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Diamond deposition using an *X–Y* stage in a d.c. plasma jet chemical vapour deposition

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Diamond was deposited using the substrate scanning mode in a d.c. plasma jet of the Ar–H_2–CH_4 system. Film thickness profiles, SEM and Raman spectra of the diamonds obtained revealed that uniformity of film thickness, crystal size and crystal quality was improved, but the deposition rate decreased with the scanning speed and the crystal quality was worse than that made in the centre of the flame without scanning.

1. Introduction

The d.c. plasma jet method is known to give the highest deposition rate of diamond [1–3]. However, the deposition area is small and the radial gradients of film thickness and film quality are steep because of its small flame diameter in the usual torch. An attempt to improve the uniformity by applying bias voltage to a substrate was not so successful [4].

In a plasma spraying method with a d.c. plasma torch, which is widely used to coat high-temperature materials at high speed, it is usual to scan a torch or a substrate to achieve deposition over a large area or in a complicated shape. Therefore, we have tried here to deposit diamond over a larger area by scanning a substrate in d.c. plasma jet chemical vapour deposition (CVD). In addition, the scanning was expected to provide another way of controlling the substrate temperature. The results of the preliminary experiments are reported.

2. Experimental procedure

The torch used was the same as used before [2, 4]. The arc discharge between a tungsten cathode containing lanthanum oxide and a water-cooled copper anode generated a stream of Ar–H_2 plasma jet. Methane was introduced into this stream through a hole in the anode. A molybdenum substrate, 20 mm diameter and 1.5 mm thick, was set in a circular pit on a water-cooled copper plate. The diameter and depth of the pit were 20 mm and 0.5 mm, respectively. The substrate was prescratched with 5–10 μm diamond paste. This copper holder was placed on an X-Y stage and scanned two-dimensionally in a plane perpendicular to the plasma flame; other important experimental conditions are summarized in Table I.

The scanning mode used is shown in Fig. 1. The range of the scan was from − 9 to + 9 mm in both (X, Y) directions, and the origin of the coordinates of this movement was set at the centre of the flame. Three scanning speeds, i.e. 0.5, 5, 50 mm s^{-1}, were used in the X-direction, the pitch in the Y-direction was 3 mm, and the speed of this switch was 16.7 mm s^{-1}. The deposition time was 17 min, which was chosen to get two return trips in the slowest scan, but it was 10 min for fixed substrates.

The substrate was heated by the torch flame up to a certain temperature depending on the distance, L, between the torch nozzle and the substrate. At the same L, if necessary, the temperature was increased by restricting the flow rate of cooling water to the substrate holder. The substrate temperature, T_s, was measured using an infrared thermometer, Minolta IR-630, with a constant value of 1 as the emissivity. Therefore, the true temperature may be higher than the value written in this paper. The target area of the thermometer was about 3 mm diameter. Under the slowest scan only, the temperature change between under and out of the flame, both at the centre and the edge of the substrate, could be measured. At higher

TABLE I Deposition conditions

Flow rate Ar	30 l min^{-1}
Flow rate H_2	10 l min^{-1}
Flow rate CH_4	0.4 l min^{-1}
Pressure of deposition chamber	140 torr
D.c. power	70 V × 140 A = 10 kW
Substrate	Mo plate, 20 mm diameter × 1.5 mm thick
Substrate temperature	840–980 °C
Distance between substrate and anode nozzle, L	60, 65 mm
Scan range	18 × 18 mm^2
Scan speed: X-direction	0, 0.5, 5, 50 mm s^{-1}
Y-direction	16.7 mm s^{-1}
Step width: Y-direction	3 mm

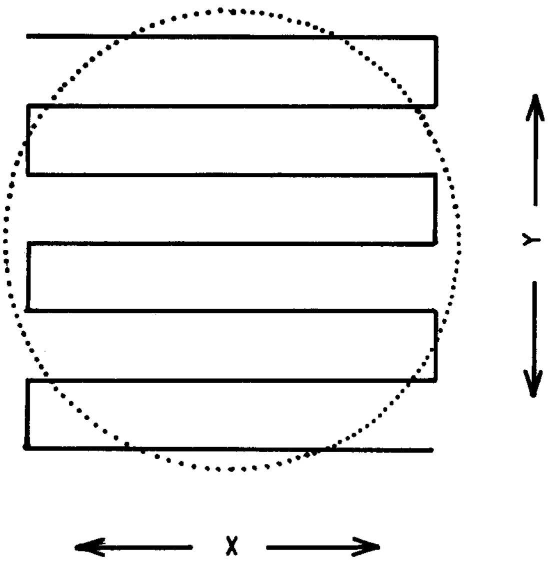

Figure 1 Scanning mode used in this experiment. The circle shows the size of the substrate.

speed, only the temperature under the flame was measured.

