

Diamond Synthesis: The Russian Connection

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Introduction

Several 40-year anniversaries of the modern area of the synthesis of diamond at high pressures and temperatures (HPHT) have come and gone. If you are a proponent of the Norton Company, this first synthesis would be somewhere between 1948 and 1950. ASEA's Feb. 15, 1953, accomplishment was noted at an international meeting in 1993 on high pressure (AIRAPT) with a small session that included papers by ASEA and General Electric (GE) representatives. The GE success in the Hall experiment of Dec. 16, 1954 (announced in February 1955), was marked only in the personal memories of the remaining members of that diamond team. DeBeers recognizes the ASEA date, but if it celebrates the 40th anniversary of its own in-house accomplishment, it will do so late in 1998; the Russians will do so on or about the year 2000. In any case, the basic, much-copied GE HPHT process is repeated thousands of times each day at sites all over the world (Figure 1) to make a product that has replaced 90% of natural diamond as an abrasive and has given to technology new superhard products in forms unavailable from the earth (Figure 2). All manufacturers are in fierce competition for a total business that probably is in the range of \$1 billion per year, and engineers spend their time primarily in finer tuning for faster growth, greater yields, lower costs, and higher quality crystals. The HPHT process seems to have survived the threat of the low-pressure chemical vapor deposition (CVD) process with respect to abrasive grain and gem-quality stones. However, the low-pressure process has some unique capabilities that obviously cannot be achieved by HPHT, and the product is finding niches in specialized applications (Figures 3 and 4).

The history of this success in industrial crystallization has been documented and revised in numerous interesting publications,¹⁻¹⁹ culminating perhaps in the fascinating story of human beings in the book, *The New Alchemy*.¹⁷ The interplay of personalities among all the players, both successful and otherwise (all of whom had shared the affliction of diamond fever, which sometimes clouds minds), is absolutely intriguing and was best written by someone who was not di-

rectly involved but knew or met most of the players while their memories were still reliable. There is no need to rehash that story. Here we have chosen to isolate a narrow theme based on the contribution of Russian scientists to the HPHT and CVD routes to diamond. Both paths share very-much-ahead-of-their-time experimental discoveries or theories and a remarkable lack of follow-up technology until it was too late to be the first to capitalize on the findings. The reasons for this are complex but include lack of communication, World War II, language barriers, bias, and perhaps, market orientation.

Part I: O.I. Leipunskii and the HPHT process

It had long been appreciated that diamond was a high-pressure mineral and that it would be useful to know the *P-T* equilibrium describing the stability of diamond with respect to graphite.²⁰⁻²² However, before 1938 sufficiently accurate thermodynamic data did not really exist to do this properly in a theoretical manner, and experimentally the world was not really ready until after 1955 (although hindsight suggests somewhat earlier). In 1938 Rossini and Jessup of the then U.S. National Bureau of Standards did careful measurements of the heats of formation of CO₂ from well-characterized samples of diamond and graphite²³ (further refined later by Prosen, Rossini, and Jessup in 1944),²⁴ and calculated the difference in free energies of diamond and graphite as a function of pressure and temperature. The Rossini and Jessup work was a major contribution, and they provided a basis for a diamond/graphite equilibrium curve that was subsequently recalculated and extrapolated by others.

The first of these revisions appears to be by Leipunskii, who made the calculations and published them in a Russian journal in 1939.²⁵ He bravely made a lin-

ear extrapolation of the Rossini-Jessup curve from 1400 K and 42,200 atm to 4400 K and 125,000 atm, a part of which is shown in Figure 5. In addition he was willing to state a pressure and temperature for the direct conversion of graphite to diamond and the same parameters for the conversion in a solvent (iron) to handle the kinetic problem in this transformation. He noted, on the basis of Bridgman's work,²⁶ that the pressure capability to achieve the solution regime (50,000 atm) existed already, that internal heating would present lesser difficulties, and that the 60,000-70,000-atm regime would be achieved in the not too distant future. His comment on internal heating apparently is based in part on his own experience since he refers to himself²⁵ and also to Basset²⁷ in this regard. Starting from Basset's data for the melting of graphite (~4000 K at one atmosphere),²⁷ Leipunskii also presented a graphite-melting line that had a slow increase in temperature with pressure and a widening error bar to accommodate parameters inadequately defined at that time.

In this same paper he was optimistic about the formation of diamond outside of its stable regime and pointed out the kinetic problems associated with nucleation of diamond in the graphite-stable region. From surface free-energy considerations, he concluded that small crystals of diamond might be more stable than graphite in the same size range. He also said that another approach to large diamonds was to sinter diamond powder. There is no evidence that he made diamonds, but he did some graphite-melting experiments at pressures up to 10,000 atm.²⁵ This assertion is corroborated by Neuhaus²⁸ and is contrary to the implication of Liander² that Leipunskii had done many experiments on carbon in silicate and metal melts.

About this time Leipunskii disappeared into the nuclear physics and chemistry programs of a Soviet Union about to be engaged with Germany in the devastation of World War II, and nothing more on diamonds was published by him until a review article on history of diamond synthesis appeared in 1984.²⁹ There is an extensive post-war bibliography for him on radioactivity, reactors, and other aspects of nuclear sci-

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Figure 1. A diamond-manufacturing facility using the high-pressure, high-temperature (HPHT) process. Courtesy of DeBeers Industrial Diamond Division.

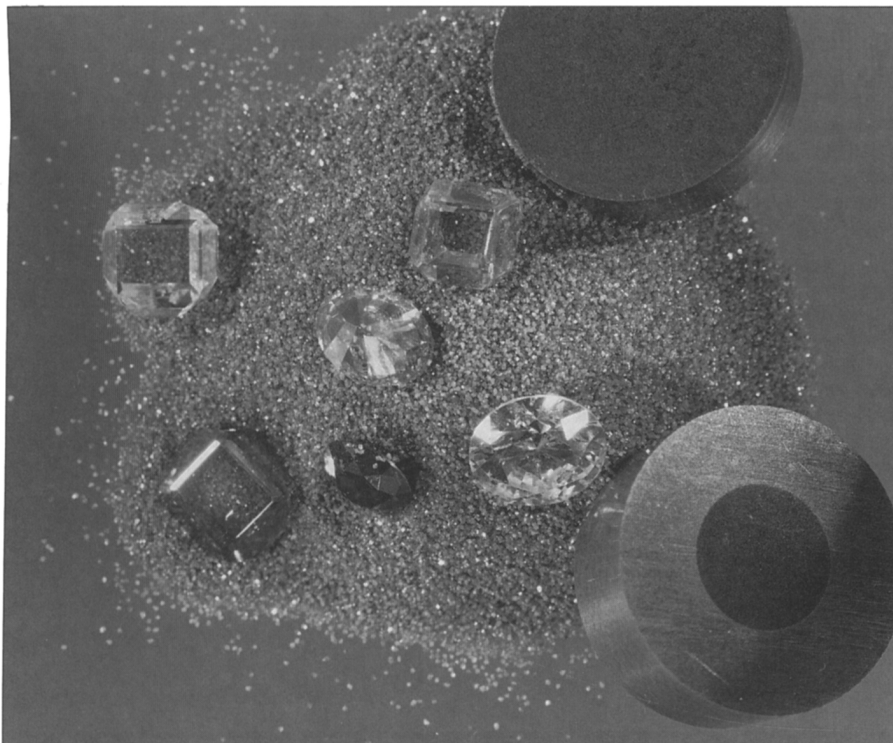


Figure 2. Diamond products synthesized at HPHT. Resting on a pile of abrasive grain are polycrystalline diamond compacts (a wire die blank and a cutting tool) and gem-quality crystals of various colors, both polished and as-grown. The maximum dimension of the largest single crystal shown is about 5 mm. Courtesy of the Corporate Research and Development (CRD) Laboratory of the General Electric Company, Schenectady, N.Y.

