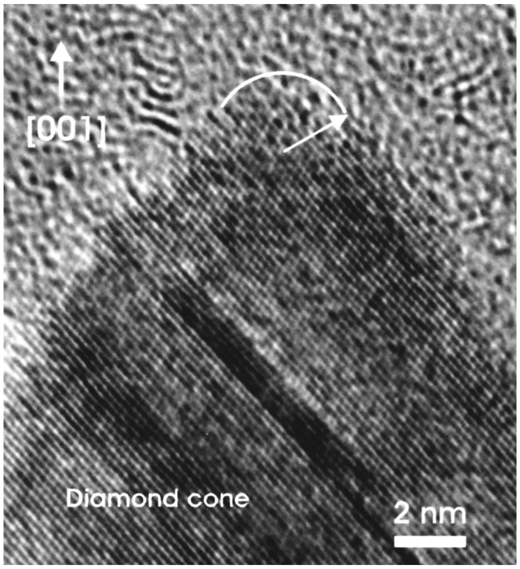

FIG. 3. High-resolution TEM image of a tip apical region shows the apical radius to be about 2 nm.

as small as 2 nm. The mechanism of the cone formation has been understood in terms of the processes related to the uneven distribution of plasma sheath, space-charge formation, and current density configured by the diamond columnar structure. Hence the methodology developed here is also applicable for manufacturing conical structures based on a wide range of materials including silicon carbides and nitrides.

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