

Diamond synthesis by thermal-plasma CVD (chemical vapor deposition)

Seiichiro Matsumoto, Ikuro Hosoya*, Yuji Manabe** and Yukinobu Hibino***

National Institute for Research in Inorganic Materials, 1-1
Namiki, Tsukuba-shi 305, JAPAN

*Idemitsu Petrochemical Co. Ltd., **Japan Synthetic Rubber Co.
Ltd., ***ULVAC Japan, Ltd.

Abstract - After a brief summary of the characteristics of thermal plasma methods for diamond synthesis, the results of our attempts to increase deposition rate and to improve uniformity of diamond films are described. Use of alcohols instead of methane did not increase the deposition rate. Deposition under substrate scanning mode improved film uniformity but was not good for high quality diamond. The positive substrate bias increased the deposition rate and the negative changed crystal morphology to a great extent.

1. INTRODUCTION

The key factor for metastable growth of diamond by CVD is the presence of super-equilibrium amount of activated species in the gas phase. Although the first methods were by thermal activations, cold or non-equilibrium plasmas have been used for diamond synthesis from the early stage, because they give suitable conditions for diamond growth, i.e., a moderate gas temperature and super-equilibrium amount of excited species. Because diamond transforms into graphite at high temperatures, thermal plasmas was at first thought unsuitable for diamond synthesis. However, after the discovery that thermal plasma also gives diamonds by cooling a substrate sufficiently, various thermal plasmas have been applied for diamond synthesis. rf induction(ref. 1) and arc discharge between two tungsten rods(ref. 2) were used at first. This was immediately followed by dc arc jet(ref. 3,4) and microwave jet(ref. 5,6). In a sense of high gas temperature and high gas pressure, combustion flame can be also regarded one of thermal plasmas(ref.7), though it will not included in this report. The thermal plasma methods have eminent advantages, i.e., diamond can grow much faster than from glow discharge methods owing to its high density of excited species derived from its high plasma density. Instead, there are some difficulties in the control of deposition temperature and of uniformness of the film, because of its high gas temperature and flame-like nature of the plasmas. In this report, at first diamond CVD by thermal plasma methods will be reviewed generally in chapter 2, and in chapters 3,4,5, we will report the results of our efforts to improve the methods by using alcohols as a carbon source, by substrate scanning and substrate biasing.

2. CHARACTERISTICS OF DIAMOND SYNTHESIS FROM THERMAL PLASMA

2.1 Deposition methods

Among a few thermal plasma methods above mentioned, dc plasma jet is (except for the combustion flame method) now most popular for diamond synthesis, probably because of ease of handling and stability of the plasma. The dc torch we have used is illustrated in Fig. 1(a). Into a plasma jet of argon and hydrogen (typically, 30+10 SLM), reactant methane (0.05-2 SLM) was introduced through a hole in the anode. Diamond was deposited on a substrate set on a water-cooled substrate holder. The pressure of the deposition chamber was 1 atm - 50 Torr and the dc power used was 8-18 kW. In addition to these most popular type of wall-stabilized torch, a dc plasma with two separated jet electrodes as its cathode and anode was applied for diamond deposition (ref. 8). It is reported that a long plasma flame can be made by their system. Lu et al. applied a triple torch reactor which coalesces three plasma jets into one larger flame for large-area deposition and more sufficient and homogeneous injection of reactant materials into the plasma(ref.

9). A cascade arc dc torch was also used, where very small flow rate of 2.5 l/min in total is notable(ref. 10).

Rf induction can produce a thermal plasma with larger volume and less contaminated than dc arc jet, though the operation is a little more complicated and the discharge is less stable. The rf torch we have used is illustrated in Fig. 2(b). Ar(15-25 SLM) + H₂(4-12 SLM), Ar(1-2 SLM) and Ar(1-3 SLM) + CH₄(0.1-1.2 SLM) were used as sheath, plasma and carrier+reactant gases, respectively. The gas pressure was 1 atm and the rf power required is 10-50 kW for 4 MHz frequency. Cappelli *et al.* used TAFE model 66 torch and deposited diamonds on a substrate which was 15 cm apart from the nearest coil(ref. 11).

