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# A Verification of Diamond Nucleation Model

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We found that our initial model agrees with most of the recent reports; however, it does not agree with some of them with respect to the kinetics of nucleus formation. This disagreement stems from the question of whether or not a nucleus precursor should be treated as an embryonic cluster.

***Key words :*** CVD-diamond, Bias, Nucleation-model

## I. Introduction

It has been more than ten years since growth diamond by chemical vapor deposition (CVD) was achieved and many researchers have conducted experiments on this topic. However, the basic mechanism for diamond nucleation has hardly been clarified due to the complexity of the diamond growth process by CVD: the process utillizes a nonequllibrium plasma reaction and proceeds under severe plasma condition.

We have analyzed a bias processing method which accelerates diamond uncleation and proposed a diamond nucleation model based on transition from an amorphous carbon cluster to a diamond nucleus. In our reports, we concluded that a low-energy ion plays an important role in diamond nucleation. Recently, many reports on diamond nucleation have been published and various views regarding diamond nucleation, including the bias effect, were presented. However, the structure of the precursor and the kinetics of nucleus formation remain unresolved. The aim of this report is to reconsider our diamond nucleation model in light of the many reports published recently.

## II. Nucleation Model from the Bias Effect Point of View

Figure 1 shows a schematic diagram of our diamond nucleation model that takes the ion irradiation effect into consideration. In the presence of applied bias, ions activated by energy in a plasma sheath undergo both internal diffusion into and surface migration on the substrate. Most activated species evaporate due to hightemperature hydrogen plasma, and some of the activated species substrate surface and form a cluster by mixing with the substrate. The structure of the cluster formed at the beginning of this process is not completely clear; however, it is considered to be a hydrogenated $sp^2$-rich amorphous carbon cluster, which can be regarded as a precursor of the diamond nucleus. these clusters are irradiated with lowenergy ions, and amorphous components are removed. At the same time, $sp^2$ bonds are trasformed sequentially to $sp^3$ bonds. After repeated transformation, an $sp^3$-rich cluster grows into a critical nucleus of 1-2 nm size, which is a diamond nucleus. A high concentration of hydrogen in plasma may induce the removal of amorphous carbon and prevent $sp^2$ bonds, judging from hydrogen assisted diamond nucleation. The

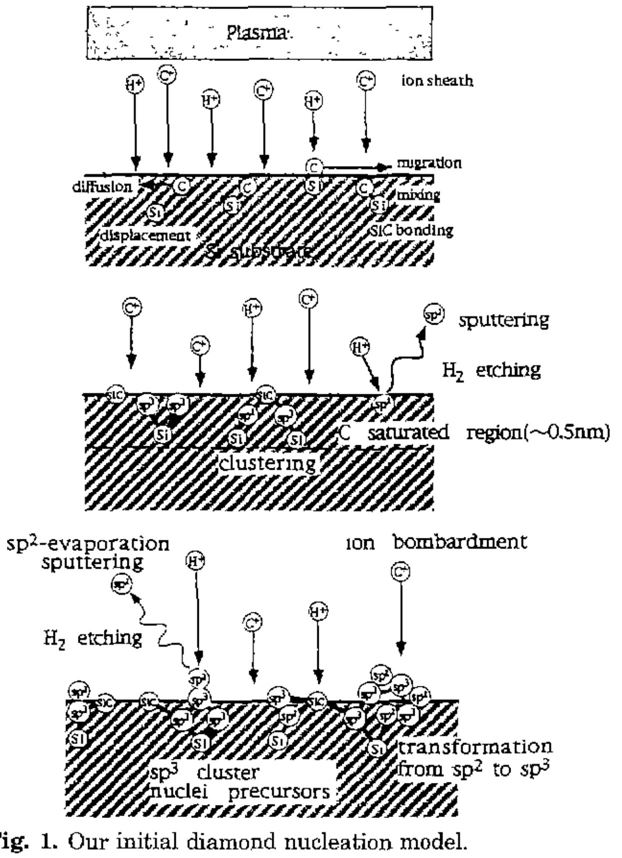


**Fig. 1.** Our initial diamond nucleation model.

explanation mentioned above outlines our diamond nucleation model based on the bias effect.[1-4]

