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Evidence for hydrothermal growth of diamond in the C–H–O and C–H–O halogen system

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Powder x-ray diffraction (XRD) and Raman evidence are presented for the formation of crystalline diamond in the "hydrothermal" pressure-temperature regime 1–5 kbars, <1000 °C. Two different methods appear to enable diamond to nucleate and grow. One—a Low Pressure Solid-State Source (LPSSS) route—utilizes special solid precursors, especially low temperature glassy carbon (GC-500), with very fine diamond seeds in sealed gold capsules with H_2O at, say, 800 °C and 1 kbar. The other includes pyrolysis of highly selected organic solid/liquid precursors (halogenated aliphatics such as iodoform) onto similar diamond seeds. In all the cases, powder x-ray diffraction evidence shows a marked increase of the diamond XRD peaks, likewise the Raman spectrum shows a strong increase of the 1331 cm^{-1} line. However, the crystals apparently are too small to be seen in the SEM. TEM diffraction data, on the other hand, seem to lend support to the possibility of all the grown diamonds being very small.

I. INTRODUCTION

The synthesis of diamonds by the GE group[1] in 1955 presumably was based on the condition that diamonds were supposed to have been made in nature, and it was soon assumed, worldwide, that diamond could *only* be made above the Berman–Simon P-T line. The Spitsyn–Derjaguin synthesis[2] method based on ambient pressure synthesis (1 atm) and its development via the Kamo *et al.*[3] microwave CVD process proved that pressure is not a necessary parameter for diamond synthesis. Obviously high pressure was not essential. Our LPSSS process[4,5] is another low pressure process proving the case. For example, mixtures of Au or Ag plus any form of carbon reacted at 800 °C at 100 Torr of H_2 form Me–C–H *liquid* alloys, from which diamond is precipitated.[6] The question we address here is as follows: besides the equilibrium High Pressures and High Temperatures (HPHT) regime and the CVD region, can diamonds be made in an intermediate pressure regime?

Starting in 1957, Tuttle and Roy unsuccessfully attempted to utilize an intermediate pressure regime to synthesize diamonds. They studied hydrothermal conditions from carbonatite-related compositions (see Ref. 7). It was DeVries[8] who for many years kept pointing out the geological evidence suggesting that diamonds could possibly be made hydrothermally. Since 1991 we have approached this goal experimentally, and in 1993, Devries, Roy, Sōmiya, and Yamada[9] presented a detailed analysis of our rationale for the potential for the synthesis of diamond under hydrothermal p-t conditions which would provide a fourth, very different, process for making diamonds. They also presented some of their results therein.[9] In this paper we report details of our results from a wide variety of approaches to diamond synthesis in the hydrothermal regime. Since most of the research on this paper was complete, a paper appeared by Szymanski *et al.*[10] also reporting the synthesis of diamond in the hydrothermal regime, albeit no details were given on the compositions involved.

II. EXPERIMENTAL

Some 200 runs have been made using a wide variety of carbon-containing starting materials, reacting with various fluids, in sealed gold or platinum capsules, under pH_2O of 1–2 kbars, and temperatures of 300–1450 °C. All samples have been examined by XRD and SEM. Where appropriate, microprobe Raman and TEM have been utilized. Our experimental hypothesis was that if carbon is exposed to atomic hydrogen from whatever source while it is being recrystallized, or formed, it can deposit as diamond. The runs may be clustered in the following families of reactions within the C–H–O–halogen system. In all cases the results have been obtained in many different runs, sometimes by two different operators.

A. Pyrolysis of hydrocarbons

A series of aliphatic and aromatic hydrocarbons have been sealed in with 5 wt.% of <1 μm diamond seeds and heated for 8–50 h at temperatures of 600–1000 °C. Special attention was paid to dodecane, adamantane, etc., which have often been considered as possibly being stereochemically favorable to diamond formation. We believe that this is an erroneous rationale, since the necessity to break the C–H bonds and the necessity to remove the hydrogen makes any similarity of the original *molecule* quite meaningless as a precursor to an "infinite" solid "molecule" *of a different composition.*

B. Reaction of carbons with water in the presence of seeds

The calculations presented in our earlier paper[8] supported the reasonable hypothesis that low temperatures, say, 400–500 °C and high pressures (≈5–10 kb) in the C–H–O system would favor high sp^3/sp^2 ratios.