The film thickness was evaluated with a surface roughness tester, DEKTAK 3030 (Sloan Co.), or calculated from the interference fringes in the infrared spectra of the film. The target area of the infrared spectra was 4 × 4 mm^2.

3. Results and discussion

The appearance of the deposits obtained without scanning and at the three scanning speeds in the X-direction is shown in Fig. 2 for three different conditions of L and T_s. The substrate temperatures for these depositions are summarized in Table II, including those at the edges. Because the values at both edges on the X-axis and on the Y-axis were not very different, only those on the left edge are given. The white scars at the edges of some of the specimens were made by scratching after deposition to measure the film thickness.

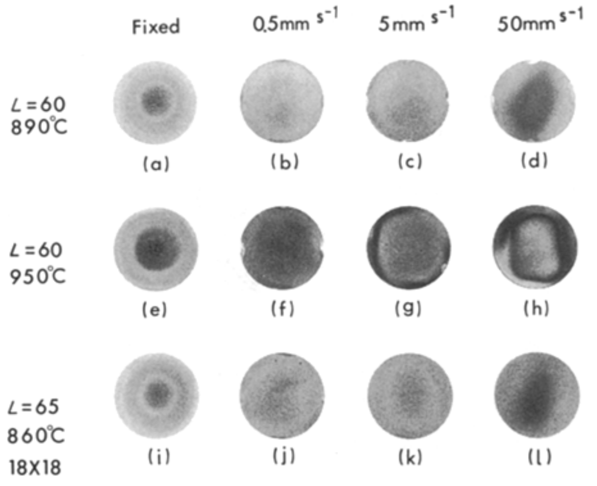

Figure 2 The appearances of diamond films obtained. L is the distance between the torch nozzle and the substrate. The temperature shown is that representative of each line and at the centre of the substrates during deposition.

TABLE II Substrate temperature during deposition (°C)

		Fixed	0.5 mm s^{-1}	5 mm s^{-1}	50 mm s^{-1}
$L = 60$	centre	890	$950 \rightleftharpoons *$	880	890
	edge	810	$880 \rightleftharpoons 685$	850	830
$L = 60$	centre	950	$950 \rightleftharpoons 790$	950	970
	edge	870	$910 \rightleftharpoons 690$	930	930
$L = 65$	centre	870	$860 \rightleftharpoons *$	865	860
	edge	790	$845 \rightleftharpoons 680$	850	800

*Not measured.

The patterns of concentric circles seen in the fixed samples are, as reported previously [4], due to the non-uniformity of film thickness and crystal size, which was induced by the small diameter of the flame and the temperature distribution. On scanning the substrate, the film became homogeneous, particularly for the samples with scan speeds of 0.5 and 5 mm s^{-1}. However, the films obtained at the speed of 50 mm s^{-1} show some non-uniformity between the centre and the outer regions.

In order to understand how the homogeneity of the films was improved by the scanning, film thickness profiles and regional differences of SEM and Raman spectra were measured. Film thickness profiles for the four samples in the first line (a–d) of Fig. 2 are shown in Fig. 3, which were measured using the surface roughness tester. Because the profiles along the X-axis (at $Y = 0$) and along the Y-axis (at $X = 0$) were not

