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Morphology of diamonds prepared in a combustion flame

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Diamonds were prepared on molybdenum substrates in a C_2H_2–O_2 combustion flame in the ambient atmosphere. The morphology of diamonds obtained were characterized with a scanning electron microscope (SEM), Raman spectroscopy, and X-ray diffraction. Changes in the morphology of the deposits on the substrate can be observed. The differences in the growth rates between {100} and {111} planes are discussed from the viewpoint of crystal habits.

1. Introduction

The combustion flame is widely known to be a kind of thermal plasma which consists of thermo-ionizations of burnt gases [1]. There has been active research into combustion flames under reduced pressure and in the soot formation since the early 1950s [2]. Hirose *et al.* first succeeded in preparing diamonds in a combustion flame [3]. The typical structure of the C_2H_2–O_2 flame [4] is shown in Fig. 1. It is composed of three regions. (a) The primary reaction zone, where premixed C_2H_2 and O_2 gases are heated to the ignition temperature. (b) The acetylene feather, which only appears in the case of excess C_2H_2 and has various radicals such as C_2, C_2H, CH_3, CH and C [5]. The length of the feather is very sensitive to the gas flow ratio. Diamonds are only synthesized in this feather [6]. (c) The secondary reaction zone, where C_2H_2 gas completely burns to stable molecular species by the air which is entrained from the atmosphere.

In this paper, the morphology of diamonds prepared in a C_2H_2–O_2 combustion flame are presented, and the differences in the growth rates of {100} and {111} planes are discussed from the changes of crystal habits.

2. Experimental procedure

The experimental arrangement is schematically shown in Fig. 2. The acetylene–oxygen burner used was a conventional one. The C_2H_2 gas was welders' grade (91.5 to 98.5%) and the purity of O_2 gas was 99.99%. The flow rates of both gases were controlled by mass flow meters. A molybdenum plate of 10 mm in diameter was used as a substrate. It was set on a water-cooled holder made of copper. The spacing between the burner nozzle and the substrate was 10 mm. The substrate temperature (T_s) was monitored with an infrared pyrometer which was insensitive to the flame emission because the monitored wavelength was limited from 0.8 to 1.1 μm. The experimental conditions were as follows. The flow rates of C_2H_2 and O_2 gases were 2.45 and 2.25 SLM, respectively, and the flow ratio of C_2H_2 to O_2 gas was 1.09. The length of the feather was approximately 17 mm. T_s was approximately 1000 °C at the centre of the substrate. There was a temperature gradient in the radial (R) direction on

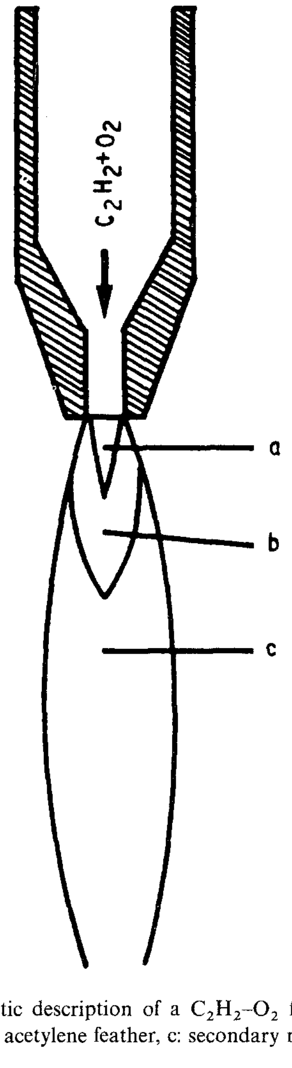

Figure 1 Schematic description of a C_2H_2–O_2 flame (a: primary reaction zone, b: acetylene feather, c: secondary reaction zone).