For calibration, crystals of highly oriented pyrolytic graphite and single crystals of diamond were treated hydrothermally in pure H_2O. Surprisingly neither showed, by SEM, any noticeable etching or redeposition up to 900 °C at 1 kbar pH_2O. Our next series of runs involved intimate mixing[4,5] of various solid carbons with 5% by weight of diamond seeds, inserting this mixture into gold or platinum tubes and adding a measured amount of water, sealing, and welding the tube and heating it at the selected p and t for 8–50 h (and recently for up to 14 days). A typical run is as follows: glassy carbon mixed with 5% diamond seeds is mixed with 32 wt. % of water so that not more than 10% of the graphite would be oxidized. In other runs the sintering temperature of glassy carbon, the percentage of water, percentage of seeds, time, temperature, and pressure were varied.

C. Pyrolysis of selected organic phases on diamond seeds

The goal here was to choose carbon-containing phases that might provide additional catalysis or easier bond breakage. The following materials have been tried, all mixed with diamond seeds in the same gold tubes: carbon tetrachloride, chloroform, 1,1,2-trichlorotrifluoroethane, CS_2, haloforms [$CHCl_3$, CHI_3, and $CHBr_3$]. Out of all the haloforms, iodoform (CHI_3) seems to be the most interesting compound in these hydrothermal experiments.

In this preliminary note we only report on a few of the successful runs in each of these areas.

III. RESULTS

Group 1. Table I selected from our data shows that there is little evidence for diamond growth in most of this set of runs. Indeed one can barely see the XRD peaks from the seeds in the final product of noncrystalline carbon + seeds.

Group 2. On the other hand, Fig. 1 shows the XRD patterns of a specific glassy carbon + diamond seeds before process. Figure 2 shows powder x-ray diffraction patterns (raw data) of a run in the presence of four drops of water (72% by weight), which showed substantial increase in the intensity of the diamond peak (d = 2.059). For the XRD, the same sample area was covered with the same amount of powder so that the peak heights of diamond should be a semiquantitative measure of the concentration of diamond in the before and after samples. The increase in diamond concentration is very substantial; moreover, the graphitic background is also very substantially altered. The color of the samples typically becomes grey from black in some runs. The same results have been obtained in several repeated runs, even when made by two separate operators a year apart. Changing the temperature to 900 °C made little difference. Indeed one run at 1400 °C showed less (or the same) growth of diamond. Very significantly, throughout these studies, runs in platinum tubes did not show the growth of diamond. This we attribute to the fact that hydrogen diffuses through Pt but not through gold, and its (H) presence is essential to the growth of diamond.

TABLE I. Starting materials used in the hydrothermal processes and the products obtained.

Starting materials	Pressure (kbars)	Temperature (°C)	Time (h)	Products (from XRD)
HOPG graphite	1	800	24	No etching, no growth
Single crystal diamond	1	800	24	No etching, no growth
Dodecane + diamond seeds	1	600	24	Amorphous carbon
Adamantane + diamond seeds	1.4	800	50	Diamond somewhat enhanced
Carbon tetrachloride + diamond seeds	1	800	24	Amorphous carbon
Glassy carbon + diamond seeds + water	1.4	800	72	Diamond peaks strongly enhnaced
Glassy carbon + diamond seeds	1.4	1450	24	Graphite peaks enhanced
Glassy carbon + diamond seeds + water	1.4	1450	24	Diamond peaks enhanced
Iodoform + diamond seeds + water	1.4	800	48	Diamond peaks strongly enhanced
Iodoform + diamond seeds	1.4	900	24	Only diamond peak strongly enhanced
Iodoform + diamond seeds	1.4	1450	24	Amorphous carbon
Glassy carbon + diamond seeds + water	1.4	800	50	Diamond peaks strongly enhanced
Furfuryl alcohol resin	1.4	800	50	Diamond peaks strongly enhanced
Phenolic resin	1.4	800	50	Diamond peaks strongly enhanced