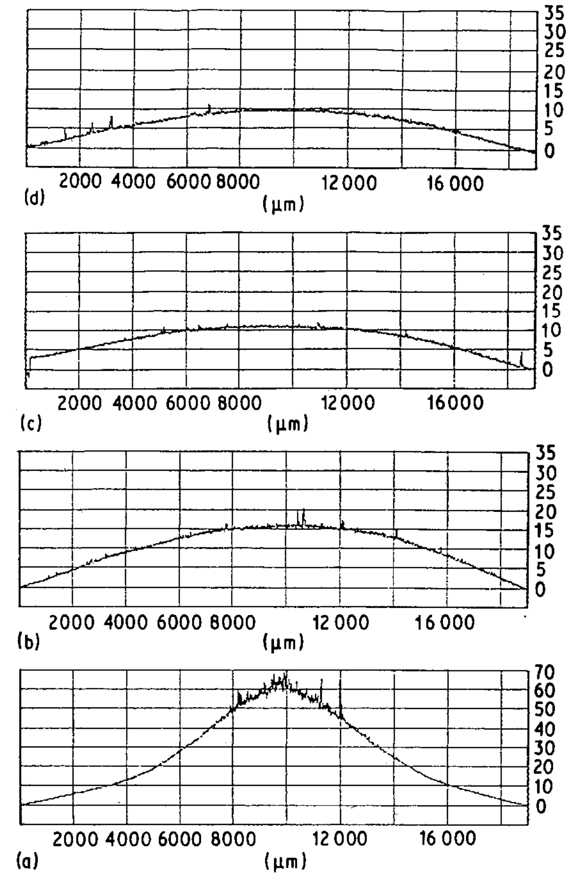

Figure 3 Change of thickness profiles with substrate scanning for specimens of the first line (a–d) in Fig. 2. Deposition time: (a) 10 min and (b–d) 17 min.

very different, only the former are shown in Fig. 3. Thus the film thickness has nearly circular symmetry about the centre of the substrate. The change in thickness in the central region with scanning speed is summarized in Fig. 4 for all the samples shown in Fig. 2. The thickness in Fig. 4 was calculated using the interference fringes in the infrared spectra. Therefore, the thickness was averaged within the target area of the infrared measurement.

It can be understood that film flatness was greatly improved by the scanning (Fig. 3) and the maximum thickness decreased with scanning speed (Fig. 4). However, there are two problems to be considered. Firstly, in spite of the fact that the centre of the flame came close to the edge of the substrate on scanning, the film thickness decreased nearly to zero at the edge. Secondly, the total amount of deposits seems to have decreased too much with the scanning, because the thickness curve after scanning is lower in all positions of the X-axis than that of the fixed sample. Note also that the deposition times were 10 and 17 min for fixed and scanning mode, respectively. At least two reasons can be put forward to explain the above results. Substrate temperature was lower at the edge region within the range of 10–60 °C depending on the deposition conditions, which could decrease the deposition rate at the edge. Also, it was necessary to peel off the film at the edge to obtain a correct baseline of film thickness, but the adhesion was so good that peeling off was difficult. However, the value of film thickness evaluated from the interference fringes suggests that the raising of the backgrounds of the thickness profiles is perhaps not necessary. Anyway, it is not yet certain if there are other substantial reasons exist for the decrease in the amount of deposition. Because these edge effects complicate the results, experiments with substrates of larger area are desirable.

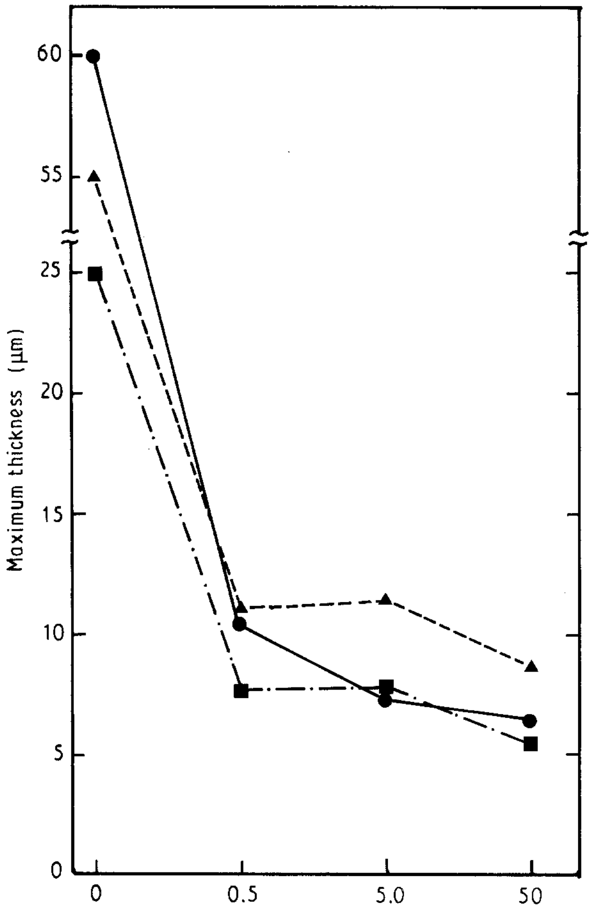

Figure 4 Change of film thickness at the centre of a substrate with scanning. Deposition time: 10 min for the fixed samples, 17 min for the others. (●) $L = 60$, $T = 890\,°C$, (▲) $L = 60$, $T = 950\,°C$, (■) $L = 65$, $T = 870\,°C$.