ence and engineering. We would like to celebrate his remarkable foresight on the conditions for diamond synthesis 14 years before ASEA, and to point out that his work was either unknown, ignored, or unappreciated by many. Furthermore it is interesting to compare Leipunskii's predictions to both the subsequent theory and experiment. We also are aware that predictions and equilibrium curves do not a diamond make. For the critical combinations of circumstances and commitment that led to a reproducible process and product, see Hazen's book.¹⁷

Leipunskii in the Literature to 1955

The Leipunskii paper²⁵ was abstracted in very brief form in *Chem. Abstracts* 35 (1941) p. 354: "Review of the literature and theoretical. The thermodynamics of crystal-diamond formation from dissolved carbon or from graphite or diamond powder at various temps. and pressures is discussed." This cryptic but adequate abstract seems to have been essentially missed or ignored by most Americans until much later. However Bridgman, who had a long-standing case of diamond fever, was one of the few who cited Leipunskii's paper early on. In an appendix to his own famous paper of 1947²⁶ (which established a marked decrease in the graphitization of diamond with increasing pressure at temperatures in the range of 2000–3000°C and showed that pressures greater than 30,000 kg/cm² would be required for the conversion), he gave a fairly detailed critique of why he couldn't agree with Leipunskii's linear extrapolations of Rossini and Jessup to higher temperatures and pressures. He distinctly left the impression of considerable uncertainty in Leipunskii's version of the *P-T* curve and felt it would bend over to lower pressures at higher temperatures. Bridgman does cite Leipunskii's prediction of <60,000 kg/cm² at about 2000°C as being in general agreement with his own expectations. It is interesting that he says not a word about the role of a solvent for which Leipunskii had predicted a synthesis at lower *P* and *T*. Bridgman's 1947 paper was published about the time of the termination of his contract, which began in 1941 to work on diamond synthesis with the Norton, Carborundum, and General Electric companies. After this, his press went to the Norton Company, and Bridgman said this would end his work on diamond.

In 1949, Mellor (in Australia) reviewed the history of attempts to produce dia-

mond in the laboratory.³⁰ Although he cited Bridgman's paper,²⁶ he makes no reference to Leipunskii but does show Goranson's proposed equilibrium curve for diamond/graphite,³¹ which curves upward to higher pressures than the Leipunskii curve. Mellor thought that J.B. Hannay's use of Li as a solvent might be worth pursuing. In 1952, Eyring and Cagle³² in the United States showed a figure in which Leipunskii's P - T curve for diamond-graphite equilibrium is compared to Bridgman's curve.²⁶ They were also concerned with the kinetics of the phase transformation and discussed the need for a catalyst to lower the activation energy, without mentioning the not-so-new suggestion of Moissan,³³ Parsons,³⁴ Ruff,³⁵ Hershey³⁶—and repeated by Leipunskii—to use an iron solvent.

Leipunskii's paper was well-appreciated by A. Neuhaus who also had the diamond bug and wrote very complete reviews in German of what was and was not known about diamond synthesis in both laboratory and natural environments. In his paper written in 1953,²⁸ he put together a composite figure that compared the P - T curves of Leipunskii,²⁵ Bridgman,²⁶ Simon,³⁷ and Wiberg.³⁸ He mentions that Leipunskii heated carbon rods in an arc at pressures to 10,000 atm and produced graphite. Neuhaus clearly accepted the concept of metal solutions for carbon and used the term "mineralizer"—an earth scientist's way of lowering activation energy—to accomplish diamond synthesis. However, he did not put much stock in metastable synthesis outside the stability region of diamond.

Although the ASEA group did not tell of their 1953 synthesis until 1955 after the GE announcement,^{39,40} it is quite likely that they knew of Leipunskii's work prior to 1953 since they had started work on diamond synthesis in 1942. In one of their publications,⁶ they suggested that one of the reasons they didn't feel they could get a patent was because of prior work, which we believe included the Leipunskii paper.²⁵ In the patent litigation of the 1960s, ASEA tried unsuccessfully to invalidate the GE patents by citing the Leipunskii information, but Liander and Lundblad described the ASEA synthesis of 1953 in some detail without reference to Leipunskii.⁴⁰ Their P - T diagram shows graphite-diamond equilibria curves by Bovenkerk et al.,⁴¹ Berman and Simon⁴², and by Liljeblad.⁴³ They prefer to describe the role of iron as a solvent rather than a catalyst^{2,40} and it is stated that diamond precipitated on cooling the solution. In 1980, in *Diamond Synthesis—the True Story*,² Liander gives