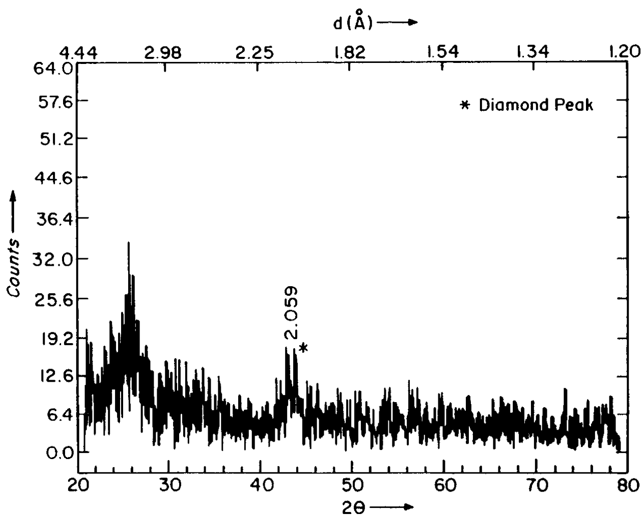

FIG. 1. X-ray diffraction pattern of glassy carbon + 5% diamond seeds before being subjected to the hydrothermal process.

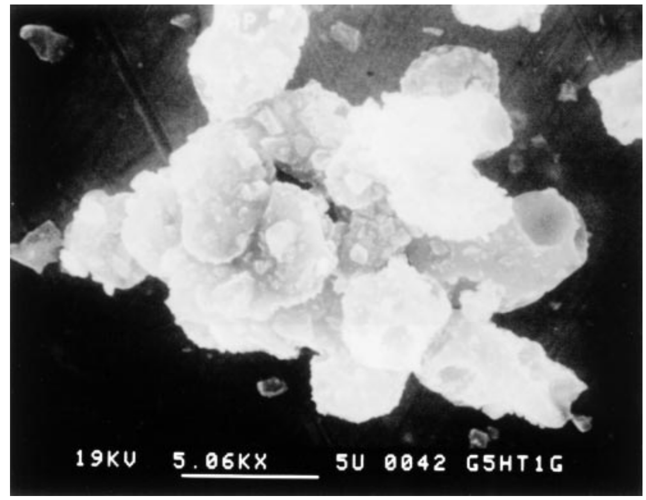

FIG. 3. SEM micrograph showing the substantial reaction of glassy carbon and clear hexagonal crystal shapes etched out of the glassy carbon.

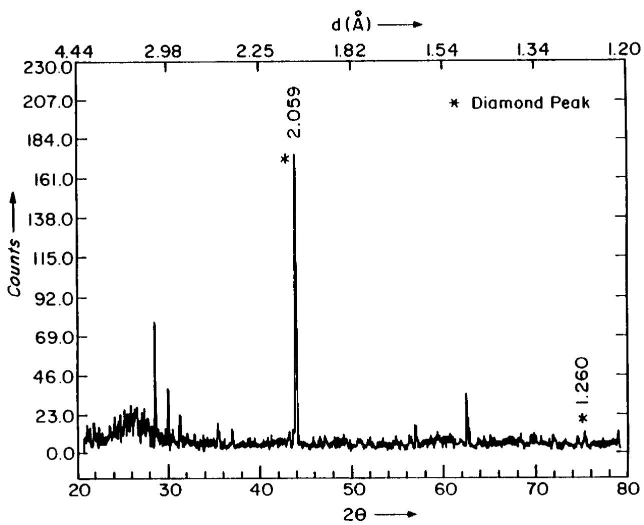

FIG. 2. X-ray diffraction pattern of glassy carbon +5% diamond seeds and 72 wt. % of water after the hydrothermal process at 800 °C, 1.4 kbar for 72 h.

The Raman spectrum in all of these samples shows a clear small diamond peak superimposed on a "graphitic" background as expected. Although it is more difficult to prove that there has not been a circumstantial concentration of seeds, the experiment has been repeated so many times with very similar results that accidental concentration is highly unlikely.

