Cooperative Effect of Metals and Diamond Powders Abrasion on CVD Diamond Nucleation Process

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ABSTRACT: A novel method of surface treatment was developed to enhance diamond CVD nucleation on non-diamond substrates. This is based on abrasion of the substrate surface using a mixture of diamond and metal powders such as Ti, Fe and Cu. It was found that the original nucleation density obtained by abrasion with diamond powder can be enhanced by few orders of magnitude by a mixed slurry. Furthermore, no nucleation enhancement was observed using for surface treatment a metal slurry alone. The enhancement in nucleation density was in the order: virgin ≈ (Cu, Fe, or Ti) < Di < (Cu + Di) < (Fe + Di) < (Ti + Di), (Di stands for diamond powder). The effects of metal particles size and metal-to-diamond weight ratio in mixed slurry, as well as the intensity of ultrasonic abrasion on CVD diamond nucleation density were studied. The effect of diamond nucleation enhancement is supposed to be due to the metal residues left on the surface after the abrasion treatment. It is suggested that these metal residues influence the rate of surface reactions of diamond precursor with gaseous species, thus facilitating the process of CVD diamond formation.

INTRODUCTION

A current issue in the CVD of diamond is its nucleation and growth on foreign (non-diamond) substrates. Many materials were tried as substrates and several substrate treatments were found to be effective

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to enhancing CVD diamond nucleation density. However, the mechanisms of diamond nucleation on foreign substrates are poorly understood and are still a matter of debate. In order to grow CVD diamond films for applications in various fields it is important to understand and control the processes involved in their formation, in particular, reactions in the gas phase and on the substrate surface. It is well recognized now that a special role in these processes is played by metals [1–5].

It is well known that various metals have different affinities to carbon [1]. Manifestations of these differences being studied in diamond CVD process may elucidate the basic processes involved in diamond nucleation and growth. It was observed that both diamond nucleation density and growth rate were dependent on the substrate's nature: metals which do not form carbides (i.e., Cu) generate high diamond nucleation density; deposition on strong carbide formers results in intermediate nucleation densities and in carbide formation prior to nucleation (i.e., Ti), and, finally, low nucleation density was observed on carbon dissolvers (i.e., Fe) [1].

Several attempts have been made to influence both the gas-phase and the surface reactions of carbon species (with each other and with diamond precursor on the substrate) by introduction of metals to plasma during CVD process. It was observed that such additives increase diamond nucleation density by 2–10 times [3]. However, understanding of these processes is poor because it is impossible to distinguish between the metal's influence on the gas-phase reactions and on the surface reactions of diamond precursor on the substrate with gaseous species.

With the idea to investigate the influence of substrate surface reactions on CVD diamond formation, a method of substrate surface preparation was found to enhance CVD diamond nucleation density. This method is based on abrasion of the substrate surface using a mixture of diamond with metal powders such as Ti, Fe and Cu. By using metal particles of different affinity to carbon in the abrasion process, in addition to damage the substrate, we aimed to chemically modify the near surface region of the substrate. As demonstrated below, for some metal additives, this treatment results in a significant enhancement, by few orders of magnitude, of the CVD diamond nucleation density.

EXPERIMENTAL

The abrasion pretreatment experiments were performed by sonification of silicon (100) substrates for 30 min in a slurry, followed by a 1 min rinse in acetone. The mixed diamond–metal slurry consisted of 0.2

Table 1. Summary of nucleation densities measured after 15 min of diamond deposition on Si substrates pretreated with mixed diamond/metal slurries. The sizes of the metal and diamond particles used, as well as the concentration of carbon and metal residues left on the silicon surface after treatment, as measured by AES, are summarized.

N	Slurry	Metal Particle Size (μm)	Atomic Concentration (%)		Nucl. Density (10^7 cm^{-2})
			Metal Residues	Carbon	
1	Di	1–3	—	5.3	1.2
2	(Ti + Di)	30–35	3.4	14.3	168
3	(Fe + Di)	1–3	1.6	13.5	5.1
4	(Cu + Di)	10	1.0	7.8	2.6

g diamond powder, 0.2 g metal powder and 20 ml of ethyl alcohol. The different metal powders, used for abrasion, and their sizes, are listed in Table 1. Diamond depositions were performed in a hot filament CVD system previously described in Reference [6] using a methane volume concentration of 1% in hydrogen, a gas flow rate of 100 sccm, a working pressure of 50 Torr, a substrate temperature of 850°C and a filament temperature of 2000°C.

