

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 in a gallium-rich melt under ambient pressure but still high temperature in few minutes paws the way. The present contribution picks up the thread and makes further suggestions, based on empirical crystallographic experience. The formation of diamond under ambient pressure as well as ambient temperature is expected to be soon possible using advanced buffer layer materials such as cubic boron nitride on Si(111) substrates. Once the catalytic formation path is fully elucidated, the rapid synthesis of large octahedral crystals becomes routine. The formation of diamond under ambient conditions may be catalytically mediated by the electronic properties of Ga₁₃ clusters in melt. It is proposed to use also gallium metal by the conventional HPHT diamonds synthesis to reduce pressure and temperature considerably.

Keywords: Diamond, Silicon, Boron Nitride, Boron Phosphide, Boron Arsenide, Melt Synthesis, Gallium, Ga₁₃ Cluster, Crystal Growth, Catalysis, Epitaxy, HPHT Method.

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 time-scale of lab-grown diamonds drops in 2025 from weeks to hours!

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/hydrogen 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 a Si atom lattice. 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 and delocalized electrons 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 their original work is recommended. However, crystal growth as atomic surface covering is ever influenced by the *Casimir-Lifshitz* effect [4] [5], and balanced dielectric properties of the materials are a prerequisite for crystal growing success.

The direct conversion of CO_2 to solid carbon even at room temperature by Ga-based liquid alloy (EGaIn: eutectic GaIn alloy (75.5% Ga, 24.4% In) with low melting point of $15.7^\circ C$ 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 silicon or boron nitride to the alloy to bind the in situ emerging carbon atoms in tetrahedral fashion onto such additives. A smaller substituted atom in contrast to Si such as BN should cause less pronounced lattice deformations on the diamond structure, but should have a similar ‘catalytic’ effect. Gallium may not be oxidized and remains unchanged, when using an equimolar mixture of CO_2 and CH_4 . The H_2O 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 substituted Si^* substrate or a buffer layer. Possible substitutions are summarized in **Table 1**.

Table 1. Lattice parameters for phases exhibiting cubic sphalerite archetype at room temperature. Shortest atomic distance: $a \frac{\sqrt{3}}{4}$.

Phase	Lattice parameter $a(\text{Å})$	Atomic distance (Å)	Ratio $a_{\text{substrate}}/a_{\text{diamond}}$	Reference
diamond	3.567	1.5445	1	-
BN	3.6153(1)	1.5655	1.014	[8]
BP	4.53781(8)	1.9649	1.272	[9]
BAs	4.8145	2.0847	1.350	[10]
$Si_{0.9}(BP)_{0.1}$	5.35	2.3166	1.500	this work
$Si_{0.88}(BAs)_{0.12}$	5.35	2.3166	1.500	
Si	5.431020511(89)	2.3517	1.523	CODATA (2022)

A vapor deposited buffer layer of BN on Si(111) is highly recommended, because the mismatch between diamond lattice and cubic BN lattice is only about 1.4%. Other possibilities include substituted silicon variants, where the cubic lattice parameter of Si is reduced from $a = 5.431 \text{ Å}$ towards $a = 5.35 \text{ Å}$. A mixed crystal between Si and BP in a molar ratio of 0.9 / 0.1 would perfectly fulfill the condition. Then the lattice parameter ratio to diamond is almost exactly 3/2 and ideal for epitaxy

$$\frac{a_{Si^*}}{a_{diamond}} = \frac{5.35 \text{ Å}}{3.567 \text{ Å}} = 1.5$$

The synthesis of a $Si_{0.9}(BP)_{0.1}$ mixed crystal may be possible under moderate pressure, by a molten salt-assisted route or chemical vapor deposition (CVD). Another possibility is the application of boron arsenide, BAs, which can be produced by a wet-chemical route [7]. From such precursor and Si one could try to grow a monocrystal of ideal composition

$\text{Si}_{0.88}(\text{BAS})_{0.12}$. Using CVD methods, a buffer layer of BN, $\text{Si}_{0.9}(\text{BP})_{0.1}$ or $\text{Si}_{0.88}(\text{BAS})_{0.12}$ composition can be deposited on a Si(111) substrate, onto which finally the diamonds grow. Also a copper-substituted Co(0001) substrate with zero-mismatch is applicable, if it can withstand the process temperature.

