

Calculated phase diagrams for activated low pressure diamond growth from C–H, C–O, and C–H–O systems

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Three-dimensional temperature (T)–pressure (P)–composition (X) phase diagrams of binary carbon-hydrogen (C–H) and carbon-oxygen (C–O) systems for activated low pressure diamond growth have been calculated. Based on an approximation of linear combination between C–H and C–O systems, a projective ternary carbon-hydrogen-oxygen (C–H–O) phase diagram has also been obtained. There is always a diamond growth region in each of these phase diagrams. Once a supply of external activating energy stops, the diamond growth region will not exist. Nearly all of the reliable experimental data reported in the literature drop into the possible diamond growth region of the calculated projective ternary C–H–O phase diagram under the conditions of 0.01–100 kPa and above 700 K.

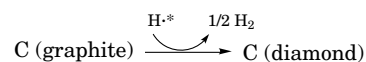
I. INTRODUCTION

Activated low pressure chemical vapor deposition (CVD) diamond growth had once been thought to be “alchemy” by some scientists.¹ According to equilibrium thermodynamics, theoretical calculations showed that if the pressure is not over 15,000 times higher than atmospheric pressure, the spontaneous transformation of graphite to diamond will be impossible.² It is well known that low pressure CVD diamond growth has been realized under different activated conditions, such as activated by hot filament, by low pressure direct current plasma, by rf or microwave discharge, by hot dc or rf atmospheric pressure plasmas, and even by combustion flames. Usually, methane or other gas hydrocarbons and hydrogen mixtures are used as carbon-containing sources, but now some papers^{3–6} or patents^{7,8} concerning the transformation of graphite to diamond have also been reported in the literature under activated CVD conditions. Therefore, the activated low pressure diamond growth should be treated by nonequilibrium thermodynamics.

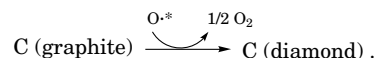
II. T - P - X PHASE DIAGRAMS OF BINARY C–H and C–O SYSTEMS

According to nonequilibrium thermodynamic coupling theorem,⁹ a thermodynamically unfavorable reaction (such as the transformation of graphite into diamond under low pressure) could be driven by another thermodynamically favorable reaction [such as the association of superequilibrium atomic hydrogen (SAH, or H^* as symbol) or superequilibrium atomic oxygen (SAO, or O^* as symbol)]. Just as pointed out by Prigogine:

“Thermodynamic coupling allows one of the reactions to progress in a direction contrary to that prescribed by its own affinity, . . .”,⁹ so the activated low pressure diamond growth could be driven by the association of SAH (or SAO) as the following expressions (similar to expressions of a lot of coupled reactions in biochemistry¹⁰):



or



For further calculations, graphite together with the driving force coming from the association of SAH (or SAO) could be treated as a whole and named “graphite activated by SAH (gra*)” for carbon-hydrogen (C–H) systems or named “graphite activated by SAO (gra**)” for carbon-oxygen (C–O) systems. It is obvious that the concentration of SAH or SAO is not equal to that of equilibrium atomic hydrogen (or atomic oxygen), so the thermodynamic data of SAH (or SAO) should be different from those of ordinary atomic hydrogen (or ordinary atomic oxygen). Therefore, thermodynamic data of activated graphite should also be different from those of ordinary graphite. Under a constant substrate temperature and a constant total pressure the ordinary thermodynamic calculating program minimizing of Gibbs free energy could still be used for the activated CVD diamond growth system, but thermodynamic data of activated graphite should be used instead of those of ordinary graphite. The thermodynamic calculation method and the derivation of thermodynamic data of graphite

activated by SAH and graphite activated by SAO had been discussed in our previous papers¹¹⁻¹⁵ and will not be repeated here. Figures 1 and 2 show three-dimensional substrate temperature (T)–total pressure (P)–composition (X) phase diagrams calculated for activated CVD diamond growth from C–H systems and C–O systems, respectively. It is obvious that there is always a diamond growth region (oblique line shadow part in Figs. 1 and 2) in each T - X cross section phase diagram at different pressures. Nearly all the influences of pressure and temperature could be quantitatively discussed on the basis of these T - P - X phase diagrams.