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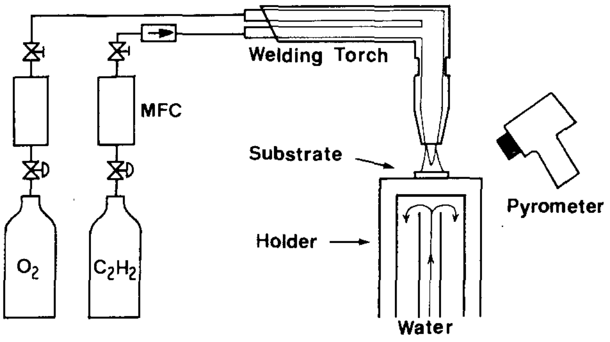

Figure 2 Schematic diagram of the C_2H_2–O_2 torch apparatus.

the substrate shown in Fig. 3. The diamond deposition took place within about 6 mm in diameter. T_s of the edge of the deposited area was, therefore, approximately 200 °C below that of the centre.

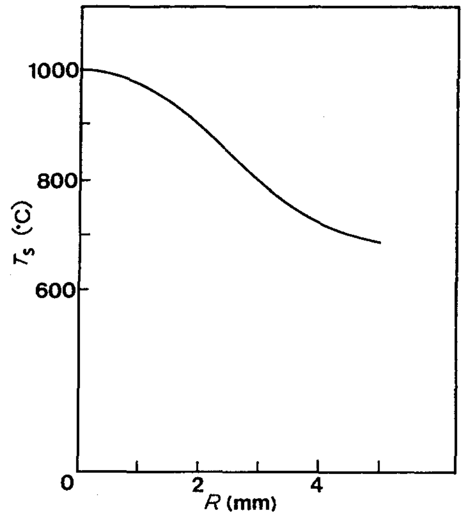

Figure 3 Distribution of substrate temperature in the radial direction on the substrate.

3. Results and discussion

Scanning electron micrographs (SEM) of diamond are shown in Fig. 4: (a) at the centre of the substrate ($R = 0$), the shape of diamonds is just like pyramid on which many pyramidal nucleations take place. These crystal planes are not smooth. (b) $R = 1$ mm, smooth {100} planes appear, however the other parts look like agglomerated powder which should be diamond-like carbon. (c) $R = 2$ mm, the polycrystalline film has shape crystal habits of {100} and {111}. The {111} planes seem to grow from the {100} planes. They may be twinned between {100} and {111}. (d) $R = 2.5$ mm, it is a polycrystal film which is composed of diamond particles with high crystallinity. As can be seen in Fig. 4d, the {111} planes mainly appear. Although {100} planes are present, the number of them is very much smaller than that of {111} planes.

Raman spectra in each part are seen in Fig. 5. From the centre to the edge of the substrate, the intensities of diamond peaks near 1333 cm^{-1} [7] strengthened, on the other hand, intensities of broad peaks due to double bond of carbon peak near 1550 cm^{-1} became weaker. This tendency agreed with the morphology of the deposits.

From the data of X-ray diffraction pattern (Fig. 6, Table I), the resultant lattice spacings are in good