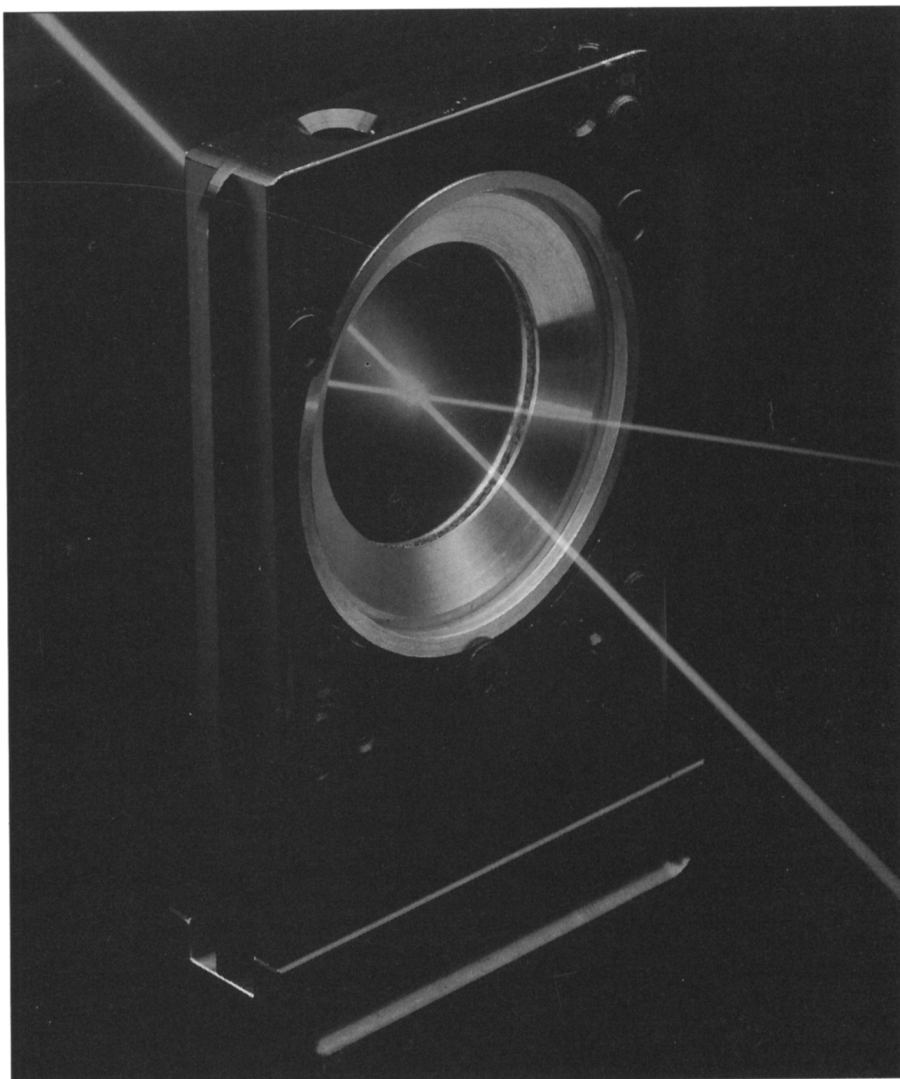


Figure 3. A 50-mm-diameter \times 0.5-mm-thick polycrystalline diamond window made by the CVD process, mounted for use in a beam-splitter application on a synchrotron. Courtesy of GE Superabrasives, Worthington, Ohio.

Leipunskii a lot of attention, along with a query to the effect that since Bridgman knew of Leipunskii's work, why didn't he get off the direct conversion kick and use Fe with carbon and make diamond since he had the pressure capability? This dig perhaps shares overtones of bitterness also found in the ASEA statement that Bridgman told them in 1951 he didn't know of any one seriously engaged in diamond synthesis.^{2,9} It is quite reasonable that he did not know since the consortium had broken up and gone their separate and secret ways.

In 1955 Berman and Simon⁴² recalculated the diamond-graphite equilibrium line from Rossini and Jessup data to

1200 K but with further refinements based on better entropy, compressibility, and thermal-expansion data. The result of this fine tuning extrapolated to higher pressures and temperatures is the curve shown in comparison to Leipunskii's and others in Figure 5. This version is universally accepted. Berman and Simon cite Leipunskii's 1939 paper,²⁵ and both extrapolations are supported by the very convincing determination of the initiation of diamond formation in various metal solvent/catalysts by Bundy et al. in 1961,⁴⁴ as indicated in Figure 5. The Berman-Simon paper appeared after the GE announcement of the successful synthesis of diamond⁴⁵ and has a con-

cluding note acknowledging that accomplishment. Berman and Thewlis later showed why Liljelblad's maximum in the curve was untenable.⁴⁶

The General Electric Company started their own diamond synthesis project in 1950. In both the GE press release of February 1955⁴⁵ and in the first publication in the open literature,⁴⁷ the Bridgman,²⁶ Neuhaus,²⁸ and the Eyring-Cagle³² papers were cited. In the 1959 paper by Bovenkerk et al.,⁴¹ the Berman-Simon line and extrapolation are shown with curves for the melting of Ni and of the Ni-C eutectic without reference to the use of iron or to Leipunskii.

Slawson is another who may have known of Leipunskii's paper via Bridgman's paper but did not mention it in 1953 when he plotted his interesting attempt at diamond synthesis via the decomposition of HgC_2 in terms of a modified Rossini and Jessup diagram with stability regions for diamond and graphite.⁴⁸ He claimed to reach 35,000 kg/mm² at room temperature but made only graphite.

B.V. Derjaguin and D.V. Fedoseev (key players in the Russian effort on CVD diamond synthesis to be discussed in Part II) in their fascinating little book, "Diamonds Wrought by Man," written for the Russian public in 1980 and translated into English in 1985 (Mir Publishers, Moscow), clearly recognize Leipunskii's contribution.⁴⁹ There are at least three other specific testimonials, two in Russian and one in German, that we know about and are worth citing here.

In 1973 in *Sinteticheskoye Almazny*, no. 2, pp. 5-8, an anonymous account (in Russian) of Leipunskii's early place in theory of diamond synthesis tells of his being awarded Diploma No. 101 in 1971 to establish the priority of his 1939 paper and the Soviet role in HPHT synthesis of diamond.⁵⁰ His contributions to both the thermodynamic and kinetic aspects of diamond synthesis both in and out of the diamond-stable region are noted, his 1939 paper is essentially reviewed, and the creativeness of Soviet scientists and engineers is praised. The many honors awarded to him are listed.

A popular article designed to appeal to the people of East Germany, "Der Stein des Leipunskii," written by Dieter Wende in *Der Ausschnitt, Wochenpost DDR*, 1056 Berlin, p. 13, 1984, has many intriguing statements.⁵¹ A subheading reads "How the Discoverer of Diamond Becomes Discovered." There is a beginning description of large and famous natural diamonds and the famous picture of the GE press with F. Bundy and

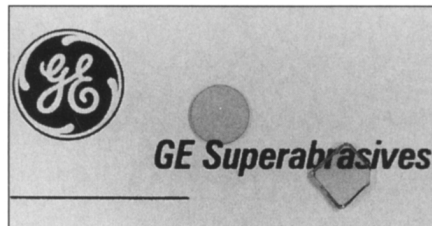


Figure 4. Comparison of transparency of chemically vapor-deposited (CVD) polycrystalline diamond (left) with single crystal (Type IIa, cube plane orientation). Both pieces are 0.3-mm thick and about 6-mm wide. The CVD diamond contains about 10 ppm hydrogen and has a thermal conductivity of about 20 W/cm-K. Courtesy of GE Superabrasives, Worthington, Ohio.

H. Strong, a section citing Leipunskii's lone contribution to diamond synthesis and his subsequent disappearance ("Wo ist Leipunskii?"), and the importance of synthesized diamond grain. However in our context, the German article gets more interesting in the sections dealing with patent litigation. According to this account, ASEA challenged the GE patents on the basis of the priority of Leipunskii's work and the alleged clear correspondence of it to the GE process. ASEA lost this argument on the basis of GE's claim that the process as described by Leipunskii (presumably his proposal for the slow cooling at high pressure) would not produce quantities of diamond as in the isothermal mode used by GE. The German article also states that after the Russians made diamond under HPHT conditions at around 1960, GE brought suit for patent violation and asked that the Russians pay a sizable penalty and stop production of synthesized diamond. Accordingly Leipunskii was asked to study the situation, was surprised that his paper already had been the center of controversy among two capitalistic firms and that so few knew of his work or cited it *even in Russia*. Wende's article claimed that in the Russian case GE withdrew its complaint on the basis of Leipunskii's priority.

Finally there is the memorial to Leipunskii, who was born in 1909 and died Jan. 7, 1990. This appeared in Russian in the proceedings of a seminar on diamond and diamond films that took place in 1991.⁵² Varnin, a man with considerable interest and experience in both HPHT and CVD diamond synthesis, wrote the memorial. Here are listed

Leipunskii's many awards and contributions to science and engineering with considerable emphasis on his diamond paper and the impact of this single contribution for which he received no specific award. The litigation begun in 1969 by GE asking the Russians to pay a penalty for patent violation and to stop exporting diamond is cited as reported earlier. Similar to the Wende article, the memorial also stated that in 1970, GE dropped the suit admitting the priority of Leipunskii. There are some nationalistic overtones expressed in the context of Soviet-U.S. competition, but all can agree on how far ahead of his time Leipunskii was in diamond synthesis. Without the intervention of World War II, the story of diamond synthesis under HPHT conditions certainly would have been different.