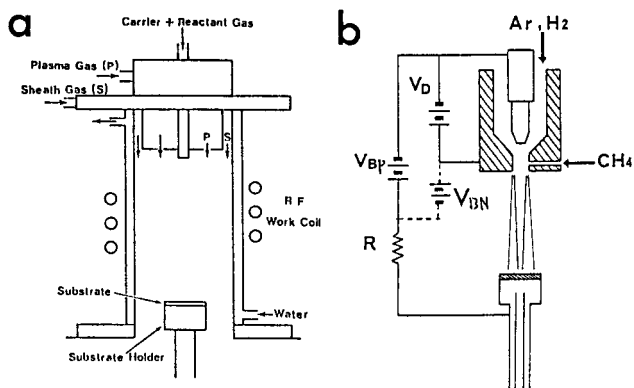


Fig.1 Arrangement of thermal plasma CVD by using a rf induction plasma (a), and a dc plasma jet(b). In b, settings of positive (V_{BP}) and negative (V_{BN}) bias are also shown.

The most popular microwave applicator, in which a quartz tube penetrates E-planes of the wave guide, was able to produce a thermal plasma of 1 atm for diamond synthesis by using a microwave of 900 MHz and 6-7 kW in power (ref. 6). However, the diameter of the plasma was very small. By the microwave torch with coaxial electrodes, a hydrogen plasma of 1 atm was generated with a small electric power of 2 kW(ref. 5). They reported that owing to the nature of microwave discharge, flame diameter can be larger, which results a larger deposition of 25 x 25 mm, and the contamination from the electrode is negligible.

The gas system used in thermal plasmas are Ar-H₂-CH₄ or H₂-CH₄ (for some dc and microwave plasmas). No use of argon is economical but the stability of the plasma is usually worse and deposition rate does not seem to increase further even when argon is free, if the percentage of hydrogen is higher than a certain level. Addition of helium to a dc jet relax radial temperature gradient resulting the increase of deposition area. Replacing the reactant methane by alcohols and acetones was reported to give high deposition rate (ref. 12), which is not fully consistent with our results. This will be discussed in chapter 2.

Pressure of the deposition chamber was in the range of soft vacuum in dc jet CVD of diamond. This is because of better controllability of deposition in such a vacuum in the deposition from the flame with high temperature gradient. Deposition rate was also highest in a soft vacuum probably because of the balance between the density and the life time of active species(ref. 9). On the other hand, in rf induction plasma, depositions under 1 atm were mostly reported. Recently, Hernberg *et al.* reduced pressure of their rf torch down to 150 Torr to get homogeneous films(ref. 13), while Kobayashi and Ono reduced pressure of a deposition chamber by conflicting a flow with a nozzle just below the torch(ref. 14).

Electric power used varies from ca. 1-50 kW. It is closely related to the flame size and hence the deposition rate and the deposition area.

The substrates were almost always cooled by setting on a water-cooled substrate holder; otherwise it is destroyed by the heat of high temperature plasma. Substrate temperature was difficult to measure by a usual disappearing-filament type pyrometer, because of high emission of the plasma. Cappelli *et al.* used a narrow band filter in 632.0 nm range(ref. 11). An IR emission pyrometer can be used for dc jet deposition. IR pyrometric measurement from the opposite side of the substrate by using an optical fiber was reported to be very accurate(ref. 14), though some temperature difference between the surface and the bottom will be present depending on the thermal conductivity and the thickness of the substrate.

2.2 Characteristics of diamond deposition and diamonds from thermal plasmas

High growth rate is the most prominent advantage of diamond CVD from thermal plasma. The value as high as 930 $\mu\text{m}/\text{h}$ was reported as a maximum growth rate by dc jet(ref. 8). However, the diamonds shown in the report has a large

degree of vertical relief and they used the top of the highest grain observed. The maximum deposition rate seems to be generally in the order of 600 $\mu\text{m}/\text{h}$. Our data are also in the same order: 9 $\mu\text{m}/\text{min}$ at 140 torr and 4 $\mu\text{m}/\text{min}$ at 1 atm. These values are even the highest in all the methods of diamond deposition. Deposition area is narrow by dc jet, ca. 8-10 mm ϕ in our case, but it depends greatly on the torch used. Klocek et al. reported a formation of a free-standing diamond film of large area, 50 x 50 mm, at a rate of 40 $\mu\text{m}/\text{h}$ in the center and 5 $\mu\text{m}/\text{h}$ at the edge, though little was reported about their torch(ref. 15). Norton Co. has advertised they can make a diamond film of 15 cm in diameter by a dc jet method. They used the techniques called magnetically mixed and spread arc (MMSARC) and magneto plasma dynamic arc (MPDARC), but the details have not been reported(ref.16).