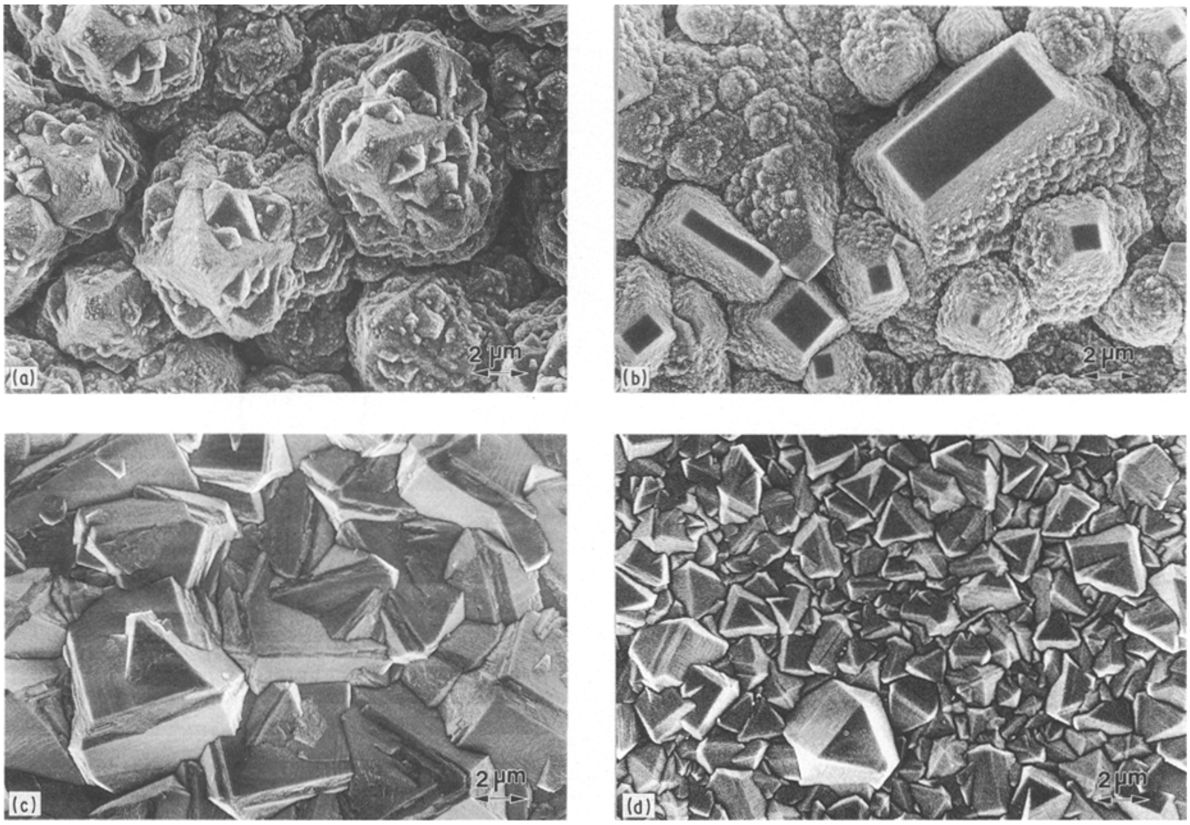

Figure 4 SEM images of diamonds deposited on a molybdenum substrate in the radial direction (a: $R = 0$ mm, b: $R = 1$ mm, *c*: R = 2 mm, *d*: R = 2.5 mm).

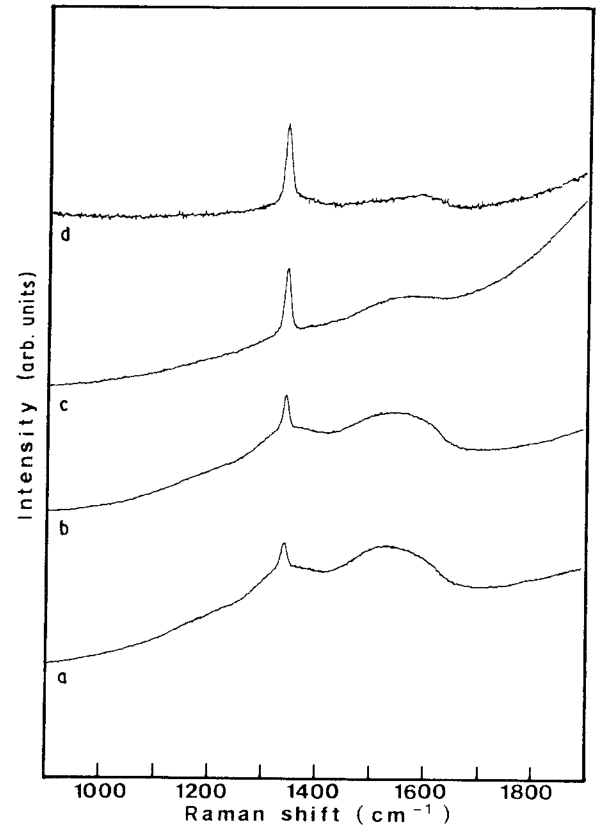

Figure 5 Change of Raman spectra from the centre to the edge on the substrate. (a: 0 mm, b: 1 mm, c: 2 mm, d: 2.5 mm)

agreement with the values reported for a diamond [8]. The diffraction from {331} was not clear, however, because of the relatively strong background of Mo_2C. Compared with the ASTM card, the disagreement of the relative intensities revealed a preferred orientation in the deposits. The lattice constant of the deposits calculated from these d values is 0.356 77 nm, and is in good agreement with the reported value [8] (0.356 67 nm). These results revealed that the deposits obtained were cubic diamonds which had, for instance, some defects such as carbon double bonds.