An Evaluation of Leipunskii's Predictions

So how did his work fare in the subsequent accumulation of new knowledge? Obviously from Figure 5 his calculated curve to 1400 K is essentially identical with the Berman-Simon version, but there is some small difference in the two linear extrapolations. Both were experimentally made more secure in the classic contribution of Bundy et al. in 1961 where Leipunskii is cited.⁴⁴ Also in 1961, Neuhaus gives us a view of his feelings when he specifically notes the essential identity of the Berman-Simon and Leipunskii version.⁵³ However, he goes beyond this by showing a *P-T* diagram with a curve labeled "Leipunskii-Simon." This is a worthy testimonial to Leipunskii's prior publication, but it is a bit awkward to include Simon without Berman since Simon's 1926 curve really is considerably displaced from the two more recent versions.³⁷ It would be nice to give Leipunskii credit somehow, but the Berman-Simon line has achieved its own immortality in this context and is a more precise evaluation.

With respect to Leipunskii's quantitative predictions of minima of *P* and *T* for direct transformation of graphite to diamond, compare his ~58,000 atm and 2000 K with Bundy's >125 kbars and >3000 K.⁵⁴ For indirect transformation (via solution), compare ~45,000 atm and ~1500 K (as read from his diagram) with the lowest *P-T* threshold for diamond formation from iron found by Bundy et al.⁴⁴ to be about 53 kbars and about 1700 K (see Figure 5). Not bad on the latter; quite a bit off on the direct transformation. As mentioned previously, the experimental data from solvents⁴⁴ supported both Berman-Simon and Leipunskii's

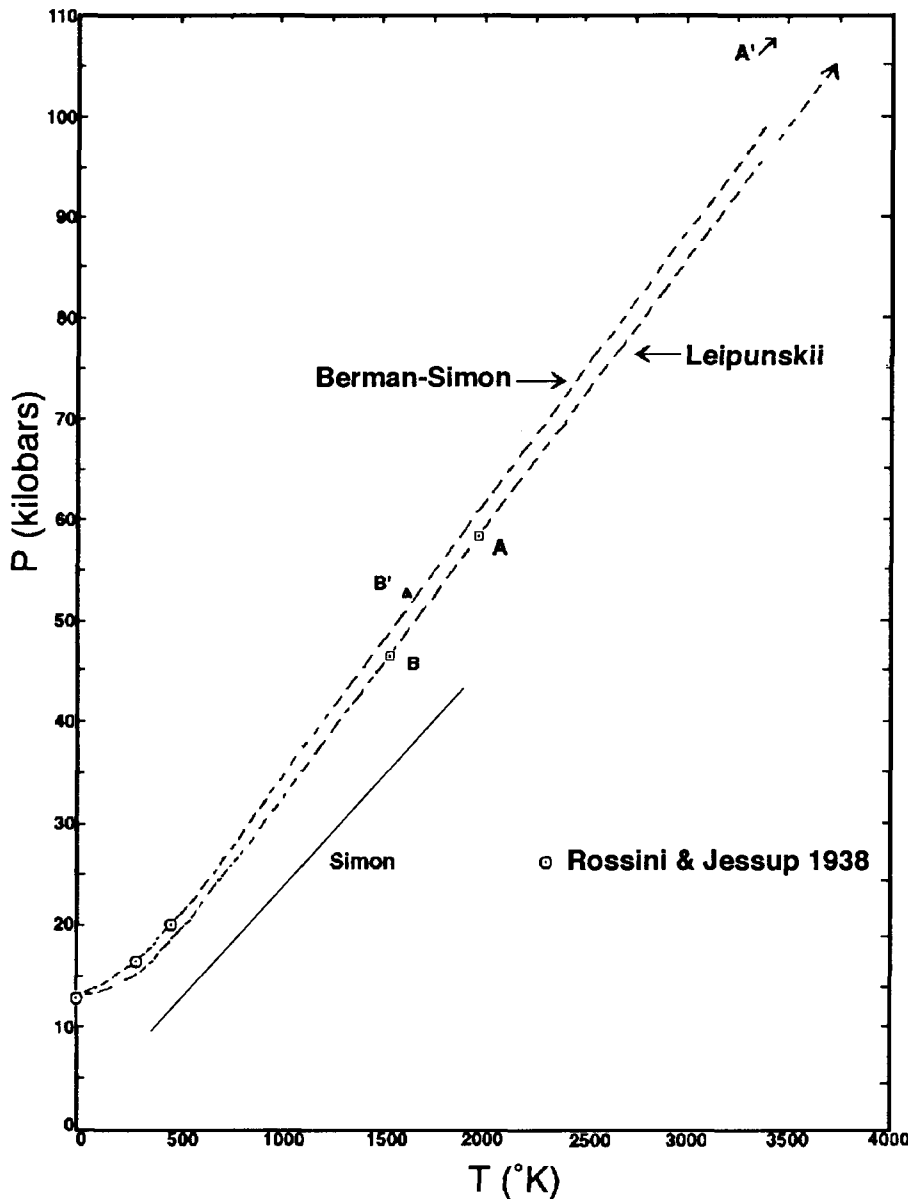


Figure 5. Equilibrium curves for diamond/graphite: Simon,³⁷ Leipunskii²⁵ and Berman-Simon.⁴² A: Leipunskii prediction for direct conversion,²⁵ A': experimental minimum for direct conversion: offscale, >125 Kb, >3,000 K;⁵⁴ B: Leipunskii prediction for indirect conversion in the system Fe-C;²⁵ B': experimental minimum for diamond formation from Fe-C.⁴⁴

skii extrapolations of the equilibrium curve for graphite-diamond within the limits of experimental error, the vagaries of pressure calibration, and the assumptions in the calculation itself.

Leipunskii believed that to grow diamonds from the diamond-stable region, it would have to be done at a slow enough rate, presumably by slow cooling, to avoid the kinetically favored formation of graphite. As Bundy²⁰ has pointed out, the successful process for making abrasive grains is isothermal,

and slow cooling does not produce the yield or quality desired. Here the driving force for diamond growth is the difference in solubility between graphite and diamond in the diamond-stable region. However, in the more nearly equilibrium process for growing large diamond crystals where the carbon source is diamond only, slow transport of carbon onto a seed crystal in a temperature gradient has been successful enough to worry the gem trade (Figures 2 and 6).⁵⁵ It may be moot if this is a verification of Leipun-

skii's concept of slow cooling.

With regard to growth of diamond from the graphite-stable region, Leipunskii was optimistic that this could be solved with attention to the critical problem of avoiding nucleation of graphite. He proposed rapid quenching of liquid or gaseous carbon and the use of seeds (also suggested for HPHT conditions). He was well aware of the previous work on CVD experiments, particularly those of Ruff,³⁵ von Bolton,⁵⁶ and others. It seems quite reasonable to assume that his opinions in this regard might have had some influence at least on the Russian scientists who later were successful with both the homoepitaxial and heteroepitaxial growth of diamond from the gas phase.