The chemical composition of the Si surfaces following different pretreatments, was measured by Auger electron spectroscopy (AES). The concentration of carbon and metal residues on the surface was calculated from the Auger spectra measured in the first derivative mode using appropriate elemental sensitivity factors [7]. Scanning electron microscopy (SEM) measurements were performed to calculate diamond particles densities on variously treated substrates after different deposition times. The nucleation density measurements at a magnification of ×1000 were performed by counting the number of individual particles deposited before coalescence of isolated particles into a continuous film occurred. The crystalline quality of the deposited continuous films was monitored by Raman measurements.

RESULTS AND DISCUSSION

Typical SEM micrographs obtained after deposition for 15 min on silicon substrates pretreated with diamond (Di) and mixed diamond/titanium (Ti + Di), diamond/iron (Fe + Di) and diamond/copper (Cu + Di) slurries are shown in Figure 1. As observed from these figures, in addition to the enhanced nucleation, the mixed slurry pretreatment results in a broader distribution of deposited particle sizes.

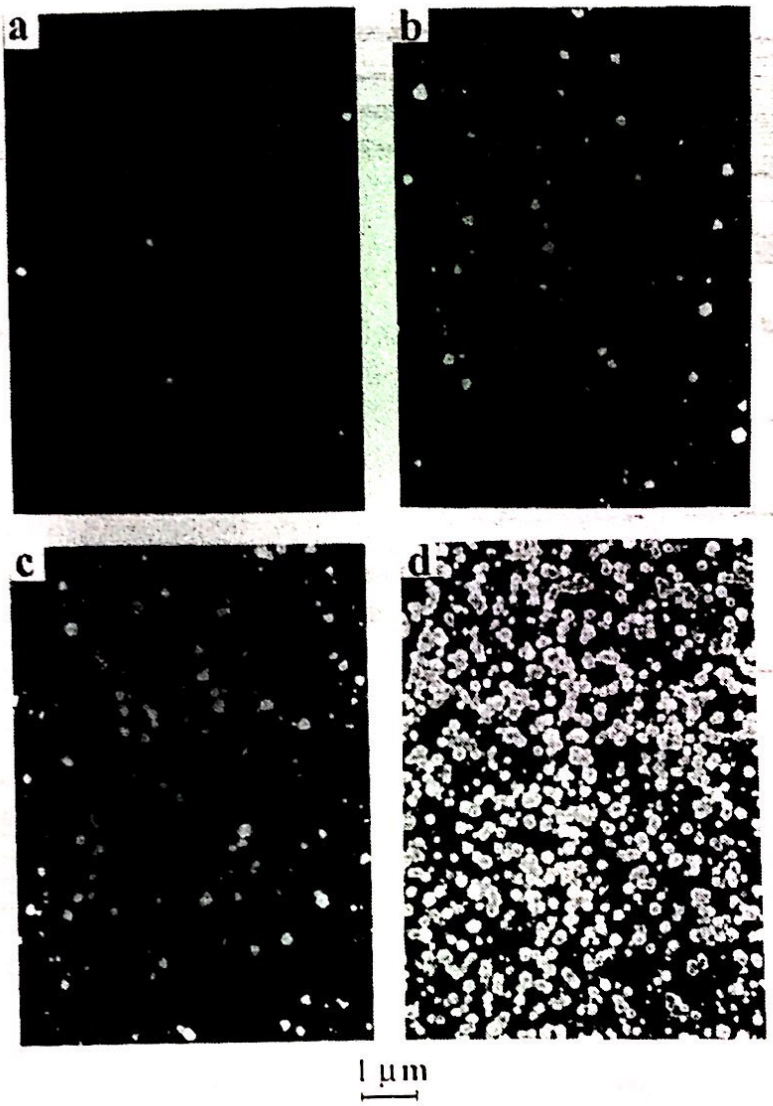

Figure 1. Scanning electron micrographs of silicon substrates pretreated in: (a) diamond slurry and mixed (b) (Cu + Di), (c) (Fe + Di), (d) (Ti + Di) slurries after 15 min of diamond deposition.