## III. Reports on Diamond Nucleation Regarding Bias Effect

The following items regarding diamond nucleation have been selected from recent publications.

a) effective ion energy[5-8]

b) acceleration of migration and carbonization reaction[9-13]

c) transition from carbon $sp^2$ bonds to $sp^3$ bonds[14-18]

d) subsplantation effect of ions[19, 20]

e) stress effect and excess heat generation effect[21-23]

f) graphite sheet coagulation effect and diamond generation from graphite edge[24-26]

g) removal of amorphous $sp^2$ component by hydrogen and prevention of carbon double bond formation[27-30]

h) effect of substrate temperature[31]

i) secondary electron effect[32]

Some of these items agree with our model; however, some of them disagree such as the structure of the precursor and the transition mechanism from carbon $sp^2$ bonds to $sp^3$ bonds. We will reconsider our diamond nucleation model by analyzing the items listed above.

## IV. Discussion

Generally speaking, the bias effect is observed in the bias voltage range of about -50 V to -200 V. This bias method is based on the compound effects of ions with various energies. Low-energy ions may exert some chemical effect such as cleaning of the substrate, surface migration and accelerating reaction, whereas high-energy ions may exert some physical effect such as subplantation and selective etching.

The initial cluster is mainly composed of hydrogenated amorphous carbon and that it is a diamond precursor. The most critical question is show the diamond precursor is transformend into a diamond nucleus. The initial cluster is an embryonic cluster; therefore a process which differs from the reaction of a solid cluster should be considered. The ion effect with lower ion energy is effective for the embryonic cluster compared to that for the solid cluster; therefore, embryonic clusters tend to be more active and reach a stable site relatively easily. This process actively promotes dehydrogenation and transformation from carbon $sp^2$ bonds to $sp^3$ bonds. For this reason, the subplantation effect of ions is considered to be relatively small. Also, the stress effect and excess heat generation effect in the cluster are small; they cannot act as a motivating force for diamond nucleation. When the cluster is graphitized, the possiblities of the graphite sheet coagulation effect and diamond generation from the graphite edge cannot be denied. Therefore, random transition from $sp^2$ bonds to $sp^3$ bonds on the cluster surface, mainly account for the mechanism of diamond nucleation.

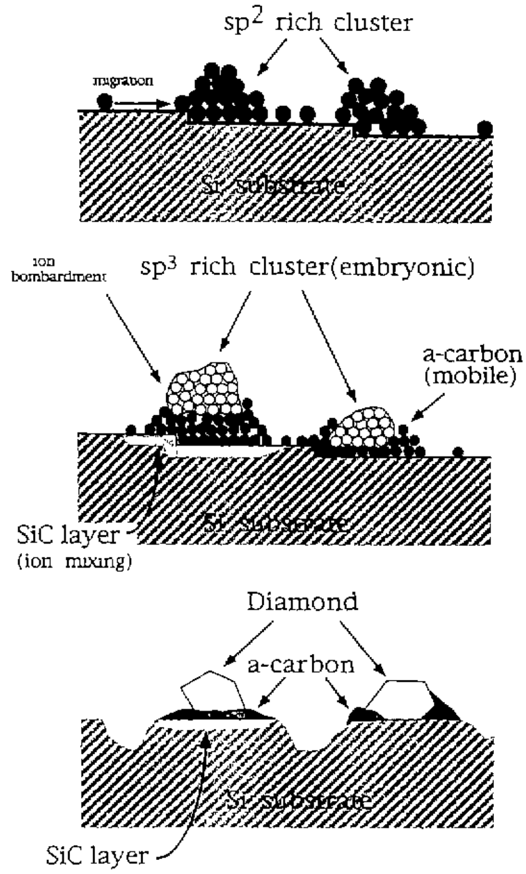


**Fig. 2.** Modified diamond nucleation model.

Finally, Fig. 2 shows a schematic diagram of our modified model that indicates the start of nucleation using an amorphous carbon cluster as the host. However, experimental demonstration of this model is very difficult, since the crystal nucleus is very small and is an embryonic cluster. Furthermore, in experiments, we observed results of completed processes but not the nucleation process itself.

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