In relation to the high deposition rate from thermal plasmas, it should be added here that formation of diamond powders by dc jet on the wall near the substrate was reported(ref. 17). The yield was very low (below 0.2% of hydrocarbons used) and it is not certain that this was due to homogeneous nucleation in the gas phase. The powders are very fine (10-100 nm in grain size) and have no crystal habits in contrast to the particles which were reported to be made by homogeneous nucleation in a microwave glow discharge and a combustion flame(ref. 18,19)

Kurihara et al. reported that substrate pretreatment is not necessary to get diamond films by dc jet because nucleation density is high owing to the high density of reactive species.(ref. 3). However, scratching is still effective to obtain smoother films. Prolonged exposure to hydrogen plasma seems to decrease the nucleation sites made by the scratching.

By rf thermal plasma, deposition area is larger than by using dc jet. Although our deposition area was limited by the substrate size (20 mm ϕ), Cappelli et al. reported the deposition of 20 cm². In stead, the rate reported is rather low, i.e., 1-2 $\mu\text{m}/\text{min}$ (ref. 1) and 50 $\mu\text{m}/\text{h}$ (ref. 11) at 1 atm. When the plasma was conflicted and expanded into a deposition chamber of low pressure, the deposition rate increased as high as 15 $\mu\text{m}/\text{m}$, though the decrease of deposition area was accompanied(ref. 14). By microwave thermal CVD, deposition rate of 30 $\mu\text{m}/\text{h}$ was reported(ref. 5).

Diamonds made by thermal plasma CVD show essentially the same morphology and properties as those made by glow discharge methods. Diamonds are obtained as microcrystals and microcrystalline films on substrates. A large degree of vertical relief with polycrystalline steeple-like towers is often seen when the nucleation density is low and the growth rate is very high. The crystal morphology changes from ball-like to euhedral depending on the ratio of CH₄/H₂, substrate position, substrate temperature, electric power used, etc. The ratio of the areas of {100}/{111} changes mainly depending on the ratio of CH₄/H₂ and substrate temperature. Euhedral crystals can be obtained by thermal plasmas with higher ratio (up to 10 %) of CH₄/H₂, probably because of high degree of hydrogen dissociation.

In Raman spectra, a broad scattering at ca. 1450-1600 cm⁻¹ usually accompanies to a sharp peak at ca. 1333 cm⁻¹, but the former can be eliminated by some proper growth conditions. Fluorescence background of Raman spectrum of euhedral diamonds from thermal plasmas is usually lower than those from microwave glow discharge in CH₄-H₂. The value of 3.5 cm⁻¹ was reported for the narrowest half width of the 1333 cm⁻¹ peak diamonds on silicon from thermal plasmas(ref. 10), while it was 2.9 and 5.4 cm⁻¹ for homoepitaxial diamonds on (100) and (110) faces, respectively(ref. 20).

Although arc discharge between the two tungsten rods co-deposited WC(ref. 21), usually by X-ray diffraction, no materials other than carbon can be found in the films made by dc jet and by rf thermal plasma. Yet, high sensitivity analysis like laser ionization mass spectrometry revealed incorporation of electrode materials in the diamond film from dc jet(ref. 22). Although their concentrations are of trace amount, it may be a problem for a use for electric devices.

There are few reports on the physical properties of the diamond films by thermal plasmas. Vickers hardness of 10,000 kg/mm²(ref. 2) and thermal conductivity of 8 W/cm·K(ref. 2) and 12.1 W/cm·K(ref. 23) were reported for a film by dc jet. The values for natural diamond IIa is 26 W/cm·K. Diamond films of a few groups made by dc jet were reported optically black, though graphitic Raman response was very little. One group attributed this to high degree of faults such as stacking faults and twinning in the film(ref. 24),

plane became very rough when the ratio=0.17. The growth rate from ethanol was nearly the same to that from methane for the same feeds, in spite of the fact that an ethanol molecule has two carbon atoms. From methanol, however, diamond nor graphite or other types of solid carbon deposited in a concentration range of MeOH similar to that of EtOH.