The measured diamond nucleation densities are summarized in Table 1. These results indicate that ultrasonic abrasion with a mixture of diamond and metal particles results, for all three metals used, in nucleation enhancement relative to that obtained following treatment with the diamond slurry alone.

Auger spectra from differently treated silicon substrates before deposition (Figure 2) indicate the presence of carbon and metals residues left on the substrate surface. The carbon and metal concentrations are summarized in Table 1 alongside the nucleation densities. As can be

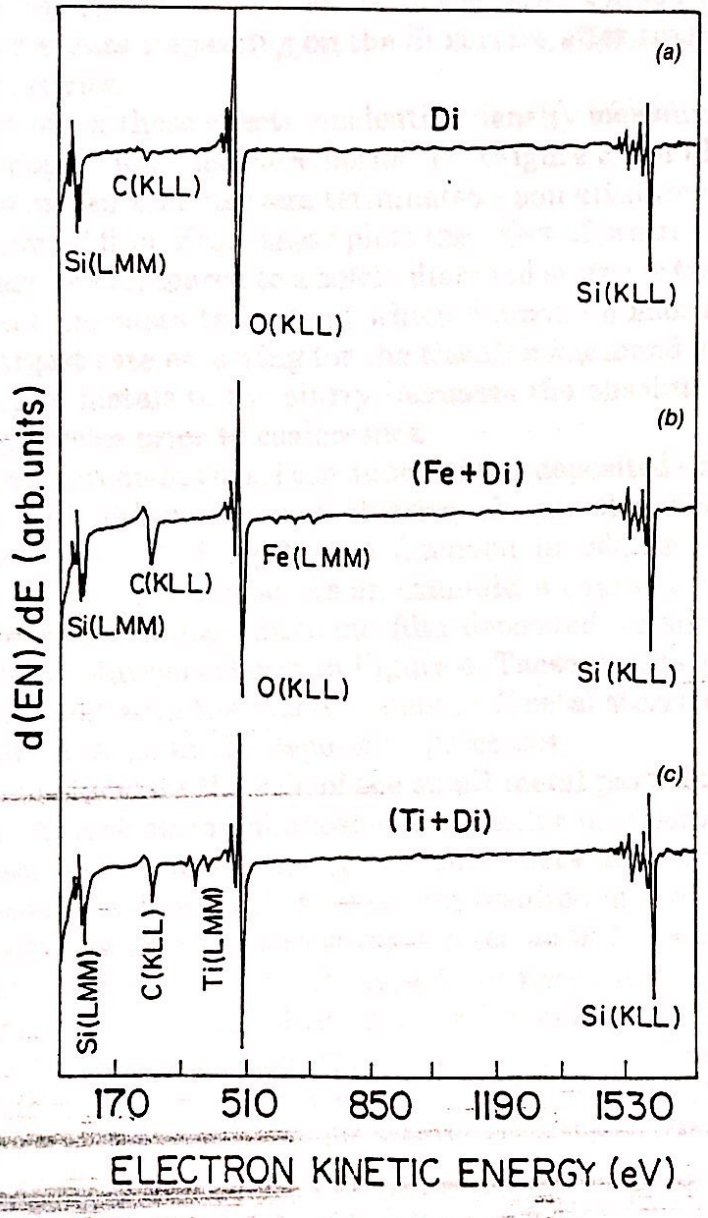

Figure 2. Auger spectra from differently treated silicon substrates before deposition.

seen from the data presented, no straightforward correlation exists between the values of the nucleation densities and the concentration of metal and carbon residues present on the Si surface subsequent to the different pretreatment. However, some trends were observed, relating the highest nucleation density values to the largest amounts of metal and carbon residues remaining on the Si surface after treatment with (Ti + Di) particles.

To further assess these effects, nucleation density measurements as a function of deposition time were performed (Figure 3). In all the cases studied, the measurements were terminated upon attainment of a continuous diamond film. From these plots the effect of pretreatment with a mixed slurry as compared to a solely diamond slurry is twofold. Such pretreatment increases the rate at which diamond nuclei are formed, with the largest rate occurring for the titanium/diamond slurry. Also, the addition of metals to the slurry increases the absolute number of deposited particles prior to coalescence.

