Enhanced nucleation density of CVD diamonds by using interlayers

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I. INTRODUCTION

It is crucial to understand the nucleation mechanism for most applications of diamond films grown by CVD. In general, the nucleation density of diamonds (N_d) is very low without any substrate pretreatment. Therefore, various pretreatments of substrate surface have been tried to enhance N_d. One common method is the diamond abrasion in which substrate surface is scratched with diamond powder or ultrasonically abraded in diamond powder suspension prior to diamond deposition. Its effectiveness in enhancing N_d is mainly attributed to the generation of residual diamond seeds. To achieve much higher N_d, the diamond abrasion method has been improved in such ways which are after all based on the increase in the density of nucelation sites (N_s), that is, the density of residual diamond seeds. However, N_d was reported to be lower in one order of magnitude than N_s from the HR-SEM experiments. This result was attributed to the atomic hydrogens which could etch away residual diamond seeds during the initial diamond deposition. Therefore, to maximize N_d as much as possible, it is necessary to develop a novel method to keep the nucleation sites from atomic hydrogen etching. In this study, we try to deposit interlayers on the diamond abraded Si substrates prior to diamond growth, for the purpose of the enhancement in N_d for the constant N_s that are prepared under the constant abrasion condition.

II. EXPERIMENTAL PROCEDURE

First, Si (100) substrate was ultrasonically abraded in an alcohol suspension of diamond powder before interlayer deposition by r.f. magnetron sputtering. After the depositions of various interlayers such as Si, Mo, Ti, Pt, Ag, TiN, and SiO_2, diamonds were grown in a typical condition of microwave plasma CVD.

III. RESULTS AND DISCUSSION

The nucleation density (N_d) was $1 \times 10^8/cm^2$ just after the diamond abrasion, however it could be greatly enhanced to $1\text{-}2 \times 10^9/cm^2$ by various 50 nm thick interlayers such as Mo, Ti, Pt, Ag, TiN, and SiO_2. Si, Mo, and Ti are known to be carbide forming metals, while Pt and Ag are not. From the XRD patterns, most interlayers were shown to be crystalline except the amorphous SiO_2 or Si interlayer. The efficiency of interlayer in enhancing N_d did not show any dependency on the nature of interlayer material such as crystal structure or its ability to form carbide during diamond growth in this study.

In contrast above results, the interlayers could not enhance the N_d [~10^4/cm^2] on the bare substrate without the diamond abrasion, indicating that the interlayers can not produce any nucleation sites of diamond by themselves. The interlayers also failed in enhancing N_d even when diamond growth was preliminary performed for 15 min on the abraded substrate followed by the interlayer deposition, drawing the guess that the N_d could be already greatly decreased to ~$1x10^8$/cm^2 before the interlayer deposition.

The role of the interlayers in enhancing N_d was investigated from the HR-SEM observation of the initial diamond deposition process on the abraded substrate with or without the Si interlyer 50 nm in thickness. On the substrate with the interlayer, white spots considered as the residual diamond seeds were observed before diamond deposition. After the deposition for 15 min, most white spots disappeared, and only small portion of them grew to diamond particles [N_d~$1x10^8$/cm^2], resulted from atomic hydrogen etching as reported before. With the futher deposition to 45 min, the diamond particles were just kept growing without any change in N_d. On the substrate without the interlayer, before diamond deposition a very smooth surface was observed without any feature such as above white spots, indicating that the residual diamond seeds are covered by the interlayer. However, white spots surprisingly appeared with high density [~$2x10^9$/cm^2] on the fissures generated on the interlayer after diamond deposition for 15 min. And they were only grown without change in density, but the fissures were disappeared after the further deposition to 45 min.

The generation of the fissures is likely to be related with the phase transformation of the Si interlayer from amorphous to polycrystalline structure during diamond deposition at T_s~850 °C. The Si surface is well known to be be etched by the plasma during diamond deposition, and then the etching rate is faster in grain boundaries than on the grains. On this basis, we speculate that the residual diamond seeds, which had been protected by the interlayer in the initial diamond deposition, could be grown through the fissures without any loss of nucleation sites as they were exposed to the plasma. It is also noteworthy that the sizes of the grown diamond particles were smaller on the substrate with the interlayer than that without the interlayer. This was attributed to the increase in the incubation time for diamond growth, which could normally proceed only after the Si interlayer being to some degree etched away by atomic hydrogens.

To investigate the effects of interlayer thickness on N_d, Si interlayers were deposited in various thicknesses 20 to 700 nm on the diamond abraded substrate. Compared with $1x10^8$/cm^2 for the just abraded substrate, as the interlayer thickness was increased from 20 nm to 500 nm, Nd was always enhanced to $1x10^9$/cm^2 except for the interlayer of 100 nm where the Nd reached a maximum value, $2x10^9$/cm^2. Interestingly, the mean size was monotonically decreased with the increase in the thickness, and the growth rate estimated from the size was decreased from ~300 nm/hr to ~100 nm/hr with the increase in interlayer thickness. Diamond was not grown at all as the interlayer thickness was increased up to 700 nm. These results indicate that there is an optimum range of the interlayer thickness for higher N_d; it is from 50 to 100 nm in these experiments. There is no doubt that the thinner the interlayer, the more quickly it can be etched away by atomic hydrogens during diamond deposition. Based on this we speculate that the 20 nm interlayer is too thin to protect all the nucleation sites generated by the diamond abrasion during the initial diamond deposition. On the other hand, as the interlayer thickness is increased, the protection of the nucleation sites, of course, may be made better. However, since the diffusion rate of carbon source through the interlayer is all the more decreased, the nucleation rate would be decreased. No diamond growth at the interlayer of 700 nm would be presumably the extreme case of the complete inhibition of the diamond growth. The monotonic decrease in the growth rate with the interlayer thickness is also attributed not only to the decreased diffusion rate of carbon source through the interlayer, but also to the increased time required for the etching of the whole interlayer.

IV. CONCLUSION

Effects of interlayers on diamond nucleation were investigated for the diamond abraded Si substrates. The interlayers were deposited by r.f. sputtering system prior to diamond growth using microwave plasma CVD. As the substrate was just abraded with diamond powder, N_d was $1\times10^8/cm^2$ that is still much lower than the nucleation sites generated by the diamond abrasion. However, it was greatly enhanced to $1-2\times10^9/cm^2$ with interlayer of 50 nm in thickness whatever interlayer was deposited among Si, Mo, Ti, Pt, Ag, TiN, and SiO_2 tried in this study. Meanwhile any enhancement in N_d was not observed as the interlayers were deposited on the bare substrate, suggesting that the interlayers do not generate any nucleation sites by themselves. It was observed by HR-SEM that the nucleation sites generated by the diamond abrasion were significantly etched away by atomic hydrogens, while they could be protected against atomic hydrogen etching by the interlayer and transformed into stable nuclei in the initial stage of diamond deposition. From these results, we conclude that the role of the interlayers in enhancing N_d is not to generate new nucleation sites but to keep the nucleation sites from the atomic hydrogen etching in the initial diamond deposition, followed by the stable growth afterwards. Both the N_d and the growth rate of diamond particles were dependent on the thickness of the Si interlayer. As the interlayer thickness was increased from 20 nm to 500 nm, N_d was always enhanced to $1\times10^9/cm^2$ except for the interlayer of 50 nm or 100 nm where the Nd reached a maximum value, $2\times10^9/cm^2$. The growth rate was monotonically decreased from ~300 nm/hr to ~100 nm/hr with the increase in the thickness. As the thickness reached to 700 nm, diamond was not grown at all.