Figure 2 summarizes the results of gas chromatography showing the composition of exhaust gases as a function of initial H_2 flow rate when ethanol and methanol were used. Ar, H_2 are excluded in this figure. The most remarkable differences in the two graphs in Fig.3 is that hydrocarbons formed from ethanol, but not from methanol. The composition of exhaust gas from methane was very similar to that from ethanol except for the absence of CO.

Figure 3 shows thermochemical equilibrium compositions calculated for the systems used for diamond deposition from ethanol and from methanol. The most significant difference in the two is that large amounts of C_mH_n and C_x species exist at 2000-4500 K and solid carbon appears at 800-2300 K from EtOH, while they are very small or missing from MeOH. Actually, the green emission from C_2 was visible from EtOH but not from MeOH. This observation of emission and the results of the gas chromatography support the idea that the composition of the gas phase in a thermal plasma is close to that of equilibrium.

The reason why we could not obtain diamond from methanol can be deduced as follows: Reactive species for diamond deposition are these C_mH_n and C_x at 2000-4000 K and they are little in the gas phase from methanol. Alternately, if other species such as methyl radical is the precursors for diamond growth as calculated by Goodwin(ref. 28), it can not be either made sufficiently in the boundary layer from the gas compositions used here. Kinetic study is also helpful for the evaluation of this idea. The experimental fact that the hot-filament and microwave glow discharge methods give diamonds from methanol(ref. 27,29) and from $CO+H_2$ (ref. 30), even from the composition (MeOH/ H_2) which does not give solid carbon in equilibrium, may be explained by the idea that reactive species can be made in non-equilibrium state in the low pressure systems. Han et al. obtained diamonds by injecting liquid methanol in counter-flow mode into an arc jet(ref. 12). The reason of the difference from our results may be, as they suggested, that the liquid droplet could be transported very close to the substrate surface and effective concentration of MeOH is higher than ours, and not equilibrium species but a mixture of radicals favorable for diamond growth could be made by the fragmentation.

4. DEPOSITION BY SCANNING A SUBSTRATE

In a plasma spraying method, it is usual to scan a torch or a substrate to get large area deposition. We have, therefore, tried to deposit diamond in larger area by scanning a substrate in dc plasma jet CVD. As a result, the film thickness and crystal size was made uniform but both total and local deposition rates decreased. Crystal quality was also homogenized, but it is worse than those of the center region on the fixed substrate.

4.1 Experimental

A molybdenum substrate (20 mm ϕ , 1.5 mm t) on a water-cooled copper holder was scanned in a zigzag mode during deposition. The range of the scan was from -9 to +9 mm in both(X,Y) directions. Three scanning speeds, i.e., 0.5, 5, 50 mm/s were used in X-direction, and a pitch in Y-direction was 3 mm. The deposition time was 17 min which gave two return trips in the slowest scan but it was 10 min for the fixed substrate.

4.2 Results and discussion

With the scanning of the substrates, the films became homogeneous. An example of the change of thickness profiles is shown in Fig. 4. It can be understood that film flatness was greatly improved by the scanning and the maximum thickness decreased with scan speed. However, the films are thin at the edge and the total amount of the deposits seems to have decreased too much with scanning, as can be understood by the fact that the thickness curve after scanning is lower in all positions of the x-axis. One of the reasons for the above two results is that substrate temperature was lower at the edge region within a range of 10-60°C depending on the deposition conditions, which could decrease the deposition rate at the edge. It is not yet certain if there are other substantial reasons for the decrease of the amount of deposition. It is necessary to use a larger substrate to eliminate the edge effects.

