



Diamond synthesis by chemical vapor deposition: The early years



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ARTICLE INFO

Article history:

Received 14 July 2014

Received in revised form 14 August 2014

Accepted 18 August 2014

Available online 26 August 2014

Keywords:

History

Diamond synthesis

Chemical vapor deposition

Metastable synthesis

Diamond crystal

Diamond film

ABSTRACT

In the two decades following World War II there was a great surge in interest in high-pressure diamond synthesis, especially in Sweden, the United States and the Soviet Union. It is less well known that during this time major efforts were also made in low-pressure, metastable growth of diamond. All of these efforts, both high and low pressure, were characterized by great secrecy and a considerable lack of transparency. General Electric made the first public announcement of successful high pressure-high temperature diamond synthesis in 1955.

The first reports of low-pressure diamond syntheses in the open literature were in 1962 (Eversole; Union Carbide Corporation) in 1968 (Angus et al.; Case Western Reserve University, Cleveland, and also in 1968 (Deryagin et al.; Physical Chemistry Institute, Moscow). In addition to skepticism about the veracity of these claims, a common view was that even if true, growth rates would always be far too slow to be of interest. Also, the apparent violation of thermodynamic laws was a continuing theme by many (but not all) during this time period. These attitudes changed dramatically in the early 1980s when the National Institute for Research in Inorganic Materials (NIRIM) in Japan (Kamo, Matsumoto, Sato, Setaka) announced diamond growth rates in the micron per hour range.

The role of hydrogen in diamond synthesis was suggested in 1966 by Lander and Morrison at Bell Labs. An understanding of the critical role of atomic hydrogen grew incrementally, through sequential growth-cleaning cycles (Angus, Gardner) and culminating in its using during growth by the Moscow group (Deryagin, Fedoseev, Polanskaya, Spitsyn, Varnin, et al.).

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Contents

1. Introduction	77
2. Phase chemistry and thermodynamic stability of diamond	78
3. High-pressure synthesis	78
4. First attempts at low-pressure diamond synthesis	78
5. The early, modern era of low-pressure diamond synthesis: role of hydrogen	79
5.1. Angus et al., Case Western Reserve University, Cleveland	79
5.2. Deryagin, Fedoseev, Spitsyn, Varnin et al., Institute of Physical Chemistry, Moscow	81
6. Start of the modern era of low pressure diamond growth	83
6.1. National Institute for Research in Inorganic Materials (NIRIM)	83
6.2. Developments during the 1980s and 1990s	83
7. A retrospective view: distractions, impediments and other directions	83
7.1. Multiple roles of atomic hydrogen	83
7.2. Distractions	84
7.3. Other directions	84
8. Final thoughts	84
Prime novelty statement	85
References	85

1. Introduction

This paper focuses on the development of diamond synthesis by chemical vapor deposition (CVD) during the latter half of the 20th century. These developments were impacted by the parallel development

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of the high pressure-high temperature process, so that is briefly mentioned as well.

Much of the original record of the early diamond CVD work is still not available. There are, however, secondary sources that have been invaluable in the writing of this paper. Gordon Davies gave an excellent account of the history and science of diamond synthesis [1], with the main focus on the high pressure–high temperature process, but with a discussion of metastable synthesis as well. The status of metastable diamond synthesis in 1979 was reviewed by Wedlake [2]. The principal groups active in the Soviet Union, Japan and the United States during the early days of CVD synthesis gave independent accounts of their activities in a volume [3] edited by Karl Spear and John Dismukes [4–6]. Two reviews by Robert DeVries cover very early studies and the work done in the Soviet Union at the Institute of Physical Chemistry in Moscow [7,8]. Spitsyn, Bouilov and Deryagin published a review in 1988 with coverage of both Soviet and other work [9]. In 1992 Yoichiro Sato and Mutsukazu Kamo described the status of metastable diamond growth with emphasis on the work in Japan [10]. In addition, there are several popular accounts of both high and low pressure diamond synthesis [11–13]. The author also acknowledges very helpful communications with Andrzej Badzian, James Butler, Robert DeVries, William Eversole, Galina Popovici, Boris Spitsyn and Valentin Varnin. Of course, all omissions and errors belong solely to the author.

The basic story line of diamond CVD is two-fold: first, understanding that diamond could be grown outside of its range of thermodynamic stability and, second, recognition of the critical role of hydrogen. In this paper, both of these threads are followed.