The change in morphology on scanning is shown in Fig. 5 for the four specimens, a–d, of Fig. 2. A, B and C indicate the centre, 4.5 and 9 mm left from the centre, respectively. The fixed sample shows morphologies similar to those in the previous report [4]: crystal size decreases from the centre to the edge and the crystal facet is not clear in C. The area of the region with these ball-like particles is smaller than that of the previous experiment [4], perhaps because of the lower concentration of methane used. The crystal morphologies were greatly changed by the scanning. The crystal size was homogenized and especially, in region A, it decreased greatly. Crystal morphology was also homogenized and crystal facets appeared even in region C. However, the smoothness of the crystal planes decreased with scanning, especially for the film with the scan speed of 50 mm s^{-1}, where it was very notable that crystal quality seemed to be worse in A than in C. The dark appearance of the sample in Fig. 3 seems to correlate with this morphology change.

Raman spectra of the specimens and regions corresponding to Fig. 5 are summarized in Fig. 6. This figure also shows that the films are homogenized by the scanning; the features of the curves are similar and the peak at ~ 1333 cm^{-1} of diamond can be seen in all the spectra of the specimens which were subjected to scanning. However, the crystal quality deteriorated as compared with regions A and B of the fixed sample, as can be seen by the decrease in the intensity of the 1333 cm^{-1} peak and the increase of the background fluorescence. This deterioration of diamond quality, as shown by SEM and Raman spectra, may be caused by the incomplete etching, while in the centre of the flame, of non-diamond structures deposited when in the outer region of the flame.

The spectra from regions A and B of specimen d with 50 mm s^{-1} scan speed have broad scatterings at ~ 1360 and 1550–1600 cm^{-1}, which indicates that graphitic carbon is included in these regions. This incorporation seems to be the reason why specimen d shows a dark appearance in Fig. 2 and poor crystal planes in Fig. 5. The Raman spectra of the specimens with other conditions of L and T_s in Fig. 2 (the second and third lines) also showed that the highest scan speed was not good for diamond quality: the intensity of the peak of diamond structure was weaker than those of the specimens with other scan speeds. However, in contrast to specimen d, the diamond peak was weaker at the edge than in the centre in specimen h, and the regional difference in Raman spectra was small in specimen l, though some non-uniformity can be seen in Fig. 2. We cannot yet deduce the reason for these results of the highest scan. There are differences

