ULTRA-HIGH-VOLTAGE TRANSMISSION ELECTRON MICROSCOPE
OBSERVATION OF DIAMOND PARTICLES GROWN FROM PLASMA-ASSISTED
CVD

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An ultra-high voltage transmission electron microscope has been used to observe the internal and interfacial structures of diamond particles synthesized by plasma-assisted CVD in cross-section for the first time. At lower CH\textsubscript{4} concentrations, 0.5\% and 2.0\%, diamond particles are half polyhedra formed by single crystals or twinned crystals. In these polyhedra, line defects composed of micro-twin lamellae or stacking faults are observed. The particle directly contacts the Si substrate at base center without an intermediate layer within the resolution limit. At higher CH\textsubscript{4} concentrations, for example at 4.0\%, the particles are half balls composed of fine crystals. These fine crystals are enveloped by amorphous carbon. An amorphous layer is observed on the surface of the diamond particles which becomes thicker on the particles deposited at higher CH\textsubscript{4} concentration.

1. Introduction

In recent years, diamond thin films have been greatly improved by using techniques such as thermo-filament CVD\textsuperscript{1}-\textsuperscript{3} and plasma-assisted CVD\textsuperscript{4}-\textsuperscript{7}. Diamond has a lot of extraordinary properties, such as a wide band gap (5.5 eV) and high thermal conductivity, which are two main advantages for fabricating high-temperature semiconducting devices. Reports on the semiconductivity\textsuperscript{8} and visible luminescence\textsuperscript{9} of synthetic diamond thin films have taken the first step for the realization of wide applications to semiconducting devices.

Among the techniques for characterizing synthetic diamond, Raman scattering, X-ray and RED have been used in identifying diamond phases, and SEM (scanning electron microscope) and TEM (transmission electron microscope) studies have shown the morphologies. Among these studies, one well-known phenomenon is the effect of the methane molar concentrations in H\textsubscript{2} on the morphologies of obtained particles and films: with increasing methane concentration, the morphologies of synthesized particles turn from euhedral to ball-like\textsuperscript{9}. There have been some studies on the morphological features of the euhedral particles; the results showed that they were formed of single crystals or twinned particles composed of 2, 5, and 20 single crystal units\textsuperscript{8}. The ball-like particles deposited at higher CH\textsubscript{4} molar concentrations have not been studied, even though studies on these particles might lead to deeper understanding of the deposition mechanism; the coexistence of the diamond phase and amorphous phase is an important point when studying the synthetic process. Obviously, if we can observe the internal micro-structures of diamond particles, it will be helpful in truly understanding the morphologies of synthesized particles and the crystal growth process. Structures of thin films are much more complex to study compared with those of particles; in addition, observations of particles are more informative for investigating the internal and interfacial structures at early stages.

In this paper, an ultra-high-voltage electron microscope (TEM) [HU-3000] operated at 2000 kV has been used in studying diamond particles synthesized using plasma-assisted CVD at different CH\textsubscript{4} concentrations. Particularly, a cross-sectional

\textsuperscript{8}Science and Technology of New Diamond, edited by S. Saito, O. Fukunaga, and M. Yoshikawa, pp. 327–332.
TEM technique is introduced for the first time to study micro-diamond particles in order to investigate the internal and interfacial structures.

2. Experimental

Diamond particles were deposited on a Si(100) wafer substrate using a microwave plasma-assisted chemical vapor deposition (CVD) technique which has been reported previously\(^7\). The reaction gas was CH\(_4\) diluted with H\(_2\), and the molar concentrations of CH\(_4\) were 0.5\%, 2.0\%, and 4.0\%. The substrate temperatures were 750–850°C. Depositions were carried out for 8.0, 2.0, and 2.0 hours for 0.5\%, 2.0\%, and 4.0\% respectively, to get about 1 \(\mu\)m particles for the sake of convenience in observation. The particles were investigated by SEM, reflection electron diffraction (RED), and Raman scattering to show external forms and to identify the diamond phase. Then the obtained particles were observed in horizontal cross-sections using ultra-high-voltage TEM [HU-3000] operated at 2 MV and a high-voltage TEM [H-800] operated at 200 kV. For horizontal sectional observations, specimens were prepared by chemical thinning. For cross-sectional observations, the specimens were first prepared by mechanical lapping, followed by Ar beam thinning at low glancing angles.