Raman measurements of all continuous films deposited on substrates pretreated with different mixed slurries, showed that the deposited films were composed of crystalline diamond in addition to a small amount of amorphous carbon. As an example, a characteristic Raman spectrum of a continuous diamond film deposited on silicon treated with (Ti + Di) slurry is shown in Figure 4. These results suggest that the pretreatment with the different diamond/metal slurries affect only the nucleation stage in the deposition processes.

In order to elucidate the role of the small metal particles present in the slurry in nucleation enhancement a similar ultrasonic treatment to that described above was performed using metal powders alone. Diamond deposition following this treatment resulted in a very low nucleation density. For all the cases studied, after up to 2 hrs of deposition, the nucleation densities did not exceed 10^5 nuclei/cm^2. These results suggest that the influence of the diamond/metal slurry pretreatment on diamond CVD nucleation and growth is of a cooperative nature. Rather, it is suggested that the metal residues promote the formation of species active in the growth process on the surface. However, nucleation and growth occur on sites produced, presumably, by the diamond slurry. To further investigate this hypothesis, the dependence of diamond nucleation density on metal particle size and on the metal-to-diamond weight ratio in the mixed slurry, was also investigated. In the case of Fe powder, increasing the particle size from 3 to 30 μm increased the nucleation density by an order of magnitude, which is illustrated in Figure 5.