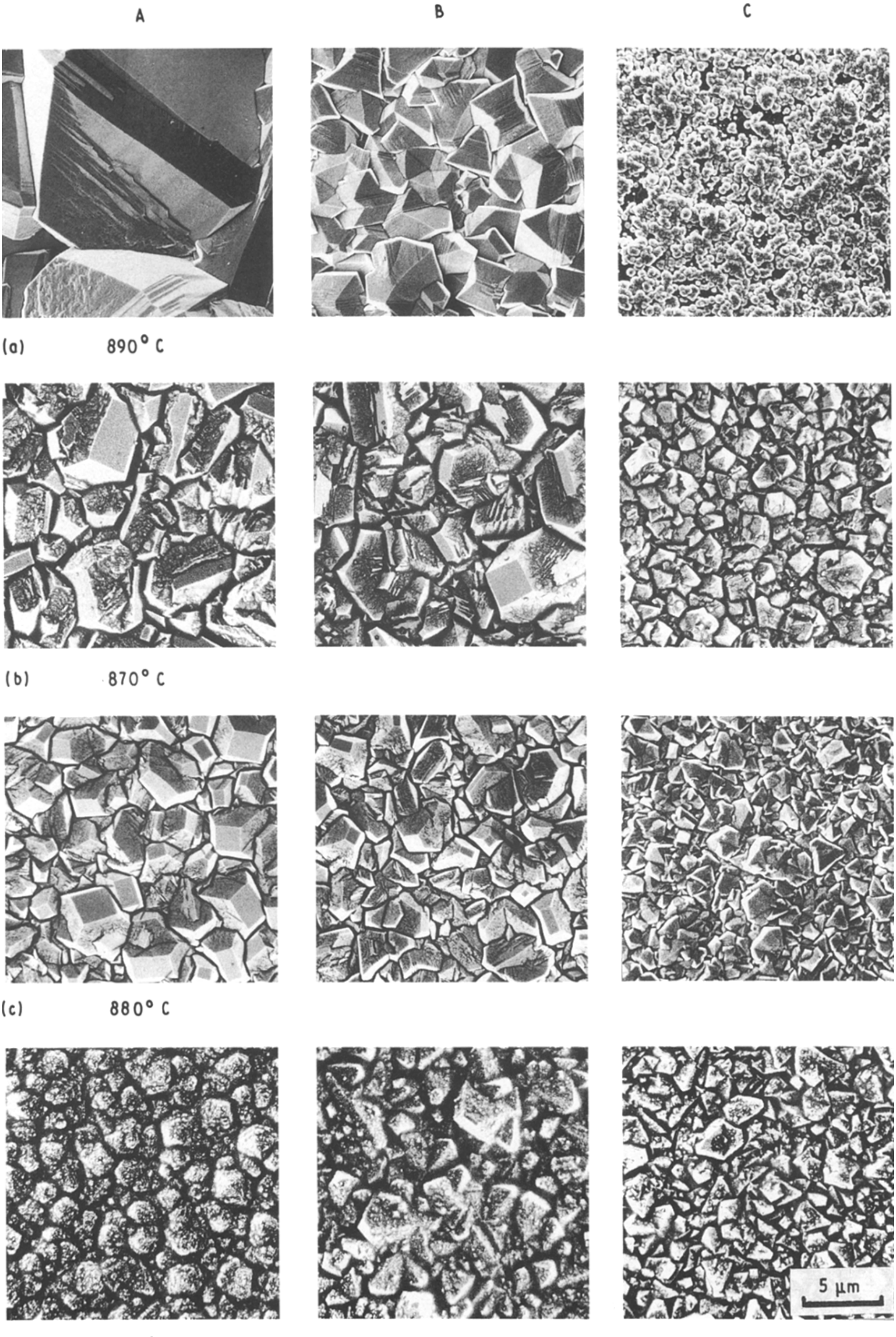

Figure 5 Change of morphology on scanning a substrate for specimens a–d in Fig. 2. A, B, C indicate the regions on the substrate, 0, 4.5, 9 mm from centre to the left, respectively.

