DIAMOND CRYSTALLIZATION FROM GAS PHASE AND CARBON ALLOTROPY

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It was became widely known due to works of H.Davy and Berzelius that there are three allotropes of carbon - diamond, graphite and amorphous carbon. The development of X-ray methods of the structure analysis has revealed that the amorphous carbon is nothing but a variant of the fine-grained graphite and can not be considered as a separate carbon modification. So the number of carbon allotropes was reduced to two thermodynamically stable under low pressures - graphite and metastable diamond. However during the last few decades the number of carbon allotropic forms has drastically increased. The metastability of diamond under low pressure is clearly manifested by the much lower upper limit of the temperature range of the deposition processes, compared with those of graphite. The most of the gas-phase processes leading to the formation of solid carbon at these temperatures are highly nonequilibrium ones. On the other hand the difference in free energy of diamond and graphite is very small compared to the value of the barrier for phase transformation. Therefore it is difficult to imagine the situation when energetic advantages of the graphite structure could be important.

The simple qualitative consideration of the process of graphite growth in the framework of the classical approach for formation and growth of crystalline nuclei shows that at low temperatures, appropriate for diamond synthesis it is difficult to realize the kinetic advantages of graphite associated with its layered structure . Moreover, under the conditions favorable for the crystal growth by normal mechanism the diamond structure can be more advantageous.

In general, solid carbon formed under relatively low temperature may contain fragments with different types of bonds. This difficulty arises when one tries to obtain a solid carbon modification weather stable or metastable with the only type of the interatomic bonds. It can be considered as a chemical aspect of the problem of diamond synthesis. It may be formulated in somewhat negative way. Instead of looking for some specific conditions appropriate for the formation of diamond type (sp^3) bonds one have to find the means to suppress the carbon deposition with other types of bonding (sp^{2}- and sp^1).

But it is not sufficient. Crystalline phases are characterized by long order in atom positions. The solution of the long order problem is a hard task for solids rich in allotropes as it is in the case of carbon.

The great number of carbon allotropes is one of the reasons why carbon can be easily obtained in amorphous state by many current deposition techniques. It also explains the great variety of diamond-like materials. It is important to stress that structure and properties of this "new" amorphous carbon are quite different from those of amorphous carbon mentioned above. This one can be considered as a new carbon allotrope. It is important that the near order of this amorphous carbon can change from one atom to another and average coordination number varies in wide range depending on deposition conditions.