Leipunskii's suggestion that at small particle sizes, diamond might be more stable than graphite has been rediscovered and debated in recent papers without citation.^{57,58}

Speculation With Hindsight

What if there had been better communication among the diamond makers, or what if WWII had not interrupted both the U.S. and Russian programs on diamond synthesis? Or what if Bridgman had a bit more of a chemist and had listened to the drumbeat about using a metal as a solvent instead of being biased toward direct conversion? Certainly both GE and ASEA and perhaps others were following that lead. Or what if Bridgman had done a little more with internal heating? All this comes into focus in the neat demonstration by Bundy of making diamond in a Bridgman anvil with internal heating and a metal solvent/catalyst.⁵⁹ As Leipunskii had pointed out, the pressure capability for the solvent experiment existed. Internal heating in pressure cells, while not as sophisticated as it was to become, was known from both his own experiments and from Basset's work.²⁷ Parsons' experiments could also have been cited in this regard.³⁴ Bridgman did do some internally heated experiments using the thermite method with which ASEA had some success in their ponderous apparatus. It is frustrating after all this to think of Bridgman and also of Gunther et al.⁶⁰ doing their "hot forging" experiments where graphite was heated outside and then rapidly put in the press for squeezing. Bridgman had a chance to appreciate all this hindsight when he went to GE in 1955 and made diamonds by himself in the Hall belt apparatus. Without the war, Leipunskii and Bridgman might have been in a race for this prize, and diamonds might have been

synthesized five years or more earlier.

However, such success is somewhat dependent on motivation. If Leipunskii's goal was simply to sum up the knowledge and develop the theory, progress in development and application might have stopped there as it appears to have done with CVD diamond in Russia. In the United States the combination of a strong driving force for a needed product and the commitment of a capitalist company certainly was a factor, but there were probably five or six groups in the world that had had cases of diamond fever and would have produced diamond for the simple reason of wanting to do it first. A thorough reading of Leipunskii's paper would have been a good start.

Part II: The Russians and the Synthesis of Diamond Under Metastable Conditions

Background History

Whereas Leipunskii appears to have played a unique lone role with ideas about diamond synthesis in the stable region, there are several Russian contributors (predominantly from one group, however) to the chemical vapor deposition of diamond far from the equilibrium conditions. Before describing that success, a brief history of this mode of synthesis is necessary to put their contributions in the proper context. Although the early attempts to make diamond were aimed at synthesis at high pressure, presumably under conditions of equilibrium, with hindsight we now know that until the early 1950s such conditions were not attained. If diamond was made by any of the early workers, it would have been in the stability region of graphite. However, there were many who believed enough in metastable growth of diamond to have deliberately chosen this direction in spite of considerable skepticism among some scientists.

At least as early as 1905, Burton—who also claimed diamond synthesis from Pb-Ca melts at 1 atm—tried the decomposition of CCl_4 at 300°C in a pressure vessel and got amorphous carbon.⁶¹ In 1910 von Bolton at Siemens claimed the formation of diamonds from the carbonization of a rubber stopper that contacted a Ba amalgam in a test tube held at room temperature for three weeks. He believed the hydrocarbon from the stopper was decomposed by the amalgam. He repeated this in a more controlled way by seeding the upper part of the test tube with very fine diamonds and passing moist acetylene over the surface of a Na amalgam heated to 100°C for four weeks.⁶² On the basis of microscopic ex-

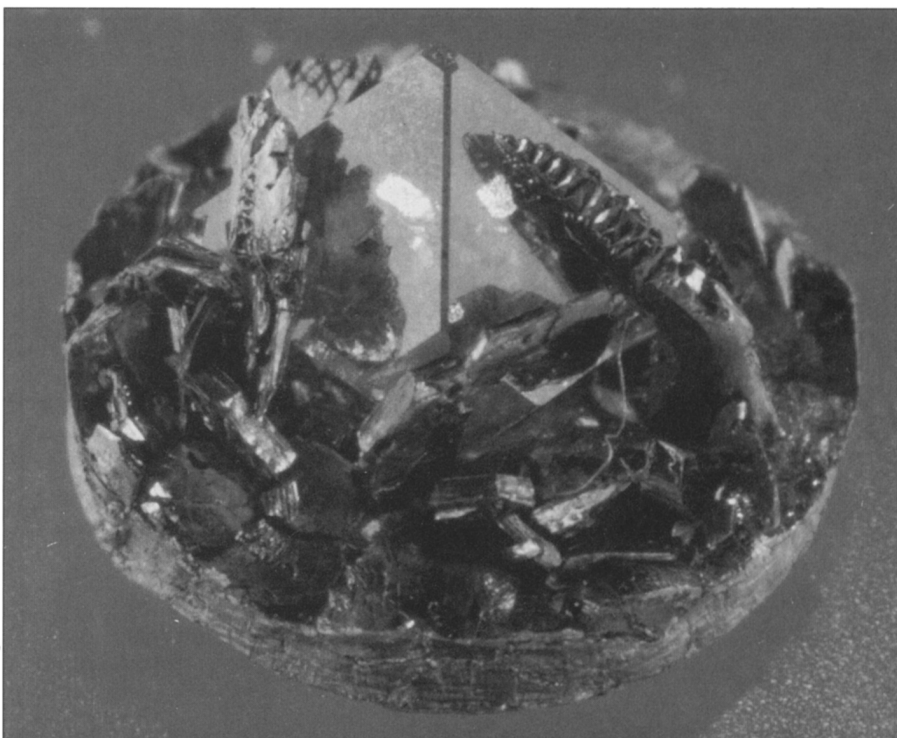


Figure 6. A gem-quality octahedrally shaped diamond grown by the thermal gradient process⁵⁵ in equilibrium with graphite that is overgrowing the crystal near the diamond-graphite equilibrium line. The diameter of base is about 8 mm. Courtesy of CRD Laboratory of the General Electric Company.

amination, he claimed the seeds had developed facets that were not previously there. The Russian researchers were aware of this study. In 1917 Ruff reported no increase in weight of diamonds heated for 14 days at 790°C in acetylene, coal gas, methane, or carbon monoxide. He also tried experiments in an electric furnace at pressures up to 3,000 atm, with graphite as the only product.³⁵ In 1921 Tammann claimed the formation of a new dense form of carbon (not diamond) from the decomposition of CCl_4 , CBr_4 , and CI_4 at 600–700°C in the presence of Hg.⁶² He clearly believed diamond could form metastably and constructed a *P-T* diagram for carbon to illustrate how diamond and graphite might coexist in a state of pseudoequilibrium.

