

Diamond Synthesis: Reflections and Suggestions

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Abstract

The synthesis of diamond under ambient conditions is a dream of mankind, but there is a realistic chance for the next time of achieving the goal. The finding of a Korean researcher team that diamonds grow under ambient pressure but still high temperature in a few minutes paws the way. The present contribution picks up the thread and makes further suggestions, based on empirical crystallographic experience.

Reflections and Suggestions

With this short contribution I return to my roots at the Institute for Mineralogy and Petrography of the TU Berlin in the 1970 years. The universally respected director was at that time *Prof. Dr. Dr. Hugo Strunz*. At that time a fake diamond maker fascinated the busy Berlin. He placed diamond splinters under his fingernails and released these in a glass, where he suggested synthesizing diamonds from solution. *Strunz* was supposed to prepare an expert opinion and ask me as experienced in physical chemistry for advice. So the apprentice explained to the master the conditions for diamond synthesis and excluded definitely the fake diamond maker's synthesis route from pure solution. Now, 65 years later, new aspects for the diamond synthesis are known and own suggestions should be written down. My contribution has triggered by a recommended contribution to the diamond synthesis, written by colleague *Kosinov* and coauthor, renowned experts in catalysis science [1]. There are given many important references.

I will not explain the synthesis of diamond under high pressure at 900-1400°C and high temperature at 5-6 GPa within the Earth's mantle, but will correct the expert babbles (German show 'Cash for Rares') about millions of years it takes a big diamond to grow, a splendid answer for stupid people. It needs weeks or still a year to form big exemplars under optimal conditions including catalytic support!

The synthesis of galena, PbS, is not comparable to the diamond synthesis. However, it may illustrate the time-scale of mineral formation. In the crystal laboratory at the University of Regensburg I synthesized big and almost perfect galena mono-crystals up to 1cm of cube length during a long weekend by a quasi-isotherm sublimation process in an evacuated quartz-glass ampoule, using a three-stage furnace and a temperature gradient of only few degrees. Thereby small starting crystals were rapidly dissolved and few big crystals were formed [2].

It is reported from a Korean researcher team about the synthesis of very small diamond crystals in liquid metal at 1 atm pressure and 1015°C in a carbon crucible within 15 minutes in a methane atmosphere [3]. The gallium-rich melt contained besides Ni and Fe some silicon that can act as seed because it has the same cubic crystal structure as diamond with tetrahedral atomic coordination. The short time-scale of formation is remarkable. The method may be applicable to enlarge diamond seed crystals. The formation process is a ‘catalytic’ prime example. Its full understanding will help to further optimize the method towards growing of larger diamond crystals, ennobling the seminal ideas of *Ruoff* and coworkers [3]. The elaborated publication covers many other possibilities of material variation.

Gallium has unusual properties and doesn’t bind carbon, but can form a very stable Ga₁₃ cluster also at high temperature. The addition of Ni and Fe to the melt may support the tendency to absorb H₂ and carbon. However, the important steps of catalytic diamond formation are surface effects, where methane is stepwise decomposed and carbon condensed to tetrahedral-coordinated carbon pre-clusters supported by Si atoms. It is recommended to offer a perfectly smooth (111)-cut Si surface as growing substrate. Instead of a carbon crucible also a silicon ($T_m = 1414^\circ\text{C}$) or SiC ($T_m = 2730^\circ\text{C}$) ampoule or rectangular tube could be useful, and some gallium could be replaced by cheaper aluminum. Last but not least, an auxiliary Pt grid could be used as growth support, in 1935 successfully applied in the flux synthesis of emerald by *IG Farben AG*, Bitterfeld in Germany. The used flux was lithium molybdate, Li₂MoO₄.

Whereas Ni and Fe are ingredients of the early high pressure synthesis, addition of trace elements like B or N found in naturally grown diamonds could be tried out, from the viewpoint of a mineralogist. Also sulfur is a trace element. Its use in a small amount could form together with some additional Zn and Ga in the melt clusters with sphalerite-type structure with the wanted tetrahedral atomic coordination. May be that also the process temperature can be decreased by such replacement. A quasi-isotherm temperature profile with a small gradient would be an alternative procedure, and larger crystals could grow at the expense of smaller ones. Nature is paragon of efficiency for such growth. Finally, we shouldn’t lose sight of superatomic double magic clusters (Ga₁₃, also Al₁₃ if Al is additionally used) with its unusual electronic transitions as mediator. The new concept of crystallogenesis of diamond developed by *Kaplunenko and Kosinov* [1] comprises the importance of electrons and the intermediate formation of C⁻⁴. The study of the original work is recommended. However, crystal growth as surface covering is ever influenced by the *Casimir-Lifshitz* effect [4] [5], and balanced dielectric properties of the materials are a prerequisite for success.

The direct conversion of CO₂ to solid carbon by Ga-based liquid alloy (EGaIn: eutectic GaIn alloy with low melting point of 15.7°C, 75.5% Ga, 24.4% In) even at room temperature is a further example of the fascinating properties of the element gallium and its relation to carbon [6]. In this way, one thing leads to another and the low temperature diamond synthesis is seen at the horizon, for instance, if you add some Si (and a trace of B) to the alloy to bind the in situ emerging carbon atoms in tetrahedral fashion onto Si. The smaller boron atom in contrast to Si should cause less pronounced lattice deformations of the diamond structure, but should have a similar ‘catalytic’ effect. In addition, B would cause a nice blue color of diamonds.

Gallium may not be oxidized and remains unchanged, when using an equimolar mixture of CO₂ and CH₄. The H₂O formed during the synthesis should be removed. It is an exciting question what will happen and whether the girl becomes a best friend under ambient conditions.

If one offers a Si wafer as substrate for diamond growth, then it is recommended using a boron-doped one. Boron substitution should reduce the cubic lattice parameter of Si from $a = 5.43 \text{ \AA}$ towards $a = 5.35 \text{ \AA}$ [7]. Then the lattice parameter ratio Si(B) to diamond is almost exactly 3/2 and ideal for epitaxy

$$\frac{a_{\text{Si(B)}}}{a_{\text{diamond}}} = \frac{5.35 \text{ \AA}}{3.567 \text{ \AA}} = 1.5$$

At the age of 87, I unfortunately no longer do experiments, but if I did, I would choose the following arrangement. A platinum grid was filled with liquid gallium ($T > 30^\circ\text{C}$) and placed just above a (111)-cut Si(B) substrate that there is just enough space for a CO₂/CH₄ gas flow to pass through, supplemented by a facility to vary the temperature. The gas flow could also be directed through some empty meshes of the grid. Before the first nucleation the gas flow should be reduced. Diamond is expected to grow with its equilibrium form {111} onto the substrate. May be *Wacker Chemistry* in Germany can provide young researchers with the optimal substrate. I am convinced that the synthesis of diamond requires neither high pressure nor high temperature.

By the way, we can once deposit the unwanted CO₂ in form of diamonds, the most dense carbon modification (a joke or coming reality?).

I end my remark with an advice. Just ignore the message 'it doesn't work'. Only use the right tools under the right conditions to uncover and decode the secrets of nature. The author himself followed this advice and proposed a microbial origin of rare *Tsumeb* minerals, including rare Ga-base compounds and diopside [8].

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