3. Results and discussions

SEM was used to investigate the morphologies of the obtained diamond particles. Figures 1(a), (b) and (c) show the SEM images; the molar concentrations of these samples are 0.5\%, 2.0\% and 4.0\%, respectively. These particles have grown to be almost the same size: about 1 \(\mu\)m. Evidently, as the concentrations of methane increase, the morphologies of synthesized diamond particles are changed, from well-shaped polyhedra which are bounded by \{111\} and \{100\} facets, to spherical particles which have no faceted planes.

TEM observations were then done of these particles with different CH\(_4\) concentrations from both horizontal and cross-sectional views.

The internal features of the particles on the substrate are studied according to their methane concentrations, since this strongly influences the external features.

3.1 At lower methane concentrations

From SEM images, diamond particles deposited at relatively lower methane concentrations, 0.5\% and 2.0\%, are of well-defined habits. Figures 2(a) and (b) are examples of TEM images taken of the particles deposited at 0.5\% CH\(_4\) molar concentration. The horizontal sectional image of Fig. 2(a) is a top view of an icosahedron; five upper \{111\} facets of the particle appear clearly. The different contrasts among these five parts are caused by different diffraction conditions. The black parts satisfy the Bragg condition while the white ones do not. A few line defects can be observed, which are found to be parallel to the two sides of each triangle, crossing themselves.

Figure 2(b) is a cross-sectional view of a particle deposited at 0.5\%. The sharper contour indicates that it is a half polyhedron with well-defined habits. This cross-sectional image of the diamond particle is constructed by contours of two \{111\} facets at the top and two \{111\} facets at each side of the particle, which cross completely without gaps between their interfaces. Some line defects are also observed from this cross-sectional image.

Another example is shown in Fig. 3, which is the upper part of a particle deposited at 0.5\% CH\(_4\) concentration, a bicrystal with well-defined habits.

\(\text{Fig. 1. Scanning electron microscope (SEM) images of diamond particles formed by plasma-assisted CVD at (a) 0.5\%, (b) 2.0\% and (c) 4.0\% methane molar concentrations.}\)
indicates that there was no obvious damage to our carefully prepared specimen during Ar beam thinning within the resolution limit of the microscope.

As the CH₄ concentration increases to 2.0%, the line defect density becomes much higher in Fig. 4, which is taken from particles deposited at 2.0% CH₄ concentration. These line defects can be summed up as four families which emerge from the base center and end separately at the four edges. This fact, that line defects start to grow from the base center of the polyhedral particle, indicates that the diamond particle begins from one nucleus on the substrate, then grows concentrically to form a polyhedron, since those line defects are traces of crystal growth, although they do not always indicate the growth direction. The same growth behavior, the concentric growth, can also be observed in the image taken from 0.5% samples shown in Fig. 2 and we will see later that this tendency appears in the particles deposited at 4.0% CH₄ concentration as well.

On the silicon side near the interface, dislocations can be observed, and there is a series of fringe rings emerging from the interface. This indicates that a stress field exists associated with the interface.

Some detailed parts of CH₄ 2.0% particles are shown in Figs. 5(a) and (b) in cross-section. These specimens are so thin that the areal density of line defects becomes lower. Figure 5(a) is the upper part of a polyhedron, a family of near parallel line defects intersecting [111] facets of the particle is

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Fig. 2. Transmission electron microscope (TEM) images of diamond particles deposited at 0.5% methane molar concentration from (a) horizontal-sectional view and (b) cross-sectional view.

Fig. 3. Cross-sectional TEM image of the upper part of a particle deposited at 0.5% methane molar concentration.