The modern era of growth of diamond under metastable conditions began in the early 1950s, primarily with Eversole in the United States and Derjaguin's group in the Soviet Union. In the 1960s they, along with Angus in the United States, comprised the major world effort on CVD diamond synthesis. Angus believes Eversole's synthesis of diamond by CVD predates any of the high-pressure claims

for precedence.^{13,64–66} According to Angus, who had access to unpublished laboratory notes at Union Carbide, Eversole started his experiments—aimed at deposition of diamond from carbon monoxide onto diamond—late in 1949 and achieved overgrowth on the seeds late in 1952 and early 1953. Confirmation of diamond was by weight gain, density, resistance to inorganic acids, chemical analysis, and x-ray diffraction. These results were reproducible but unavailable to the public until Eversole's U.S. patents, which were filed July 23, 1958 and issued April 17, 1962.⁶³ The results are referenced by all his contemporary and subsequent workers. In Germany, Meincke, who acknowledges Eversole for some chemical analyses, claimed diamond formation from some carbon arc experiments in 1958.⁶⁷ He also acknowledges the support of Union Carbide and the Office of Naval Research in Washington, D.C.

In between Eversole and Angus, and contemporary with the Russian work, are the contributions of Brinkman⁶⁸ and of Hibshman,⁶⁹ and the Siemen and Halske patents.^{70,71} Included in these works were some ideas that are close in

concept to successful methods developed later, and the Russians were aware of this prior art. Brinkman filed a patent in 1960 on transport of hot carbon atoms onto a cooler diamond-seed crystal through a temperature gradient using liquid metal in one process and a vacuum or inert-gas phase in the other. In the latter case the carbon source can be a hot graphite surface such as a furnace tube, which also heats the seed crystal.⁶⁸ He addresses the problem of avoiding graphite nucleation, but apparently not successfully enough to produce a viable process.

The Siemens and Halske Company filed patents on Sept. 5, 1962 describing the decomposition of a variety of hydrocarbons (including halogenated ones) transported in an inert carrier gas or in hydrogen from a higher temperature to a lower temperature zone where the presence of cubic carbide-forming metals was reported to assure the deposition of diamond rather than graphite. The catalyst metals could be present as solids or in organometallic compounds.^{70,71} These patents covered other modifications such as using a solid carbon source reacting with a gas and also activating the reaction zone by electrical discharge. There is no evidence of exploitation of this patent position, but in the context of later work, at least some of these phenomena seem to have been reproduced.

Hibshman, a research associate with Esso Research and Engineering had his photograph and work in a column in the March 9, 1968 *New York Times*. The article described his patent filed Jan. 20, 1964 on growth of diamond seeds from carbon monoxide and hydrogen in the presence of catalyst metals (Pt, Ni, Rh, Au, Ni).⁶⁹ He described "active nascent carbon" as a carbon atom or radical containing carbon having a free-energy potential higher than that of the diamond that is subject to growth under the conditions of the process. He listed many ways to produce this form of carbon, including vaporization of a solid source, but preferred the decomposition of CO. Hydrogen in the carbon-containing gas enhanced the growth rate in the presence of the catalyst metals. Hibshman, with considerable foresight, clearly states he believed *the role of the metals in the presence of hydrogen was to produce atomic hydrogen, which he believed destroys nuclei of nondiamond carbon*. Again, although there was no exploitation of this work, its reproducibility was later established indirectly by others. In the sense of being well ahead and unappreciated, Hibshman's foresight with respect to the role of atomic

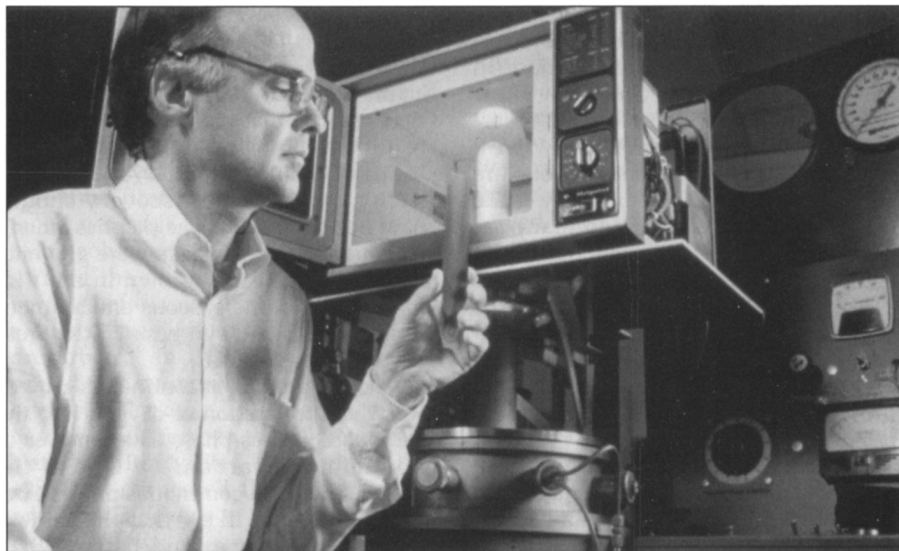


Figure 7. Tom Anthony with the microwave oven he used to create atomic hydrogen in a plasma for the CVD of diamond. Courtesy of the CRD Laboratory of the General Electric Company, Schenectady, N.Y.

hydrogen in CVD deposition of diamond is somewhat comparable to that of Leipunskii's emphasis on the role of Fe with respect to synthesis under HPHT conditions.

Angus, who is still very actively working on CVD diamond, played an important role in the Russian connection. He clearly was among the early believers as indicated by a 1966 government report,⁷² and he confirmed Eversole's results and submitted a paper on growth of diamond-seed crystals in 1967.⁷³ He applied for several patents with his colleagues in June 1968.⁷⁴⁻⁷⁶

Angus' studies were watched closely by others—especially by the General Electric Company. At the then Research Laboratory of GE in Schenectady, N.Y., belief in the synthesis of diamond in the metastable region took the form of a project that ran in parallel with the HPHT effort from 1950 to 1957. Oriani and Rocco wrote a summary report of this work in 1957,⁷⁷ and the project was terminated in view of the success of the HPHT project. One of the members of the latter group once said something to the effect that at times they thought the metastable approach was closer to success than theirs. Most would agree that in terms of what is now known about the CVD conditions for diamond synthesis, GE was operating in the proper region although no claims of success were made. It was important for any diamond maker to monitor a possible competitive

process. However, every time an evaluation was made, the growth rates or throughput were so low compared to the high-pressure process that the viability in terms of production of abrasive grain was deemed no contest—a conclusion that still appears to be true. There was some evaluation of what one could do with thin films if they were available, and some contact was made with those making sputtered diamondlike films. However, the material at that time was inadequate for testing, and nothing further was done. GE continued to monitor developments but did not get back into metastable synthesis of diamond until 1984, at least two years after the Japanese researchers' successful reproduction of the Russian work. T. Anthony made diamond by this process at the GE Research and Development Center in October 1985 (Figure 7).

The Russian CVD Diamond Connection

In 1956 Spitsyn and Derjagin filed an Authors' Certificate (patent application) on the formation of diamond by pyrolysis of CBr₄ and CI₄,⁷⁸ a mode that was tried earlier by others in various modifications.^{35,62} This patent, not issued until 1980, had its origin with Spitsyn when he was a student at Tomsk University. He later came to Moscow to work first under Roginsky and later under Derjaguin. The pyrolysis of carbon halides appears to have been no more successful than it

was for others, but it marks the beginning of an intense commitment by Derjaguin's surface phenomena group (in the Institute of Physical Chemistry of the Academy of Sciences in Moscow) to formation of diamond by CVD at low pressures. Several members of this group are still active in this field, and they made key discoveries and pursued many aspects of CVD diamond before the impact of their work was rediscovered in the late 1970s and early 1980s by the rest of the world. From 1965 to 1993 it is estimated that at least 50 different scientists were involved, and they produced at least 110 papers, three books, and several patents.