From the viewpoint of crystal growth, the crystal planes of slower growth rate finally remain. The morphological changes mentioned above, therefore, revealed that V_{100}/V_{111}, the ratio of growth rate of {100} to that of {111}, increased with the decrease of T_s in the radius direction on the substrate. This fact should be clear from the observation of diamond particles deposited on a non-polished substrate. Fig. 7 shows the resultant particles: (a) at the centre of the deposited area and (b) around the centre. The shapes of polyhedrons composed of {100} and {111} planes change in corresponding to the growth rates of each plane. Fig. 8 shows the results of calculations [9]. As V_{100}/V_{111} changes, the crystal habits change

TABLE I Observed interplanar spacings and reported values

Observed		Reported (ASTM 6-675)		
d (nm)	I_{obs}	d (nm)	I/I_1	hkl
0.206	100	0.206	100	111
0.1260	40	0.1261	25	220
0.1078	12	0.10754	16	311
0.0891	19	0.08916	8	400
—	—	0.08182	16	331

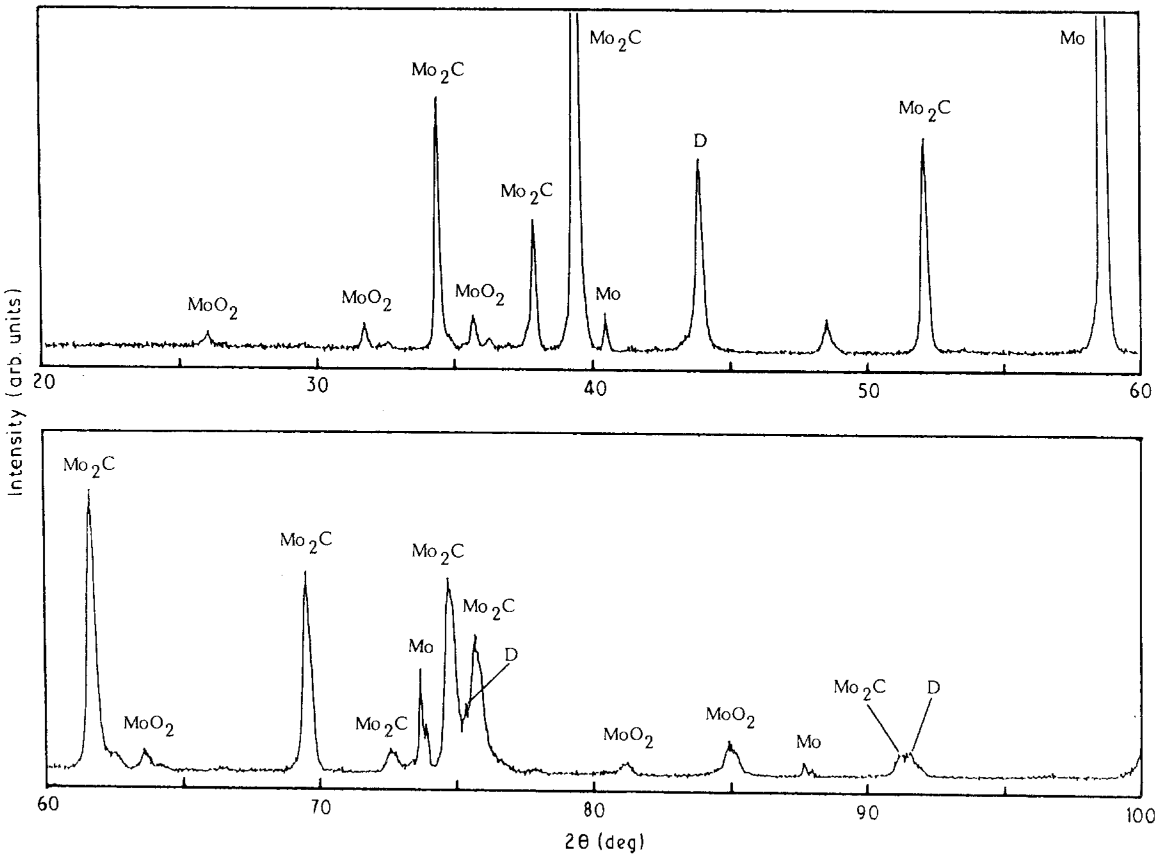

Figure 6 X-ray diffraction pattern of diamonds deposited on a molybdenum substrate. D denotes reflections of diamond.

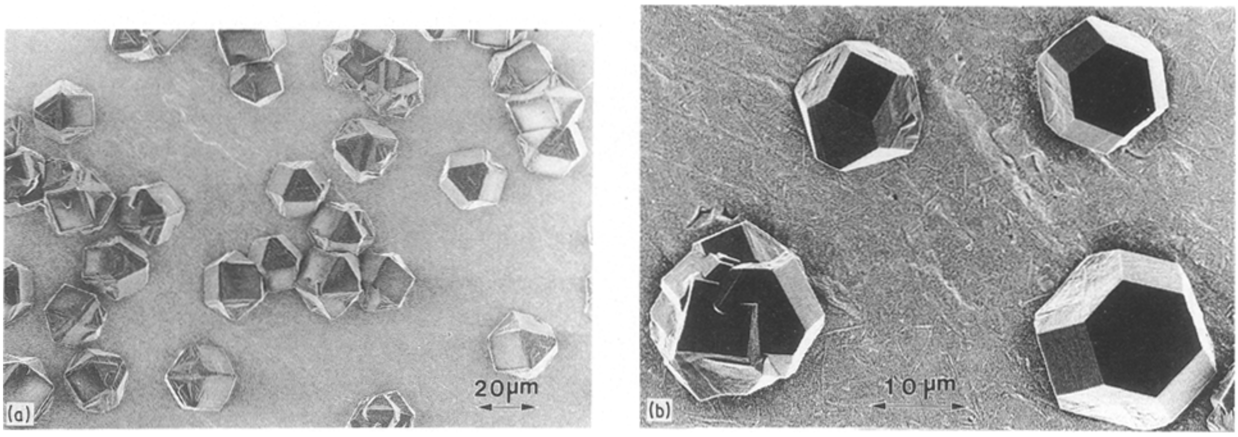

Figure 7 SEM images of diamond particles deposited on a non-polished molybdenum substrate (a: centre of the deposited area, b: around the centre).