III. PROJECTIVE PHASE DIAGRAMS OF TERNARY C–H–O SYSTEM

In the past decade, a lot of CVD diamond experiments were from C–H–O systems. Bachmann *et al.*¹⁶ had summarized the literature experimental data into an empirical plane ternary carbon-hydrogen-oxygen (C–H–O) composition phase diagram, in which there was a “well-defined” diamond growth domain. No satisfactory theoretical explanations were found in the literature, though several papers focused on its discussions.¹⁷⁻¹⁹

For comparison of our calculated results with Bachmann’s phase diagram, two things should be done. The first, a linear combination approximation of thermodynamic data for C–H and C–O systems, should be introduced for the calculation of the main part of the ternary C–H–O phase diagram. For instance, for a C–H–O system with a constrained ratio of H/O = 1 one can take average values of thermodynamic data for both C–H and C–O systems. In this way three-dimensional T - P - X phase diagrams for C–H–O systems with any constrained ratio of H/O could be obtained. The second, projections of all of these three-dimensional T - P - X phase diagrams, including Figs. 1 and 2, along

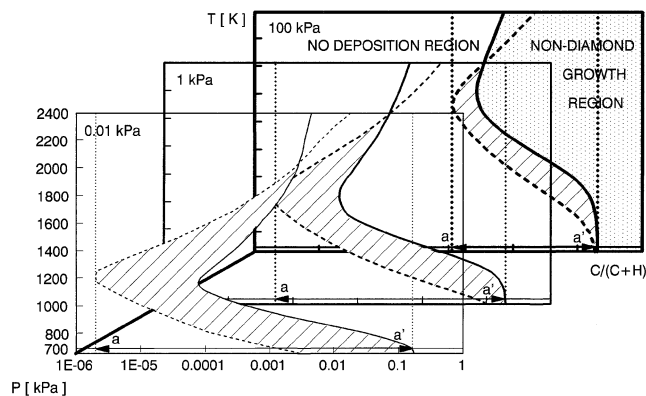


FIG. 1. Three-dimensional substrate temperature (T)–total pressure (P)–composition (X) phase diagram calculated for activated CVD diamond growth from C–H systems. Oblique line shadow parts are the diamond growth region at pressures 0.01, 1, and 100 kPa, respectively.

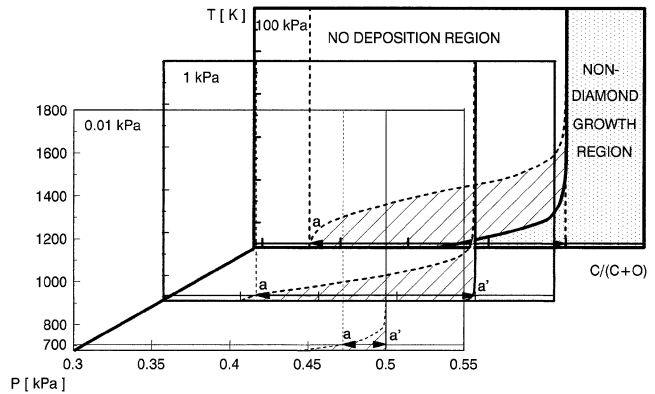


FIG. 2. Three-dimensional substrate temperature (T)–total pressure (P)–composition (X) phase diagram calculated for activated CVD diamond growth from C–O systems. Oblique line shadow parts are the diamond growth region at pressures 0.01, 1, and 100 kPa, respectively.