Scanning electron micrographs do not show any of the typical cubo-octahedra found in CVD growth above the 0.5 μm range, and no distinctive faceted growth on the seeds. However, several SEM photos (see Fig. 3) show the very substantial reaction of glassy carbon and clear evidence for hexagonal crystal shapes etched out of the glassy carbon. These hexagonal plates

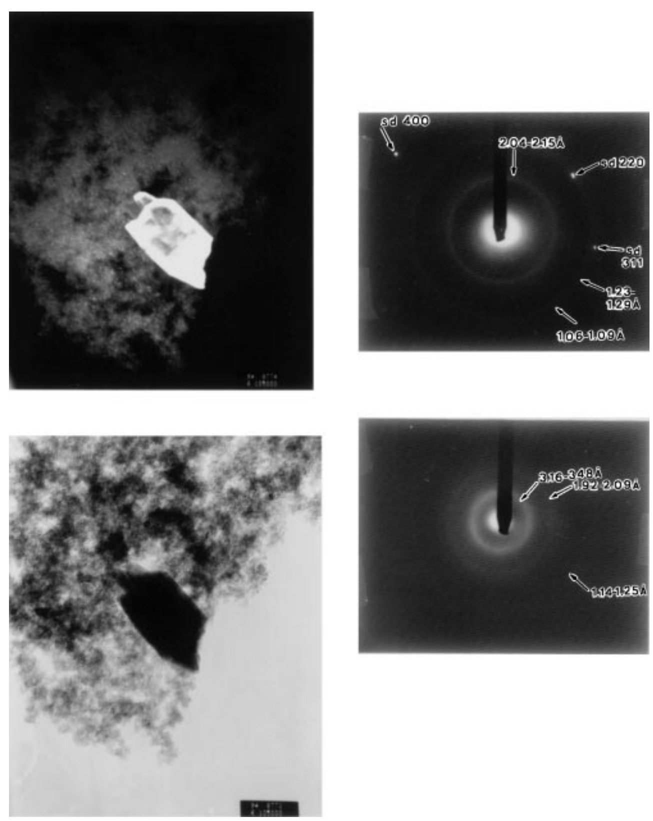

FIG. 4. On the left are the bright-field and dark-field images showing a seed (with possible overgrowth) and fine bright spots (in the dark-field photo). TEM selected area diffraction pattern taken of the hydrothermal transformed GC500 sample at 800 °C and 1.4 kbars, showing both the presence of the spotty pattern from the single crystal seeds and the broadened rings from very fine diamonds. The calibration pattern of graphitic starting materials shows more of the same rings.

have not been isolated separately for TEM structural analysis. They may be so thin that they "float" away.

In TEM we cannot locate individual euhedral crystals of diamond distinctively different from the seeds. On the other hand, wide area electron diffraction patterns show broadened reflections around the *d* values for diamond quite distinct from the typical amorphous graphitic carbon. Moreover, the dark-field photos consistently show a reasonable concentration of very fine (few nm) probable diamonds. These data are presented in Fig. 4. Our interpretations are consistent with the presence of extremely small diamond crystals in fairly high concentrations. The small size of these crystals is paralleled in a most interesting way in the *very* small sizes of diamonds found by Sobolev and Shatskii[11,12] in metamorphic (roughly in the *p-t* range of hydrothermal) rocks.

Group 3. In some cases, these reactions proved difficult to execute since the halogen sometimes attacked the platinum (e.g., in chloroform and bromoform). The most successful results were obtained using iodoform in gold. The work was again repeated by two operators a year apart, with the same results. Figures 5 and 6 show the "before" and "after" XRD data. In this case, of course, the crystalline iodoform peaks dominate in the "before" sample, and the diamond peak is barely visible. In the "after" case, again the XRD 2.059 and 1.261 peaks are greatly enhanced, with amorphous C and I_2 making up the rest of the material balance (same net composition). Figures 7 and 8 show the Raman spectra before and after the process. Again TEM shows no large crystals, but a large number of very small crystals.

IV. CONCLUSIONS

The evidence presented above, we believe, shows albeit not yet unambiguously, that diamonds have been