The crystal morphology greatly changed by the scanning. SEM photographs of

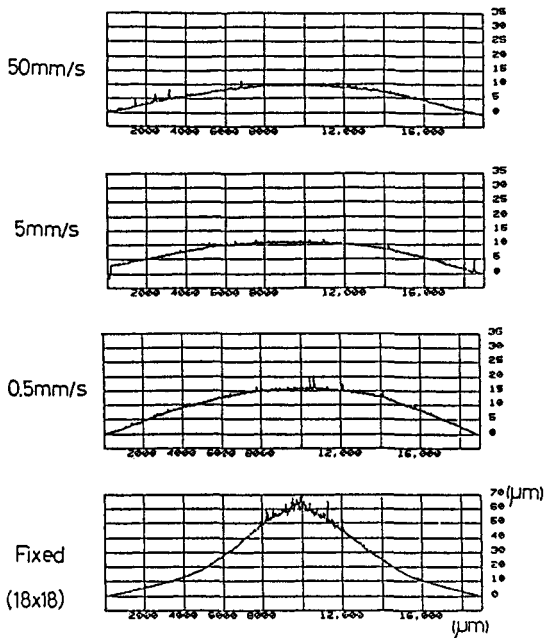


Fig.4 Change of thickness profiles with substrate scanning. Deposition time is 10 min for a and 17 min for b,c,d.

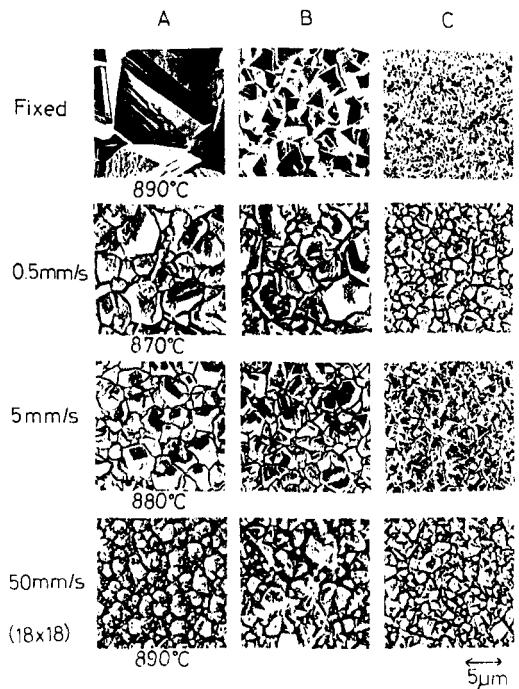


Fig.5 Change of morphologies by scanning a substrate. A, B, C indicate the regions on the substrate from center, middle and edge.

the specimens in Fig.4 are shown in Fig.5. A, B and C are from the center, 4.5 and 9 mm left from the center, respectively. The crystal size were made uniform. Especially, in region A, it decreased much. Crystal morphology were also homogenized and crystal facets appeared in region C also. However, the smoothness of crystal planes decreased with scanning, especially for the film with the scan speed of 50 mm/s, where it is very notable that crystal quality in A is worse than in C.

Raman spectra also showed that the films are homogenized by the scanning; the features of the spectra are similar and the peak at ca. 1333 cm^{-1} of diamond can be seen in all the spectra of the specimens with scanning. However, the crystal quality deteriorated as compared with the center region of the fixed sample. These deterioration in quality of diamond as shown by SEM and Raman spectra may be caused by the incomplete etching, during in the flame, of non-diamond structures deposited at the outer region of the flame. The Raman spectra also showed that graphitic carbon is included in the A and B regions of the specimens with 50 mm/s. This incorporation seems to be the reason why the specimen with 50 mm/s shows poor crystal planes in Fig. 5.

5. SUBSTRATE BIAS EFFECTS

To improve the uniformity of film thickness and of quality in the films from dc jet, the substrate was biased positively and negatively during the deposition. The positive bias increased the deposition rate more than twice but did not improve the uniformity. The negative bias did not increase the deposition rate but changed the crystal size and morphology increasing imperfections in the crystals. Too high bias voltage overheated the substrate(positive) or sputtered the deposits and substrate(negative).

5.1 Experimental

Arrangements of the bias applications are shown schematically in Fig. 1. Applied voltage and current for the bias were 0-500V, 0-1A and 0-280V, 0-0.5A for the positive and negative biases, respectively. Other operating conditions were the same as in section 2. V-I characteristics of these biases indicated that auxiliary discharge occurred between the substrate and the primary discharge by the dc jet, although the appearance of the discharge was

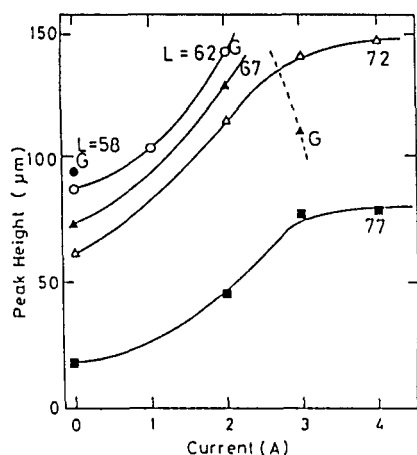


Fig.6 Increase of maximum film thickness with positive substrate bias under different torch-substrate distances(L).