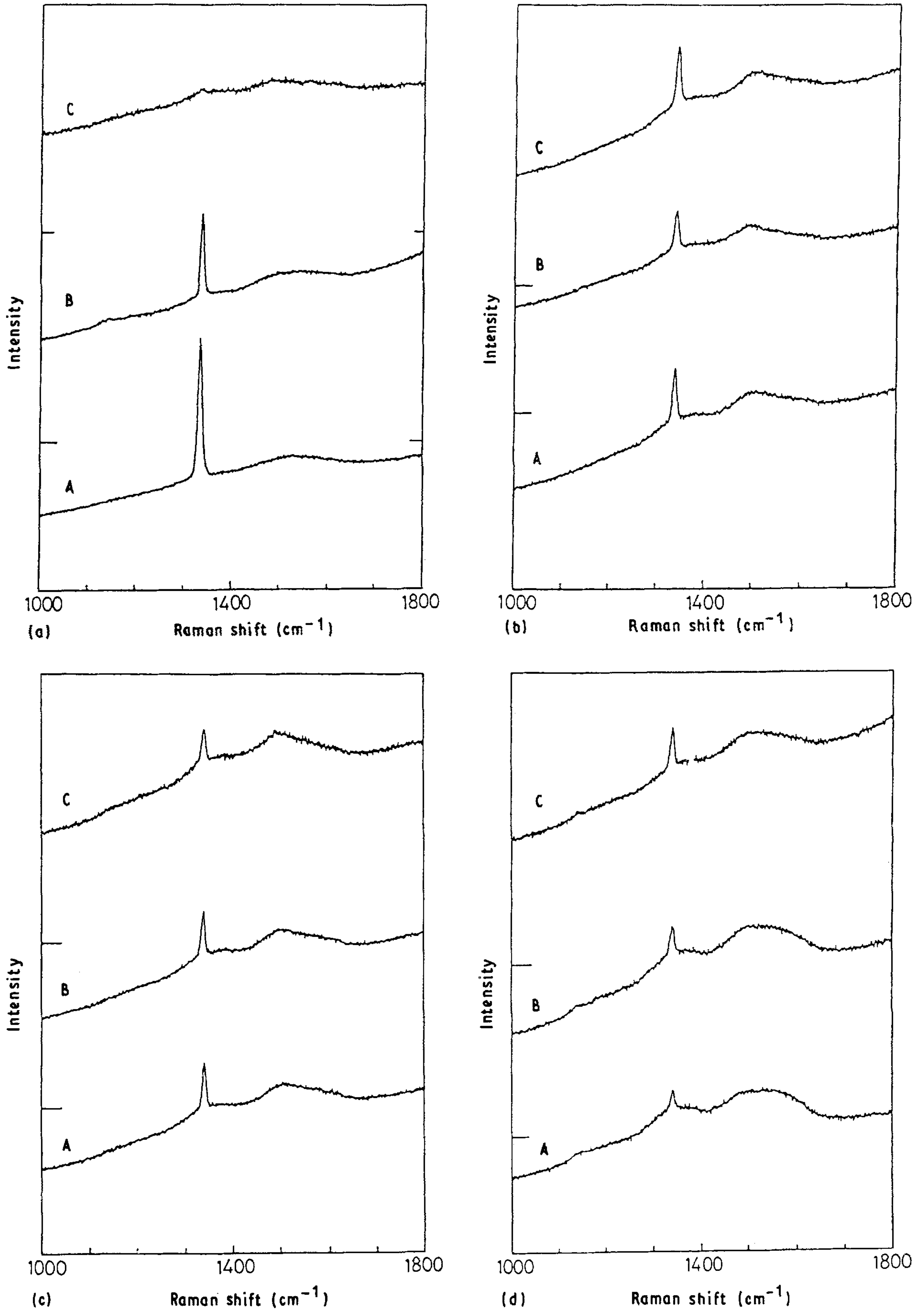

Figure 6 Raman spectra of specimens a–d in Fig. 2. A, B and C are the same in Fig. 5.

in substrate temperature and stagnation time of the flame in the centre and the edge. To determine the effect of temperature more accurately, it is necessary to use a thermometer which can follow the temperature change quickly and measure temperature distribution over a larger area and in the same view. Anyway, the highest scanning speed was not good either for deposition rate or for film quality.

Although non-diamond structures were incorporated by the substrate scanning, these diamond films will be sufficient for some applications such as hard and protective coatings. Adhesion of the films to the substrates appears to be good, though it was not evaluated quantitatively. To improve the crystal quality, it may be effective to set an aperture above the substrate which shields the substrate from the outer region of the jet flame [5].

The substrate temperature control by the scanning was not effective, because scanning, even at the highest speed, did not homogenize the temperature distribution of the substrate.

4. Conclusions

Diamond deposition on 20 mm diameter molybdenum substrates with a scanning mode of $18 \times 18\,\mathrm{mm}^2$ scan range and 0.5–$50\,\mathrm{mm\,s}^{-1}$ scan speeds, gave the following results.

1. The uniformity of film thickness and crystal size was improved.
2. Both total and local deposition rates were decreased, partly due to the low substrate temperature at the edge, but experiments with larger substrates are necessary to clarify this.
3. Crystal quality was also homogenized, but the quality after scanning was worse than that of the central region on the fixed substrate, presumably owing to the incorporation of non-diamond structure deposited when in the outer region of the flame. However, even these improvements in homogeneity will be useful for some applications.
4. Most importantly, a high scan speed of $50\,\mathrm{mm\,s}^{-1}$ was not good and caused incorporation of graphitic structure.

References

1. K. KURIHARA, K. SASAKI, M. KAWARADA and N. KOSHINO, *Appl. Phys. Lett.* **52** (1988) 437.
2. S. MATSUMOTO, *Ext. Abstr. MRS Meeting*, **EA-15** (1988) 119.
3. N. OHTAKE and M. YOSHIKAWA, *J. Electrochem. Soc.* **137** (1990) 717.
4. S. MATSUMOTO, I. HOSOYA and T. CHONAN, *Jpn J. Appl. Phys.* **29** (1990) 2082.
5. P. KOIDL, Fraunhofer Institute fur Festkorperphysik, Freiburg, Germany. Personal communication (1991).

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