There were two separate approaches to CVD diamond within Derjaguin's group. By 1965 Fedoseev had joined with Derjaguin and had begun, with several colleagues, a long series of investigations on the pyrolysis of methane while Spitsyn had taken the path of chemical-transport reactions since about 1961.⁷⁹ These studies must be considered in the context that the codeposition of graphite along with diamond was a major barrier to progress starting with Eversole. *Two discontinuous stages were required to produce a recognizable overgrowth of diamond: a growth cycle followed by a cleaning cycle to remove nondiamond carbon. The linear growth rates under these conditions were of the order of 0.001 $\mu\text{m}/\text{h}$. The second important limitation was the limitation to deposition on diamond only.* The breaking of both of these barriers and the consequent marked increase in growth rates (1–10 or more $\mu\text{m}/\text{h}$) by the Derjaguin group about 1971–72 made possible the current intense activity in CVD diamond.

Derjaguin, Fedoseev, and colleagues attacked these problems with some innovative ideas to diminish coprecipitation and to develop a continuous process. For example, they tried a periodically pulsed light beam to heat and cool the diamond in the presence of a carbon-containing gas.^{80,81} The light-beam pulses from a xenon lamp had a duration of 1.3×10^{-2} s to vary the oversaturation of carbon so that the oversaturation pulses were shorter than the time required for the formation of nuclei of nondiamond carbon. The time interval between pulses (0.5 s) was controlled to allow resorption of the nuclei of nondiamond carbon. A patent was filed on this process on July 26, 1967,⁸⁰ and work on this process was still being reported in papers and patent applications as late as 1973. A curious result of these studies was the report of growth of diamond whiskers by the vapor-liquid-solid (VLS) mecha-

nism.^{81,82} Even as late as 1975 in the famous article in *Scientific American*,⁸² these whiskers were being described and claimed as diamond from x-ray-diffraction studies. The reproducibility of this result is unknown, and little has been heard of it since about 1975. Certainly such an important discovery should have been exploited. The skeptics among us believe these whiskers were graphite, which is quite easily grown in the VLS mode in the same gaseous environment used for diamond synthesis in the presence of certain metals.

Another attempt at continuous growth was the introduction of oxygen into the carbonaceous gas phase as a remover of nondiamond carbon.^{83,84} One of the patents implies a continuous process, but it appears more likely that the growth process could be extended somewhat, but still requiring a later cleaning step. There are several, more recent studies by others that confirm a beneficial effect of introduction of certain amounts of oxygen into the process, but a continuous process with oxygen alone has not been substantiated. Another direction taken by the Russian group from about 1968 to 1971 was the use of metalorganics as the carbon source, and the advantages of higher growth rates and decreased graphite deposition were claimed.⁸⁵ The introduction of metals per se or as metalorganics has been mentioned earlier.^{68–71}

With the chemical transport mode, between 1966 and 1969 Spitsyn achieved a milestone with the growth of 1–2- μm -thick films of diamond on a single-crystal diamond seed.⁷⁹ He was influenced by a paper on the kinetics of the reaction of hydrogen with graphite at high temperatures and the species that would be present as determined from thermodynamic calculations.⁸⁶ He passed hydrogen over hot graphite (somewhat related to Brinkman's earlier approach)⁶⁸ and carbon ("in status nascendi") was deposited as diamond on the cooler seed diamond about 0.1 mm away with linear growth rates up to almost 1 $\mu\text{m}/\text{h}$.^{79,87–91} A patent application no. 987912 was filed on this process on April 21, 1971 with an issue date of Sept. 10, 1990.⁹²

As will be seen in the next section, the deliberate introduction of atomic hydrogen into the reactor became the key to the production of CVD diamond at relatively high growth rates compared to earlier experiments. On the basis of thermodynamic calculations, the Spitsyn experiment probably contained some atomic hydrogen.^{86,92} With hindsight we know in addition that because of the serendipitous presence of Re wires hold-

ing the seed diamond, there was the possibility of *in situ* production of atomic hydrogen. Although in hindsight we know the presence of atomic hydrogen undoubtedly made possible the success of the chemical-transport experiment, *there is no evidence that the importance of this gas species was recognized at that time.*

The Russian-Angus Atomic H Connection

In 1971 at a conference in Kiev, Angus presented a paper and described his work on deposition of B-doped diamond.⁹³ The last paragraph of his paper states that atomic hydrogen was a better remover of nondiamond carbon than molecular hydrogen, which everyone had used up to this point in the cleaning stage of the cyclic process. He made atomic hydrogen by introducing a hot filament into the cleaning step following the growth stage. This transfer of information appears to be the key to the breakthrough achieved by the Russian group, and our reconstruction is based on conversations with Varnin.⁹⁴ Fedoseev attended the Kiev conference and conveyed the information to the group in Moscow. Varnin picked up the idea and proposed incorporation of atomic hydrogen *in situ* in the reactor when diamond was being codeposited with nondiamond carbon, thereby eliminating the cleaning step. Polankaya was directed by Fedoseev to work on this. It must have been soon after (perhaps late 1971 or early 1972?) that diamond was deposited as visible, faceted crystals without the need for diamond seeds and at much higher growth rates than the cyclic process. In their 1971 booklet on synthesis of diamond from the gas phase,⁹⁵ Derjaguin and Fedoseev showed micrographs of faceted, epitaxial diamond films that were of sufficient substance to do hardness, diffraction, refractive index, and density measurements and to observe spiral dislocations on the (111) surface.⁹⁶ However, the actual process for these films is not clear and may have been from pyrolysis of $\text{CH}_4\text{-H}_2$ mixtures.

However, the role of atomic H is clearly stated in a paper submitted in 1974 (published in 1976) on epitaxial diamond graphite (note: nondiamond substrate).⁹⁷ This paper was available in English translation in 1976. Derjaguin, Spitsyn, and Bouilov reported on deposition on Cu and Au, with micrographs, in 1976.⁹⁸ They were able to determine the relative growth rates of the (111) and (100) crystal faces. Now one could hold and see a piece of diamond made at low pressures without having to deal with the skepti-

cism based on resorting to weight gain and diffraction. However, this paper was in Russian and described a chemical transport reaction in a closed system without mention of atomic hydrogen.

The difficulty of clearly defining the breakthrough from the literature is apparently related in part to a strict curtailment of publication from 1971 to 1975, and perhaps to deliberate obfuscation, because the unsolicited article in *Scientific American* in 1975 on the cyclic process also said nothing about atomic hydrogen, faceted crystals, or nondiamond substrates.⁸² The role of dilution of CH₄ by H₂ and its effect on the growth rate of diamond was discussed in a series of papers by Derjaguin et al. in 1973 without mention of atomic H.⁹⁹ With the hydrogen addition there was a longer growth time for diamond, and soot and graphite formation were retarded. In these experiments it was found that the process could be monitored by measuring the electrical conductivity of the product as diamond and graphite grew simultaneously. These concepts do not convey the idea of common use of atomic hydrogen as an *in situ* scavenger of nondiamond but may simply represent parallel investigations. Obviously if the role of atomic H was appreciated, it was left out of these publications.