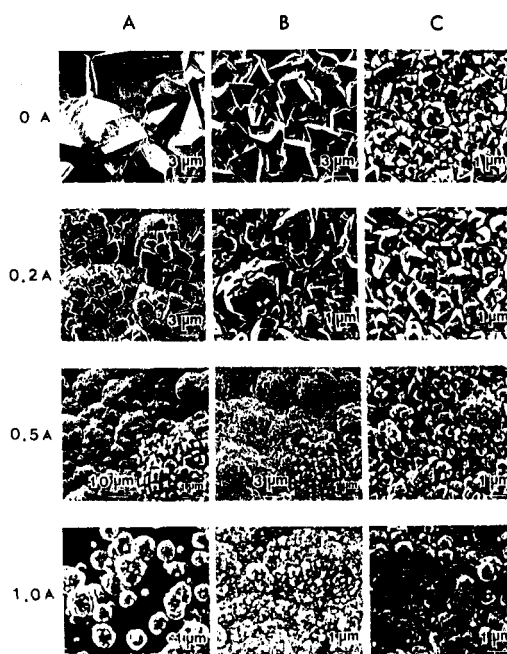


Fig.7 SEM images after deposition with various negative bias in dc plasma jet. A(center), B(middle) and C(edge) indicate the regions on the substrate.

different for these two biases: the glow of the flame of the jet was enlarged to the substrate by the positive bias, while emission of the electron seemed to dominate at the edge of the substrate holder by the negative bias.

5.2 Results and discussion

The positive bias increased the deposition area and deposition rate of diamond. Figure 6 summarizes the increases of maximum film thickness with bias current for various torch-substrate distances(ref. 31). This increase of deposition rate is presumably caused by the enhancement of the dissociation of the gas phase near the substrate by the auxiliary discharge. However, this enhancement seems most strong above the center of the substrate as was observed by the elongation of the glow from the flame tail. This is probably the reason why deposition was accelerated mostly at the center of the substrate and the uniformity of thickness was not improved.

The negative bias did not increase the deposition rate of diamond but changed the morphology of diamond obtained to a great extent. Figure 7 shows SEM images of four samples with and without bias. Without bias, the crystal size decreased from the center(A) to the outer(C), and the predominant planes changed from (100) to (111). When the bias was applied, in region A, the morphology changed from large crystals with (100) predominated planes through mosaic(with (100) planes) to ball-like. Higher magnification shows that the balls are composed of small crystals with (100) and (111) planes, whose [100] axis orientate perpendicular to the outer surfaces of the balls. In region B, steps increased at first and then became ball-like which is also made of submicron size crystals with facets. In region C, the crystal size did not change so much, but surfaces of the crystals became rough with increasing bias current. When higher bias(1 A) was applied, the film was not already continuous in region A, and faceted crystals could not be seen in all regions.

X-ray diffraction revealed that all these films are composed of or contain diamond and none of them showed peaks of graphite. However, the crystal quality decreased with bias current(voltage). The Raman spectra also revealed the deterioration of diamond quality with bias current(voltage). It is notable that in spite of the very low intensity of the diamond peak at 1333 cm^{-1} in the Raman spectra, the sample obtained with a bias current of 0.5 A is composed of crystals with distinct facets as shown in Fig. 7.

These observed changes of morphology and crystal perfection were presumably caused by enhanced ion bombardment by the negative bias to the substrate, which increased defects on the growing surface resulting secondary nucleation and the decrease of crystal size. Because the ball-like structure in Fig.7 seems to reflect initial nucleation density of diamond on the substrate, it will be effective to increase this initial nucleation to get smoother diamond surface by using this bias effect.

6. CONCLUDING REMARKS

The techniques of thermal plasma method are not yet sufficient to prepare diamond films for practical use, especially for electronic devices. For large area and uniform deposition with high speed, for high quality films, further research works for better control of the processes, for new methods and techniques, on growth mechanism, etc. will be necessary.

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