2. Phase chemistry and thermodynamic stability of diamond

It is now well known that diamond is thermodynamically stable with respect to graphite only at high pressures. Rossini and Jessup [14] in the United States, Leipunskii [15] in the Soviet Union and Berman and Simon [16] in the United Kingdom worked out the carbon phase diagram in the mid 20th century. Leipunskii's contributions have often been ignored, especially by American and European workers.

It has been less well appreciated that, although diamond is thermodynamically unstable with respect to graphite at ambient pressures, the magnitude of this instability, as measured by the difference in Gibbs free energies, is very low. In fact, at one bar and 1400 K, a typical temperature used in diamond CVD, the difference in free energy between diamond and graphite is only ~8 kJ/mole. For comparison, at 1400 K the value of kT is ~11 kJ/mole. In practical terms, this means that both phases have essentially the same free energy. Therefore, whether diamond or graphite forms during chemical vapor deposition does *not* depend on their relative thermodynamic stability, but instead on the rates of nucleation and growth of the two phases.

Some, but not all, early workers realized that diamond synthesis outside of its thermodynamically stable region was possible. An important case in point was Percy Bridgman, widely regarded as the father of high pressure science. Following the announcement of successful diamond synthesis by General Electric, Bridgman wrote an article in *Scientific American* [17] in which he said,

“... we cannot say that when a carbon compound decomposes, or when carbon is precipitated from solution, the form of carbon that separates will be the form thermodynamically preferred. We know from the thermodynamic potential that graphite is ordinarily the preferred form, but this does not enable us to say that the actual precipitate will be graphite and not diamond. As a matter of fact there are many known instances in which an element's unstable form, corresponding to diamond, separates from a solidifying liquid or solution in preference to the more stable form.” [17]

Other workers, e.g., Ubbelohde and Lewis [18], reached a similar conclusion.

“Neither has the direct deposition of carbon as a diamond lattice or as diamond layers or as a diamond nuclei ever been reported, though this should be possible in principle.”

Nevertheless, there was still wide spread belief that one could only synthesize diamond at high pressures. One example of that attitude was exemplified by Neuhaus, who stated [19],

“Metastable nucleation and growth of diamond are in practice excluded for reaction-kinetic reasons. Its synthesis can only be sought in the stable region.”

3. High-pressure synthesis

Following the Second World War, major projects on diamond synthesis in the P/T range of thermodynamic stability were undertaken by Allmänna Svenska Elektriska Aktiebolaget (ASEA) in Sweden and the General Electric Corporation in the United States. A major motivation of these efforts was to eliminate the dependence for a critical material on countries that were perceived to be unfriendly or potentially unstable. These efforts culminated in the public announcement [20] by General Electric in 1955 that diamond had been synthesized, followed by a publication in *Nature* describing the work [21].

In retrospect, it now appears that Halvard Liander and Erik Lundblad at ASEA actually grew diamond at high pressure earlier than GE, but delayed announcing their results [1]. However, the gold standard for assigning priority to scientific contributions is publication, and on this basis GE deserves priority. Furthermore, it was the General Electric process that dominated the industrial diamond industry for many years. One consequence of the announcement by GE was the termination of significant efforts to grow diamond by CVD at both GE and the Union Carbide Corporation.

4. First attempts at low-pressure diamond synthesis

There were sporadic attempts to deposit diamond from a gas or plasma phase throughout the early and mid 20th century. Von Bolton attempted to grow diamond by the decomposition of ethylene in the presence of mercury vapor [22]. Schmellenmeier decomposed acetylene in a glow discharge [23]. His carbon films showed the two strongest diamond X-ray lines; the strongest graphite lines were absent. There is a strong probability that Schmellenmeier succeeded in forming diamond, most likely as very small, defective crystals. Another significant effort was that of Meincke [24,25] who deposited carbon from carbon arcs. Meincke exchanged samples with William Eversole, who was working at the Union Carbide Corporation in the United States. Although some of these attempts may have been marginally successful, none have been followed up, and they did not play a major role in subsequent developments.

The two most important attempts to synthesize diamond at low pressure during the 1950s were those at the General Electric and Union Carbide Corporations. The details of the General Electric project have never been revealed except for an informal, public talk by Guy Suits [26]. The GE effort was apparently very serious. Many methods were tried including vapor transport of carbon from a heated graphite filament onto a diamond substrate, thermal gradient transport of carbon in liquid metals, chemical vapor deposition from CO, CH₄, CCl₄ and CBr₄, and electrodeposition of carbon from molten carbonates. No diamond growth was observed in these experiments, but the eventual possibility of low-pressure diamond growth was not excluded. The GE low pressure effort was terminated almost immediately after the successful high pressure synthesis in 1954 [27].

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