A similar effect was obtained when the relative weight of the Fe

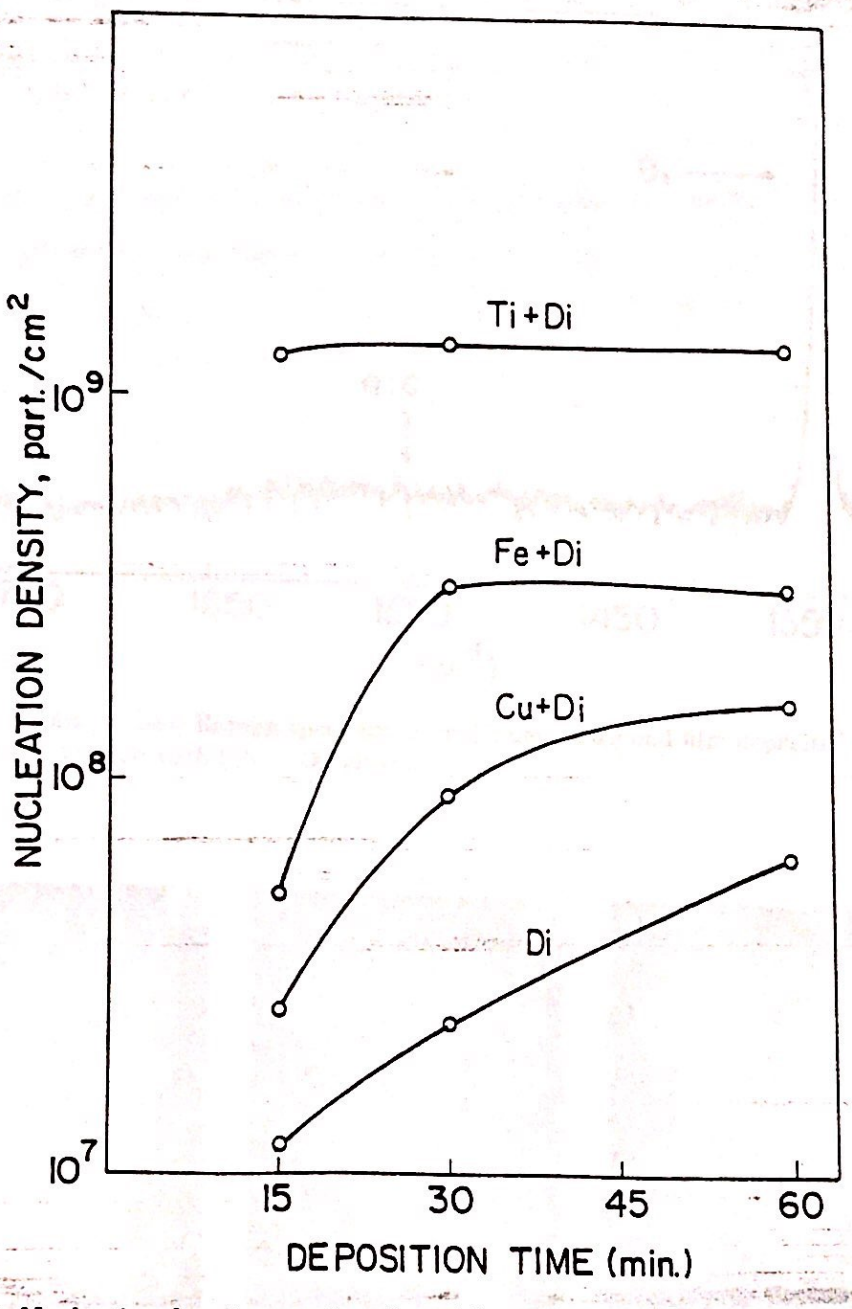

Figure 3. Nucleation density as a function of deposition time measured for differently pretreated silicon substrates. The measurements were terminated when a continuous film was obtained.

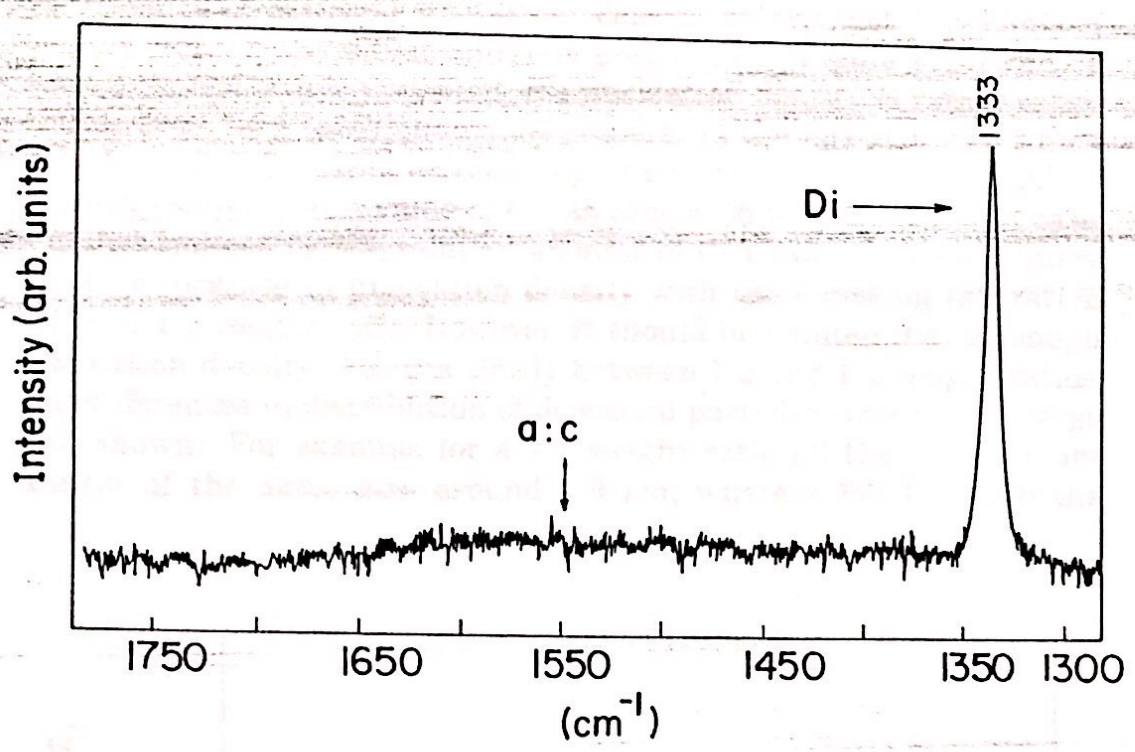

Figure 4. Characteristic Raman spectrum of continuous diamond film deposited on silicon substrate treated with (Ti + Di) slurry.