coordinates of T and P onto the abscissa of X should be made. For instance, after a projection in Figs. 1 and 2 along the ordinate of T onto the abscissa of X at 700 K a series of two-head arrows a - a' could be obtained, as shown in Figs. 1 and 2. The composition ranges of a - a' are possible diamond growth ranges at corresponding pressures (i.e., 0.01, 1, and 100 kPa). Make another projection of these a - a' arrows along the pressure ordinate onto the corresponding composition abscissa at pressure 100 kPa, and one gets possible composition ranges for activated CVD diamond growth from different C–H–O systems under conditions above 700 K and in the range of 0.01–100 kPa. Connecting all minimum values of a and all maximum values of a' , respectively, by two solid bold lines, one can obtain a calculated ternary C–H–O composition phase diagram, as shown in Fig. 3. The calculated conditions (above 700 K and in a range of 0.01–100 kPa) are very close to those of Bachmann’s diagram (above 400 °C and in a range of 0.1–760 Torr). Therefore, nearly all of the experimental data summarized by Bachmann drop into the possible diamond growth region (between two solid bold lines) of the calculated phase diagram. A newer experimental point (open square in Fig. 3) of diamond nucleation²⁰ drops inside our possible diamond growth region, but not inside Bachmann’s diamond domain (between two dotted lines in Fig. 3). The influence of temperature on the phase diagram has already been calculated. It is shown that the diamond growth region narrows with increase of the substrate temperature. The theoretical projective phase diagram with a narrow range of T and P (1100–1500 K, 1–10 kPa), as shown in Fig. 4, agrees exactly with Marinelli’s empirical result based on his critical experimental data.²¹ The possible diamond growth region above 1300 K (not shown in the paper) is very close to the H_2 – CO tie line in the triangle phase diagram. That is owing to the formation of a stable

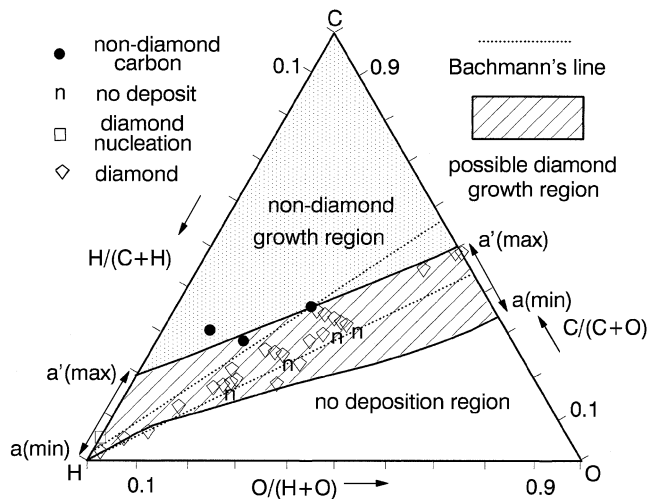


FIG. 3. Projective C-H-O ternary phase diagram for activated low pressure CVD diamond growth. Oblique line shadow part is the possible diamond growth region at pressures between 0.01 and 100 kPa and above 700 K.

CO above 1300 K. The gas composition excluding CO is similar to a mixture of ~1% methane in hydrogen, which is a typical gas source composition for activated diamond growth.¹⁹

IV. DISCUSSION

Some have the point of view that the growth of activated CVD diamond is controlled only by kinetics, not thermodynamics. It is incorrect, because kinetics and thermodynamics compensate each other from different sides, but not against each other. As a basic point of view in physics and chemistry, any practical kinetically possible process must be thermodynamically possible

