Vapor Deposition of Diamond Particles from Methane

To cite this article: Seiichiro Matsumoto et al 1982 Jpn. J. Appl. Phys. 21 L183

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Vapor Deposition of Diamond Particles from Methane

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(Received February 9, 1982; accepted for publication March 20, 1982)

Microcrystalline diamond has been formed on silicon or molybdenum substrates by vapor deposition from a gaseous mixture of methane and hydrogen. Cubo-octahedral or multiply-twinned crystals were obtained. The structure of the deposits was identified by electron diffraction and Raman scattering.

The considerable effort that has been devoted to the synthesis of diamond has been motivated by the unique combination of properties exhibited by this material. These properties include great hardness, high thermal conductivity, high electrical resistivity, optical transparency and semiconductivity induced by impurity doping. Besides high pressure techniques, currently used for commercial production of diamond, attempts have been made to make diamond by chemical vapor deposition (CVD),\(^1\)\(^\text{–}\)\(^3\) ion-beam techniques,\(^4\)\(^\text{–}\)\(^6\) and plasma-induced vapor deposition.\(^7\)\(^\text{–}\)\(^9\)\(^\text{–}\)\(^1^0\) The carbon films obtained by these techniques are often termed diamondlike, since they show, to some extent, properties similar to those of diamond. Unambiguous identification of the structure of these films, however, is difficult owing to the amorphous nature of the films or the appearance of forbidden reflections and of reflections from structures other than diamond in electron diffraction.\(^5\)\(^,\)\(^6\)\(^,\)\(^8\)\(^,\)\(^9\)

On the other hand, Deryagin et al.\(^1^1\) reported that octahedral or cubo-octahedral diamond crystals can be grown on non-diamond substrates such as copper and gold by chemical transport in a closed system. Recently, a more detailed account of the growth features, characterization and possible growth mechanism has been given by Spitsyn et al.\(^1^2\) Diamond crystals were grown on diamond, silicon, tungsten and molybdenum at growth rates of up to 5 \(\mu\)m/h. The importance of the role played by atomic hydrogen was pointed out, but the details of the deposition technique were not given. In this paper, we report that diamond crystals can also be grown on non-diamond substrates by CVD in a flow-system.

Deposition was carried out by passing a mixture of gaseous methane and hydrogen through a deposition chamber, in which a tungsten filament was mounted near the substrate, as shown in Fig. 1. Silicon wafers or molybdenum plates were used as the substrates. Observations by SEM were made with the deposits obtained under the following conditions: methane concentration, ca. 1 vol %; total gas pressure, 10–100 Torr; flowrate, ca. 10 ml/min, temperature of deposition chamber, 800–1000°C; filament temperature, ca. 2000°C. The temperature of the deposition chamber was measured by a thermocouple in contact with the silica substrate holder, as shown in Fig. 1. Thus, the temperature at the substrate surface may be higher than the temperature measured by the thermocouple as a result of radiation from the filament.

After deposition runs of 3 hours' duration, diamond particles up to 3 \(\mu\)m were formed as shown in Fig. 2(a). There appeared to be little difference in the growth characteristics between silicon and molybdenum substrates. Multiply-twinned crystals as well as cubo-octahedral crystals were observed. The morphologies resemble that observed with crystals deposited by chemical transport in a closed system.\(^1^1\)\(^,\)\(^1^2\) Film-like regions are also formed by the contact of crystals, as Fig. 2(b) shows. The density of nucleation appears to depend strongly on the substrate conditions, and preferential growth along scratches or edges was often noted.

The structures of the deposits were identified by reflection electron diffraction. As Fig. 3 shows, spotted rings were observed; the pattern consists of diffraction spots from more than a hundred particles. As Table I shows, the \(d\)-values obtained from the diffraction rings are in good agreement with the reported values for cubic diamond except that the 222 double diffraction ring appears in the diffraction pattern.

Raman scattering of the deposits was also observed as support for the structural identification. The spectra were recorded at room temperature using a Spex Ramalog.
Fig. 2. Scanning electron micrographs of diamond deposited on silicon. (a) Diamond particles deposited at 790°C (micrograph taken by tilting substrate). (b) Film-like region formed at 880°C.

Table I. Comparison of observed interlayer spacings with reported values.

<table>
<thead>
<tr>
<th>Observed</th>
<th>Reported (ASTM 6-675, Diamond)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d$ ($\text{&quot;A}$)</td>
</tr>
<tr>
<td>2.06</td>
<td>s</td>
</tr>
<tr>
<td>1.26</td>
<td>s</td>
</tr>
<tr>
<td>1.08</td>
<td>s</td>
</tr>
<tr>
<td>1.03</td>
<td>w</td>
</tr>
<tr>
<td>0.89$_2$</td>
<td>w</td>
</tr>
<tr>
<td>0.81$_8$</td>
<td>m</td>
</tr>
<tr>
<td>0.727</td>
<td>m</td>
</tr>
<tr>
<td>0.685</td>
<td>m</td>
</tr>
<tr>
<td>0.633</td>
<td>w</td>
</tr>
<tr>
<td>0.603</td>
<td>m</td>
</tr>
</tbody>
</table>

* Calculated from the reported value of $a_0=3.5667$ Å.

1401 spectrometer with a back-scattering geometry. The 488.0 or 514.5 nm lines of an argon ion laser or the 441.6 nm line of an He–Cd laser were used for excitation. In the Raman-shift range of 300–2500 cm$^{-1}$, the spectra consist of Raman peaks due to diamond as well as to the substrate, and background due to weak luminescence, as Fig. 4 shows. Raman scattering from to amorphous

![Fig. 3. Reflection electron diffraction of diamond particles deposited on silicon.](image)

![Fig. 4. Raman spectrum of as-grown specimen on silicon substrate. 441.6 nm line of He–Cd laser was used for excitation.](image)
carbon or silicon carbide was also observed in some of the specimens. Closer examination showed that the Raman line of diamond is located at 1334.5 cm$^{-1}$ with a full width at half maximum (FWHM) of about 10 cm$^{-1}$ (measured at the spectral slit width of 3 cm$^{-1}$). Single crystals of natural diamond or diamond synthesized under high pressure and high temperature using a metal catalyst give the Raman peak at 1332.5 cm$^{-1}$ with an FWHM of about 3 cm$^{-1}$.

This difference suggests that the crystals obtained in the present experiment have an internal strain and structural imperfections which are absent in common forms of diamond.

Acknowledgement

The authors are grateful to Mr. M. Tsutsumi for performing the SEM observations.

References