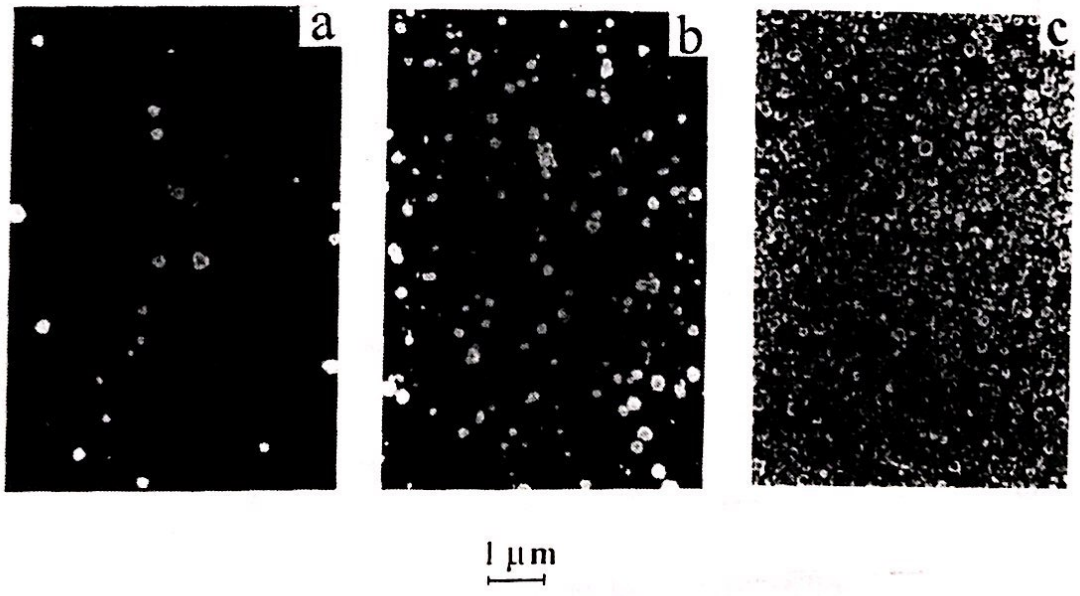

Figure 5. SEM micrographs of silicon substrates abraded with (a) diamond and mixed (Fe + Di) slurries with Fe particle size (b) 3 μm and (c) 30 μm.

powder was increased in the mixed (Fe + Di), slurry treatment. The dependence of diamond nucleation density on the metal-to-diamond weight ratio in the mixed slurry is presented in Figure 6. As can be seen from the graph presented, the nucleation density is rather sensitive to even very small quantities of metal in the mixed slurry, which is indicated by its rapid increase (approximately 5 times) for metal-to-diamond weight ratio value of 0.1 as compared with the pure Di case. Further increasing the relative amount of Fe powder in mixed slurry leads to increase in nucleation density with the following saturation above a 1:1 weight ratio. However, it should be pointed that although nucleation density changes slowly between 1:2 and 1:1 weight ratios, the differences in distribution of deposited particles sizes is very large (not shown). For example for a 1:1 weight ratio all the particles are almost of the same size around 0.9 μm, whereas for 1:2 ratio the