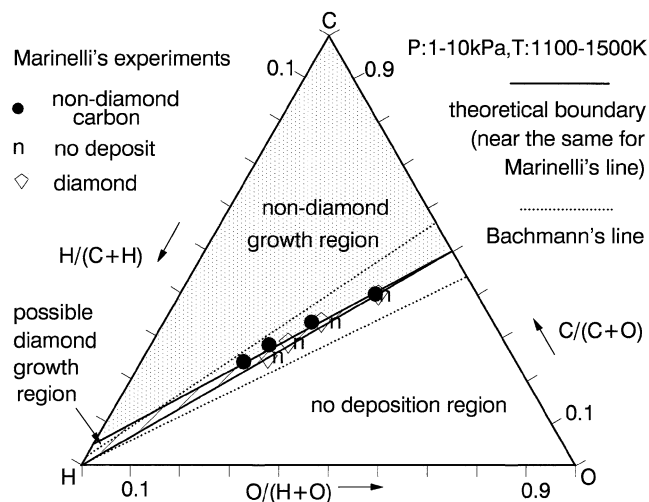


FIG. 4. Projective C-H-O ternary phase diagram in a narrow range of T and P (1100–1500 K, 1–10 kPa) for activated low pressure CVD diamond growth. Agreement between our theoretical phase boundaries and Marinelli's critical empirical phase lines is excellent.

without any exception, but, inversely, a thermodynamically possible process may be kinetically impossible, or its kinetic rate approximately equals zero. A famous example is $(2H_2 + O_2)$ mixture. The formation of water from the mixture is highly thermodynamically possible even at room temperature, but in fact the kinetic rate of the water formation reaction nearly equals zero; i.e., the reaction is kinetically impossible at room temperature without a catalyst (such as platinum black) or an initiation (such as a spark).

One can also find the following words in a textbook: "In the last century all experiments for transformation of graphite into diamond failed of success. Later thermodynamic calculations showed that only if the pressure is over 15000 times higher than atmospheric pressure the transformation of graphite into diamond is possible."²² These words were based only on equilibrium thermodynamic calculation. Thermodynamics consists of equilibrium thermodynamics and nonequilibrium thermodynamics. The calculation based on nonequilibrium thermodynamics in this paper shows that the transformation of graphite into diamond is possible under activated low pressure CVD conditions. The conclusions coming from equilibrium thermodynamics and nonequilibrium thermodynamics can be opposite each other, but both of them obey the first and the second thermodynamic laws. That is, *conclusion* depends on *condition*.

About the coupled reactions there was a question for some why the driving force coming from the association of SAH (or SAO) does not accelerate the transformation of diamond to graphite, but accelerates only the transformation of graphite to diamond. That is due to the different structures between graphite and diamond. Graphite is of unsaturated sp^2 structure with big π bonds, while diamond is of saturated sp^3 structure with σ bonds. During the presence of SAH (or SAO), additional reaction of atomic hydrogen is much easier to take place for unsaturated graphite. Therefore, the clusters on graphite surfaces (unsaturated aromatic benzene-like structure) are much easier to be etched away, and to form gaseous hydrocarbons (such as methane, acetylene, ...) with superequilibrium (also called supersaturated) concentrations to diamond. The species (i.e., CH_3 , ...) coming from the pyrolysis of these gaseous hydrocarbons will only form or enlarge the saturated clusters on diamond surfaces (saturated aliphatic cyclohexane-like structure), but will not form or enlarge the graphite clusters, if the concentration of SAH (or SAO) is over a certain value. The kinetic barrier and mechanism of the coupled reactions in the activated CVD diamond process have been discussed in our other paper.²²

According to the mechanism mentioned above, it is also very clear that the transformation of a graphite source to diamond production is not via a direct solid-solid phase transformation process, but via a

gaseous intermediate process. The superequilibrium activated particles play a very important role in CVD diamond processes, just as mentioned by many scientists in this field.

On the ternary phase diagrams, if a planar triangle phase diagram includes experimental data at different temperature and different pressure, such as Bachmann's diagram, it must be a projective phase diagram. Different phase regions (i.e., non-diamond carbon deposition region, diamond growth region, and gas region) will partially overlap each other. It is not necessary to exclude non-diamond carbon deposition data and no deposition data out of the possible diamond growth region. On the other hand, up to now no reliable experimental diamond growth data over the CH₄-CO tie line have been found in the literature. Bachmann's upper border phase line of the diamond growth region might be too low at the hydrogen-rich corner and too high on the oxygen-rich side.