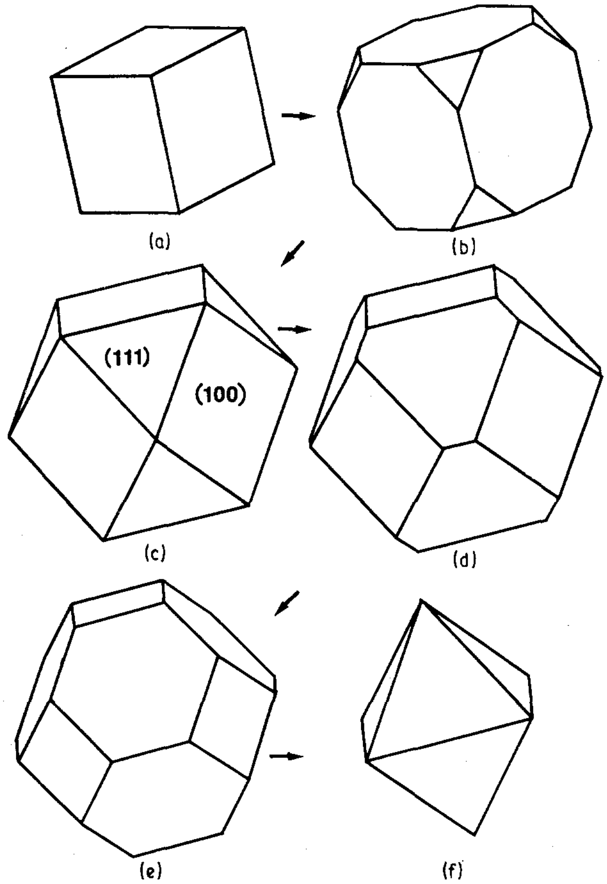

Figure 8 Change of crystal habits from the result of calculations (V_{100}/V_{111}, the ratio of growth rate of {100} to that of {111} (a: $1/\sqrt{3}$, b: 0.7, c: $\sqrt{3}/2$, d: 1, e: $2/\sqrt{3}$, f: $\sqrt{3}$).

from cubic ($V_{100}/V_{111} < 1/\sqrt{3}$) to octahedral ($V_{100}/V_{111} > \sqrt{3}$), via intermediate cubo-octahedral ($1/\sqrt{3} < V_{100}/V_{111} < \sqrt{3}$). The shapes of deposited particles at the centre were mainly (c) with rough planes. Around the centre, they were (d) and (e) with smooth planes. It was revealed, therefore, that the change of the ratio V_{100}/V_{111} was the same tendency mentioned above. This tendency was the same one in the morphology of diamonds synthesized by other chemical vapour deposition (CVD) methods [10, 11].

Growth steps appeared on crystal planes should be the strong suggestion of a mechanism of crystal growth. A lot of bunching steps on {100} planes were observed as shown in Fig. 9. The directions of the steps were parallel to the edges of planes. In some cases, there are clearly spiral steps as shown in Fig. 9 (b). These steps revealed that the crystal growth took place by the Frank mechanism [12], that is, it should take place by a spiral growth using a screw dislocation.

In summary

1. The morphological changes of diamonds deposited on a molybdenum substrate were observed in corresponding to the temperature gradient in the radial direction.
2. The relation between the ratio of growth rate of {100} to that of {111} and the substrate temperature was the same as in diamonds synthesized by other CVD methods.

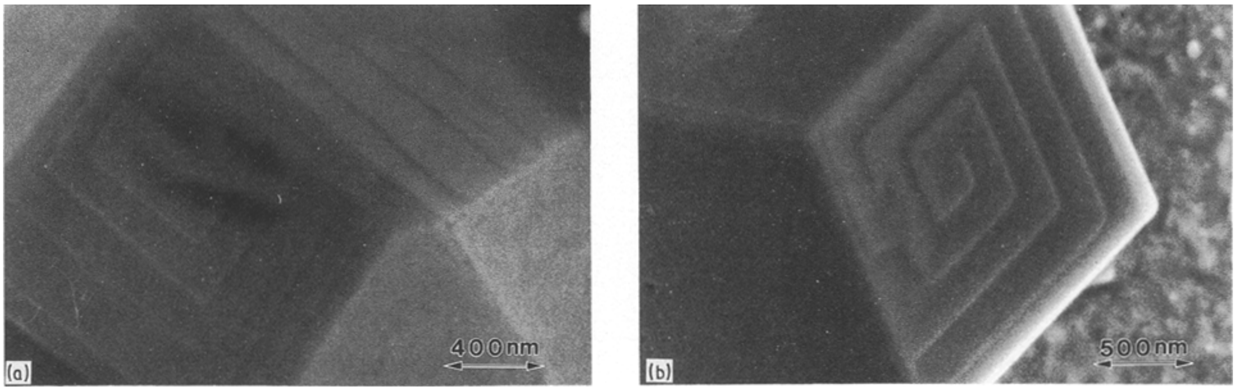

Figure 9 Typical examples of steps on {100} planes.

3. The spiral growth steps appeared on the {100} planes revealed that the crystal growth took place by the Frank mechanism due to a screw dislocation.

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