Influence of the silicon surface treatment by plasma etching and scratching on the nucleation of Diamond grown in HFCVD – a comparative study

Ansari SG, Seo Hyung-Kee, Kim Gil-Sung, Shin Hyung-Shik

Thin film technology lab, School of chemical engineering, Chonbuk National University, Chonju, Republic of Korea, 561756

Since the discovery of the chemical vapor deposition as a mean for the growth of diamond films, large efforts have been put to grow ever better quality films of forms of diamond. This technique has been proven to be a very versatile tool, which is used to synthesize highly oriented diamond thin films, fullerene and decorated and branched carbon nanotubes in the past. An important step of this evolution was the nucleation enhancement with various surface pretreatments, which resulted in increased nucleation density and growth rate. It is realized that the nucleation and growth processes are strongly affected by such pretreatment methods viz. scratching, seeding, electrical biasing, ion implantation, laser irradiation, carburization etc. Amongst all, scratching of the substrate with diamond powder is most efficient. A recent approach to enhanced diamond growth is based on the use of halogen based mixtures or noble gases during the growth as well as seeding of the substrate with carbon nanotubes.

In the present work, a comparative study is carried out using the surface treatment by plasma etching and scratching using 1 μ m diamond paste. Silicon surface plasma etching was carried out using Cl₂ ion-assisted etching at 50, 100 and 150W of the plasma. AFM study shows variation in roughness from 31nm to 110nm with different techniques. Scratching results in a random scratch whereas plasma etching gives a uniform etching, which can be favorable for enhanced growth.

Growth of diamond was carried out on chemically degreased Si (100) substrate using hot tungsten filament chemical vapor deposition system. Mixture of H_2/CH_4 , in the ratio of 100:1 vol%, was used with total flow rate of 100 sccm maintaining a constant pressure of 30±2 Torr, throughout the deposition process. Growth was carried out for 2 hrs at the substrate temperature of ~900°C whereas filament temperature was kept as 2400°C. XPS spectra of the substrate just before deposition indicate presence of peaks corresponding to S1_{2p}, Si_{2s}, C_{1s} and O_{1s}. After deposition, only C_{1s} phase is observed.

It is observed from SEM images that the film morphology, grain alignment, nucleation density and growth rate changes with different surface treatments. It is realized that the scratching with diamond paste as well as plasma etching results in well faceted crystallites with a predominance of angular shaped grains corresponding to <100> and <110> crystallite surface (Fig.1). Surface etching with 150W plasma results in best growth rate in comparison with 50 and 100W plasma (Fig. 2). This may be due to the enhanced topographical irregularities induced by etching action of the Cl₂ ions necessary for the fixation of nucleation sites.

Surface Nucleation density, as estimated form SEM images, with scratching and plasma etching is found to be $\sim 25 \times 10^{12}$ cm⁻² and $\sim 42 \times 10^{12}$ cm⁻² respectively. This shows that nucleation enhancement in both the cases are similar.



Fig.1: Growth of diamond on the scratched surface of Si with $1 \ \mu m$ diamond paste.



Fig.2: Growth of diamond on the 150W plasma etched surface of Si.

Micro Raman spectroscopy supports the SEM result giving a sharp peak related to diamond at \sim 1332 cm⁻¹ in both the cases.

The plasma etching method has advantages over scratching as it can be industrialized easily and results in a very uniform and large area surface etching. A detailed study is required to utilize this process for the growth of diamond.