At the age of 87, I unfortunately no longer do experiments, but if I did, I would choose the following arrangement. The meshes of a platinum grid are filled with liquid gallium ($T > 30^\circ\text{C}$) and placed just above a (111)-cut Si^* substrate that there is just enough space for a CO_2/CH_4 gas flow to pass through, supplemented by a facility to vary the temperature or apply ultrasonic energy. The gas flow could also be directed through some empty meshes of the grid. Before the first nucleation takes place, the gas flow should be reduced. Diamond is expected to grow with its equilibrium form {111} onto the substrate. May be *Siltronic* (*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 CO_2 in form of diamonds, the most dense carbon modification (a joke or coming reality?).

Quasi-freestanding graphene can be prepared on Ni(111) by Cs intercalation, enlarging the formerly interlayer distance between graphene and substrate from 2.1 Å to about 6 Å, because the strong hybridization between the transition metal z^2 orbital and the carbon p_z orbital is lowered [11]. Intercalated Ba atoms should act similarly. We find Ba frequently as trace element in natural diamond. Its effect as minor constituent for the diamond synthesis should be investigated. We can try to transfer such quasi-freestanding graphene layer to a Si(111) substrate, buffered with a BN layer, on which the carbon layer possibly curls to a diamond layer, where the C-C distances increase from 1.42 Å to 1.54 Å due to the coordination number increase from 3 for graphene to 4 for diamond. If we have learned to grow diamonds under ambient pressure and temperature, then we can possibly produce large exemplars with a seed technique, like growing of synthetic pearls on an aragonite seed. We would use a small octahedral Si^* (BN) seed crystal with perfectly oriented {111} form.

Recently, *Li and coauthors* summarized results of diamond nanostructures at different dimensions and give extended references [12]. Synthesis methods and applications were concisely described. The variety of forms that diamond can develop is fascinating. *Matar and Solozhenko* predicted just now an orthorhombic ultra-hard C_{12} structure that should be denser than diamond [13]. So the story of carbon allotropes goes on.

Speaking about aluminum addition to a gallium melt, it is recommended to use a ratio of Ga / Al = 12 / 1. The formation of stable icosahedral Ga_{12}Al clusters in the melt is expected, and such clusters should have excellent electronic and catalytic properties (jellium model constitution). The *Casimir-Lifshitz* effect is the reason why carbon is distancing itself from gallium, but gallium nevertheless supports at distance the twisting of a carbon layer into a diamond layer. The circumsphere radius of an icosahedron with unit edge length is compared to the metallic radius ratio of the gallium and aluminum atoms giving a well adaption

$$r_{circ} = \frac{1}{2}\sqrt{3 + \varphi} = 0.9510 \approx \frac{r_{Al} + r_{Ga}}{2 \cdot r_{Ga}} = 0.969$$

where φ is the golden mean: $\varphi = \frac{\sqrt{5}-1}{2} = 0.6180339887$.

The study of a didactic contribution about Au₁₃ gold clusters may be helpful for laypeople [14]. Aluminum is also a trace element found in natural diamonds in some ppm by weight [15]. Trace elements in minerals guide us to synthesis options.

Suppose we had synthesized a fancy blue diamond with boron color centers in form of an octahedron of edge length 1 cm. It would have a weight of 8.25 Carat

$$V \cdot D = \frac{\sqrt{2}}{3} \cdot 3.50(g) = 1.65(g) = 8.25 (Carat)$$

Besides the new melt synthesis method, the established high pressure-high temperature facility possibly can be improved by the application of gallium metal to reduce pressure as well as temperature. The leading company *Pure Grown Diamonds (Gemesis Inc.)* should keep in mind such synthesis route.

I finish 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 [16].

Conclusion

This contribution supports the thesis that diamonds can grow under ambient conditions of pressure and temperature by varying the recent experimental work of Korean researchers. The assumption is based on crystallographic experience, including interesting buffer materials such as boron nitride on silicon substrates for ideal crystal growth conditions. Gallium used as melt may electronically mediate the rapid catalytic formation of diamond at boron nitride substrate surfaces.

Conflicts of Interest

The author declares no conflict of interests regarding the publication of this paper.

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