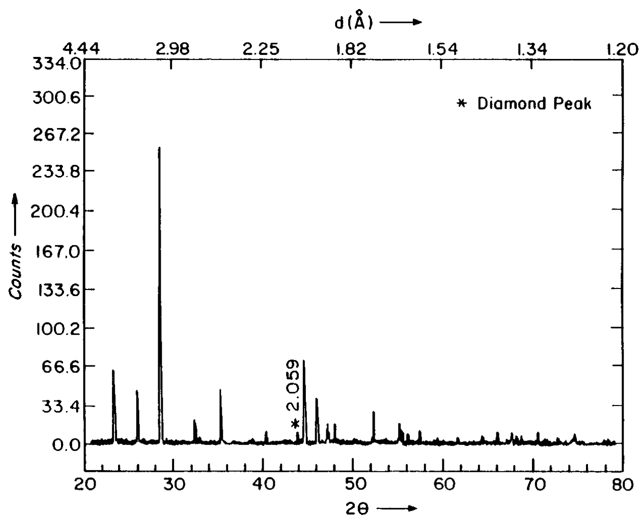

FIG. 5. X-ray diffraction pattern of iodoform +2% diamond seeds prior to the hydrothermal process.

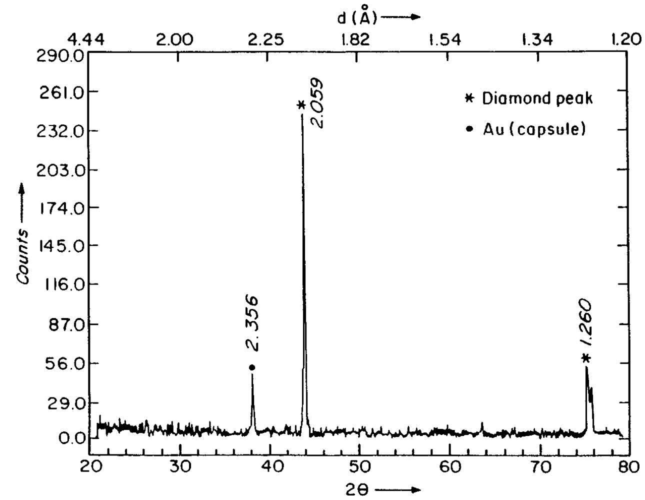

FIG. 6. X-ray diffraction pattern of glassy carbon iodoform +5% diamond seeds and 72 wt.% of water after the hydrothermal process at 800 °C, 1.4 kbar for 48 h.

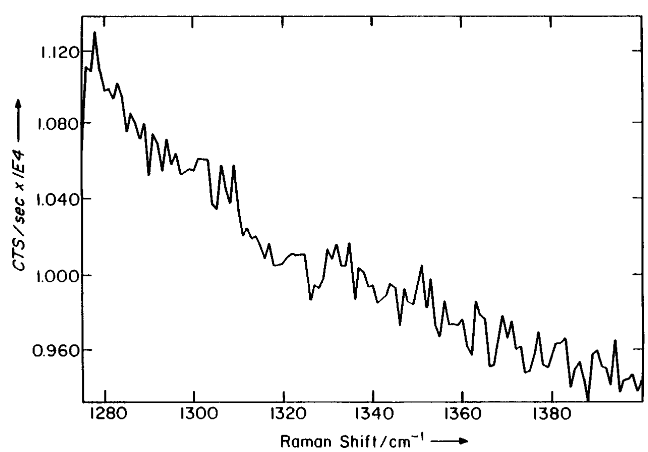

FIG. 7. Raman spectrum of iodoform +2% diamond seeds before being subjected to the hydrothermal process.

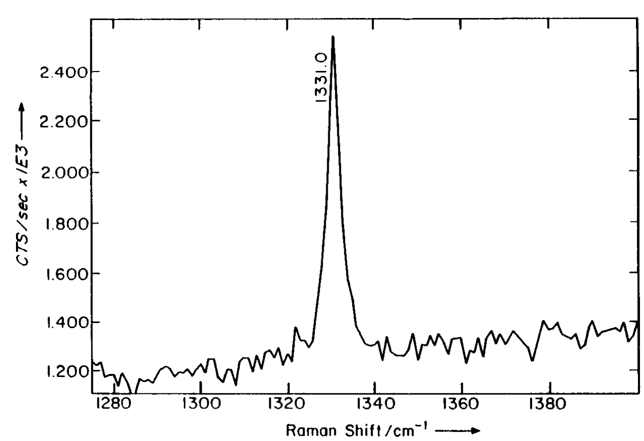

FIG. 8. Raman spectrum of iodoform +2% diamond seeds after being subjected to the hydrothermal process at 800 °C, 1.4 kbar for 48 h.

grown in yet another pressure-temperature—the hydrothermal—range.

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