The particle shows nearly perfect internal microstructure without obvious defects within the resolution limit of the electron microscope. The strips on the right part, parallel to the edges, are caused by thickness variations of the specimen. Figure 3

Fig. 4. Cross-sectional TEM image of a particle deposited at 2.0% methane molar concentration.
observed. As pointed out, these defects are not formed by ion milling, but are created within the particle itself during growth. These line defects are thought to be micro-twin lamellae and/or stacking faults parallel to the \( \langle 110 \rangle \) direction.

Figure 5(b) is the base center area of a particle. Though the thinner specimen leads to a lower line defect density as mentioned above, another type of less-straight, diffuse line defects becomes clear. A family of the defects ends at the interface between the particle and Si substrate, as shown in Fig. 5(b), and we do not find any intermediate layer at the base central interface. The diamond particles grow directly on the Si substrate, so an intermediate layer cannot be observed, at least not within the resolution limit of the microscope. Conversely, an intermediate layer which is about 2–3 nm in thickness is found at the off-center interface, as indicated by the arrow in Fig. 5(b). From Fig. 4, the same intermediate layer can also be observed; it continues from the off-center interface to as far as the free surface where no diamond particles are formed. We suppose that this is an amorphous layer formed during deposition. During plasma CVD discharge, a negative sheath potential is set up, and many kinds of ions and clusters bombard the substrate. This kind of bombardment transforms the Si surface from crystalline to amorphous. When a diamond particle grows over this layer, it is observed as an intermediate layer.

3.2 *At higher methane molar concentration*

At either 0.5% or 2.0% CH\(_4\) concentration, the morphologies of the particles are faceted by \( \{111\} \) and \( \{100\} \) surfaces, and the internal features are line defects composed of micro-twin lamellae or stacking faults. As the CH\(_4\) molar concentration increases to 4.0%, the SEM image of Fig. 1(c) shows that the particles are like spheres without observable facets. The external surfaces are uneven, with hills and valleys.

Figures 6(a) and (b) are horizontal and cross-sectional TEM images of particles deposited at 4.0% CH\(_4\) concentration. The particles appear as half-spheroids cut by the Si substrate, about 600 nm in diameter and about 310 nm in height. The horizontal TEM image shows that a “frill” of about 30 nm is found around the particle. Such coverage layers are observed in almost all the samples from either horizontal section or cross-section for all the CH\(_4\) concentrations, and it is thicker on the particles deposited at higher methane concentrations. As the observations were carried out at very high vacuum, about 10\(^{-7}\) Torr, this layer is too thick to be a contamination layer. Raman scattering indicates that an amorphous phase exists for even those particles with well-defined habits, though the broad peak which indicates the amorphous phase goes down when the CH\(_4\) concentration is low. Of course the amorphous structure can be surmised in the body of the crystals, but from the results of TEM observation, the much greater possibility is that it exists at the surface layer, or at least that there is more amorphous phase in the surface layer than in the body of the particle. This observation is very interesting because it may lead us to understand some important problems concerning the mechanism of diamond synthesis using plasma-assisted CVD.

Well-defined habits cannot be found in either
reasonable explanation is that diamond phase may be transformed from the amorphous phase.

4. Conclusions

(1) At lower molar methane concentrations, diamond particles are half polyhedra with well-defined habits. Line defects are observed in the particle bodies, and the defect density reduces as the CH₄ concentration decreases. These line defects are composed of micro-twin lamellae or stacking faults.

(2) A diamond particle grows concentrically from a base center where the diamond nucleates. The particle grows directly on the substrate without an intermediate layer on the base center area. An amorphous layer is observed on the off-center interface.

(3) On the Si side of the interfacial area, dislocations have been observed, and fringe rings are found to emerge from the interface.

(4) At higher CH₄ concentrations, the particles are half-spheres composed of fine crystals. These fine particles are enveloped by amorphous carbon.

(5) On the surface of diamond particles, an amorphous layer is observed. It is about several tens of nm and thicker on the particles deposited at higher CH₄ concentrations.

REFERENCES