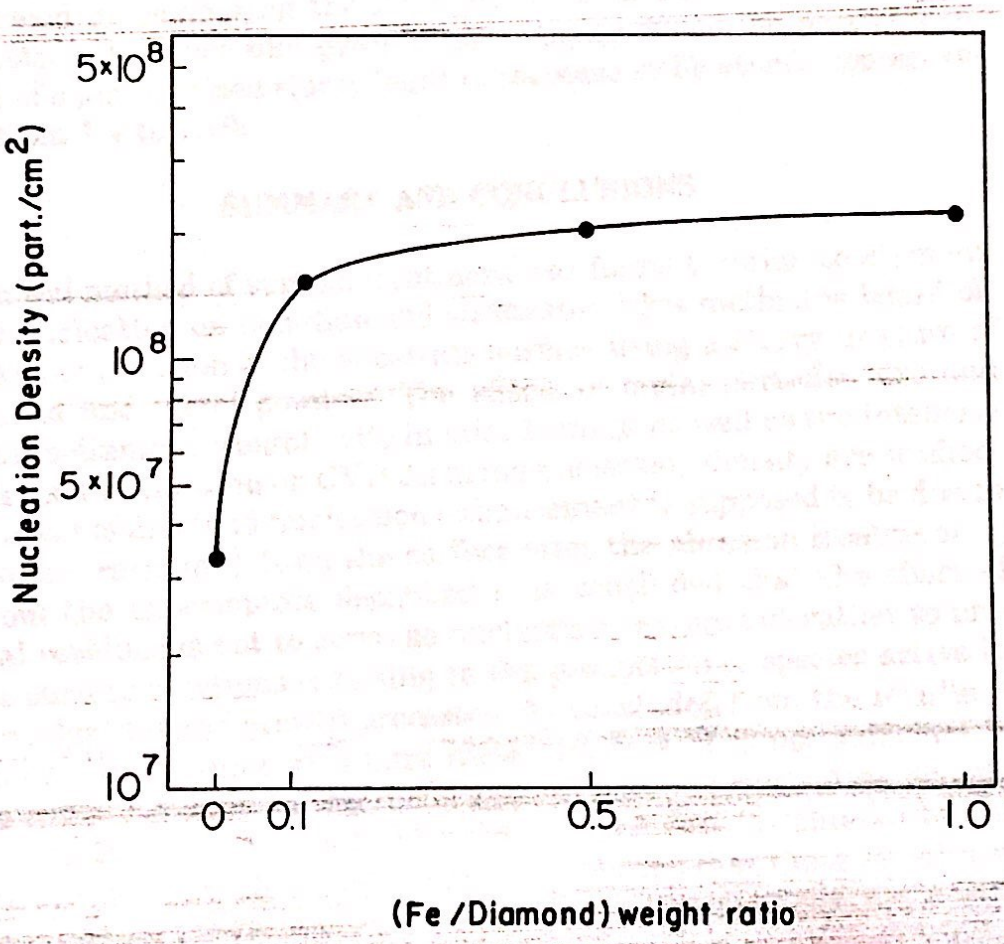

Figure 6. Nucleation density as a function of metal-to-diamond weight ratio in a mixed slurry when the metal used is Fe.

particles sizes distribution is much broader and falls between 0.4 to 0.9 μm.

In addition, the influence of intensities of ultrasonic treatment on CVD diamond nucleation density was studied. It was observed that increasing the power of ultrasonic abrasion from 60 to 140 Watt increases the CVD diamond nucleation density on both, treated with pure diamond and with mixed diamond/metal slurry substrates. For example, for silicon substrates treated with mixed (Ti + Di) slurry, the density of diamond particles observed was enhanced from $4 \cdot 10^8$ to $1.7 \cdot 10^9$ cm^{-2} after 30 min deposition.

The variations in nucleation densities and growth rates of individual diamond particles described above may be related to the quantities of metal left on the substrate surface by abrasion process. Indeed, for larger amount of metal residues–both diamond nucleation density and growth rate of individual diamond particles are higher. This result is confirmed by comparing the AES results with the data on diamond nucleation densities and growth rates. Using 30 μm Fe particles instead of 3 μm in mixed slurry leads to increase in Fe atomic concentration from 1.4 to 7.1%.

SUMMARY AND CONCLUSIONS

A novel method of surface treatment was found to enhance diamond CVD nucleation on non-diamond substrates. This method is based on ultrasonic abrasion of the substrate surface using a slurry mixture of diamond and metal powders. The effects of metal particles size and metal-to-diamond weight ratio in mixed slurry, as well as the intensity of ultrasonic abrasion on CVD diamond nucleation density are studied. The effect of diamond nucleation enhancement is supposed to be due to the metal residues left on the surface after the abrasion treatment.

From the experiments described it is concluded that the effect of metal residues is not to serve as nucleation centers but rather to promote surface reactions resulting in the production of species active in the nucleation and growth processes. As concluded from the results of substrate treatments with pure metal powders, it is not sufficient to have metal residues on the surface to enhance the nucleation density but nucleation sites have to be produced and this is achieved by the treatment with the diamond slurry. It is believed that these metal residues influence the rates of surface reactions of diamond precursor with gaseous species through facilitation of conversion of sp- and sp^2- bonded carbon fraction to sp^3 one, thus contributing to both diamond nucleation and growth processes.

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