V. CONCLUSIONS

All of the calculated phase diagrams are only for diamond growth systems under activated conditions (stationary nonequilibrium conditions), so that these phase diagrams are called phase diagrams of stationary nonequilibrium states. Once a sufficient supply of external activating energy stops, diamond growth regions (or possibly diamond growth regions in projective phase diagrams) will no longer exist. The new concept of phase diagrams of stationary nonequilibrium states is an important extension and a new challenge to the traditional concept of classical equilibrium thermodynamics. It could be useful also for syntheses of other metastable materials (such as *c*-BN, *β*-C₃N₄, ...) and even for the bioprocesses in living things.

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REFERENCES

1. K. E. Spear, *Earth Mineral Sci.* **56**, 53 (1987).
2. X-C. Fu, W-X. Shen, and T-Y. Yao, *Physical Chemistry*, 4th ed. (High Education Press, Beijing, 1990), p. 421, p. 15.
3. N. Setaka, in *Diamond Materials*, edited by J. P. Dismukes and K. V. Ravi (The Electrochemical Society, Pennington, NJ, 1993), p. 1.
4. R. Roy, H. S. Dewan, and P. Ravindranathan, in *Diamond Materials*, edited by J. P. Dismukes and K. V. Ravi (The Electrochemical Society, Pennington, NJ, 1993), p. 601.
5. B. V. Spitsyn, in *Diamond Materials*, edited by J. P. Dismukes and K. V. Ravi (The Electrochemical Society, Pennington, NJ, 1993), p. 345.
6. S. Jou, H. J. Doerr, and R. F. Bunshah, *Thin Solid Films* **253**, 95 (1994).
7. Japanese patent, JP-63117993, May 21, 1988.
8. Japanese patent, JP-63117995, May 21, 1988.
9. I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes*, 3rd ed. (Interscience Publishers, New York, 1967), p. 25.
10. R-Q. Shen and Q-M. Gu, *Biochemistry* (High Education Press, Beijing, 1993), p. 300.
11. J-T. Wang and J-O. Carlsson, *Surf. Coat. Technol.* **43/44**, 1 (1990).
12. J-T. Wang, C-B. Cao, and P-J. Zheng, *J. Electrochem. Soc.* **141**, 278 (1994).
13. J-T. Wang and P-J. Zheng, *Chinese Sci. Bull.*, Chinese ed. **40**, 1056 (1995); English ed. **40**, 1141 (1995).
14. J-T. Wang, P-J. Zheng, Q-H. Yang, and H. Wang, in *Diamond Materials IV*, edited by K. V. Ravi and J. P. Dismukes (The Electrochemical Society, Pennington, NJ, 1995), p. 13.
15. J-T. Wang, Z-Q. Huang, Q-H. Yang, D. W. Zhang, and Y-Z. Wan, in *Proc. 13th Int. Conf. on CVD*, edited by T. M. Besmann, M. D. Allendorf, McD. Robinson, and R. K. Ulrich (The Electrochemical Society, Pennington, NJ, 1996), p. 727.
16. P. K. Bachmann, D. Leers, and H. Lydty, *Diamond Relat. Mater.* **1**, 1 (1991).
17. I. Pinter, A. Tebano, A. Paoletti, and P. Paroli, *Diamond Relat. Mater.* **3**, 126 (1993).
18. N. A. Prijaya, J. C. Angus, and P. K. Bachmann, *Diamond Relat. Mater.* **3**, 129 (1993).
19. N. M. Hwang, J. H. Hahn, and G. W. Bahng, *Diamond Relat. Mater.* **3**, 163 (1993).
20. M-Y. Mao, X-F. Jin, T-P. Wang, J-F. Xie, S-S. Tan, W-Y. Wang, X-K. Zhang, and Z-C. Zhuang, *Appl. Phys. Lett.* **66**, 16 (1995).
21. M. Marinelli, E. Milani, M. Montuori, A. Paoletti, A. Tebano, G. Balestrino, and P. Paroli, *J. Appl. Phys.* **76**, 5702 (1994).
22. J-T. Wang, Z-Q. Huang, Y-Z. Wan, D. W. Zhang, and H-Y. Jia, *J. Mater. Res.* **12**, 1530 (1997).