In 1977 in their book on growth of diamond and graphite from the gas phase, Derjaguin and Fedoseev clearly stated that atomic H acts preferentially on graphite and that the combination of the two processes in one reactor allowed growth of thick layers adequate for property measurements.¹⁰⁰ No mention is made that nondiamond substrates can be used. In 1981 Spitsyn cites the enhanced nucleation of diamond on carbide-forming substrates and notes linear growth rates of 1–5 μm/h.¹⁰¹ This growth rate can be compared with the maximum linear growth rate of 0.45 μm/day (~0.02 μm/h) reported in a study of the kinetics of diamond growth in methane with and without hydrogen additions in 1976.¹⁰² The Russian explanation of the effect of atomic H during the codeposition of diamond and graphite was the preferential removal of nondiamond carbon so that more diamond can be recovered. Hibshman would have been pleased to hear this support for his theory. Since then, there have been other functions assigned to atomic H. However, whatever the mechanism, the reality of diamond from a potentially commercially viable low-pressure process was finally achieved by the introduction of atomic H into the methane-

hydrogen reaction. Additional Russian interest in producing atomic H *in situ* is indicated by the glow-discharge work of Varnin in 1975¹⁰³ as well as his use of an electrical field.¹⁰⁴ Fedoseev reported on gasification of carbon in a glow-discharge hydrogen plasma in 1979.^{105,106}

A final first for the Russians in diamond synthesis at low pressures was yet to be achieved. In 1979 Fedoseev described the crystallization of spherical particles of diamond by condensation of a pulsed-laser discharge in a liquid hydrocarbon.¹⁰⁷ In 1983, Fedoseev et al. reported that by merely exposing graphite or carbon black to a CO₂ laser pulse, diamonds would form in the laboratory ambient.¹⁰⁸ R. Roy visited Derjaguin's lab in 1985 and witnessed the conversion. In addition Fedoseev et al. demonstrated that hexagonal BN and quartz could be converted to their respective more dense forms, cubic BN and coesite and/or stishovite, by the same process.¹⁰⁹ Alam, Debroy and Roy experimentally confirmed and extended Fedoseev and Derjaguin's pioneering work on laser synthesis of diamonds.^{110,111} At a Gordon Conference in 1990 where Fedoseev presented these results, a skeptical audience was convinced by hearing confirmation of the phenomenon. Since then, others in India and Japan have taken the process even further^{112,113} and have grown crystals to 20 μm by this process.

The Russian-Japanese-American Connection

Matsumoto and Setaka at NIRIM in Japan started a research program in 1974 on CVD diamond and followed the Russian work in the literature. At least by 1981,¹¹⁴ this group had reproduced the single-step process with nondiamond substrates using different ways to produce atomic H. Their use of a microwave plasma to atomize the hydrogen was a major advance toward simplicity and reproducibility.^{115,116}

Attention was focused on the spectacular Japanese results by a serendipitous event. On a mission for Japan's Science and Technology Agency, Roy was making a periodic visit to NIRIM where S. Kimura took him to a laboratory to show him a diamond layer (confirmed by Raman and x-ray diffraction data) on a four-inch silicon wafer. This observable physical object with faceted crystals made a deep impression on Roy as it was soon to do to scientists and managers worldwide. On his return to the United States, Roy became the evangelist for CVD diamonds in the West, alerting government agencies and industries

alike to the Russian-Japanese achievement. A.M. Diness of the Office of Naval Research was persuaded to fund this "high-risk" work to duplicate the Japanese results at Penn State, and their first diamond films were produced late in 1985 using Toshiba microwave hardware. Publication in the scientific press was received with extreme skepticism at the U.S. universities, although all that was claimed was duplication of results present in the literature for almost 10 years. The corporate world, on the other hand, showed a very keen interest. In August 1986, three dozen research representatives assembled at the Materials Research Laboratory at Penn State to learn about the synthesis of diamond by CVD. On August 13, 1986, the *New York Times* carried a front-page story on this event, and that publicity nucleated a torrent of activity on CVD diamond in the Western World, and diamond fever was rampant. The rest of this story has been described adequately elsewhere.^{117,118} Perhaps the icing on the cake for this revival was the innovations of Hirose, who first showed that the carbon source could be composed of organic compounds, including sake,¹¹⁹ and then demonstrated in 1988 that the oxyacetylene torch could be used to grow diamond.¹²⁰ The latter permits all of us to make diamonds in the garage or in front of a science class and to properly toast the success at the same time.

Summary

Russian scientists made significant contributions to the theory and practice of diamond synthesis from both equilibrium and metastable conditions. In the case of HPHT synthesis, Leipunskii's quantitative predictions were many years ahead of the practice that eventually supported much of his foresight. Most did not know of his work until several years later, and even those who were aware were either nonreceptive or simply ignored it. The ideas did not fall on fertile ground for some. There is no question that World War II and the language barrier delayed both effective communication and experimental work in this field all over the world. For the Russians there was little chance of putting Leipunskii's ideas to practice until well after the war, even if there was an intent to do so. In principle there was a small U.S. interest during the war, but it did not develop into a serious commitment until the late 1940s or early 1950s. There were several competing groups eager to solve the diamond-synthesis problem, and they would probably have independently con-

verged on a solvent/catalyst solution, as did the ASEA group.

The early Russian contributions on synthesizing diamonds far from the region of thermodynamic stability were contemporary with others in the United States. However, the Russian commitment of many very good scientists over an extended period of time was an advantage that provided an environment conducive to both generation and acceptance of new ideas. The key advance was the introduction of atomic hydrogen into the reactor chamber by Spitsyn, Fedoseev, Derjaguin, et al. Without this innovation, CVD diamond might still be inspiring the same skepticism that Eversole and Angus and others had to face, and the fantastic growth of this mode of synthesis after about 1982 would not have taken place. The Russian system failed however to exploit a lead time of almost 10 years, and it was the Japanese who demonstrated reproducibility, told the world, and introduced their own engineering innovations. Some of us in the United States should also learn a lesson from this experience about taking off the blinders and accepting new ideas. The Russians read the western literature with more purpose than we did theirs, and this in an era when there was more reading of the literature than there is now.

Although two entirely different approaches to the synthesis of diamond exist, that is, in (high-pressure) and out (low-pressure) of the region of its thermodynamic stability, in a sense there is a common phenomenon. In both cases, as this historical review has shown, there is a key role for a "solvent/catalyst" for kinetic purposes: a metal in the high-pressure process, and atomic H in the low-pressure process. In the context of modern understanding of diamond, many believe that its hydrogenated surface is a thermodynamically stable entity. The extension of this is that CVD deposition of this phase is not described by "metastability" at all. This means that in *P-T-X* space where *X* is H (and perhaps even when *X* is Fe), the stability region of diamond may be in for some modification in the future. The concept of some sort of a common denominator is muddled somewhat by the synthesis of diamond by laser in the absence of hydrogen. There is still much to unravel.

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