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저압 다이아몬드 제조에서의 열역학 문제
(Thermodynamic Problems in the Low Pressure Synthesis of Diamond)

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Intensive studies have been done on the low pressure synthesis of diamond though the underlying principle has not been understood yet. Two unusual phenomena take place in the process. One is the dominant formation of the metastable diamond over the stable graphite. The other is the deposition of the less stable diamond with the simultaneous etching of the stable graphite. These phenomena were previously approached by the atomic hydrogen hypothesis, which is based on the fact that the atomic hydrogen etches graphite much faster than diamond. But the atomic hydrogen hypothesis is against the thermodynamic concept. The charged cluster model, which is thermodynamically sound, is suggested to explain these phenomena.

The first phenomenon can be approached by the capillary effect in the nucleation stage. The pressure built up inside the nucleus can be high enough to make diamond stable than graphite. The second phenomenon, however, cannot be approached by the capillary effect since the diamond deposits on the graphite substrate, which has no capillary effect, while the graphite substrate is being etched. Such experimental observations lead to the thermodynamic paradox violating the 2nd law of thermodynamics.

The CVD phase diagram of the C-H system shows that the solubility of carbon in the gas phase is minimum at around 1350 K. Thus, the carbon solubility in the gas phase increases toward the substrate temperature of around 1150 K. If the gas phase nucleation takes place, the carbon solubility in the gas phase tends to be minimum at around 1350 K and will increase toward the substrate temperature. The carbon-depleted gas phase will etch both diamond and graphite at the substrate temperature. The thermodynamic paradox can be avoided if it is assumed that the deposition takes place by the clusters nucleated in the gas phase and the etching takes place by the atomic unit. The weakest point leading to the thermodynamic paradox is the implicit assumption that the diamond deposition is done by the atomic unit.

The charges such as ions and electrons produced by the gas activation process of plasma or hot filament are suggested to be the strong heterogeneous nucleation sites in the gas phase. The fact that the gas phase nucleation is enhanced by the presence of ions is well known in the famous Wilson-cloud chamber and the bubble chamber experiments. It is suggested that the invisible nanometer sized diamond clusters formed in the gas phase make the dense diamond film. It is also suggested that the deposition by the charged clusters is the general phenomena in the thin film process where an appreciable amount of charge is produced.