

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

Shafeeque G. Ansari, Mushtaq Ahmad Dar, Young-Soon Kim, Hyung-Kee Seo,
Gil-Sung Kim, Rizwan Wahab, Zubaida A. Ansari**, Jae-Myung Seo* and Hyung-Shik Shin[†]

Thin Film Technology Laboratory, School of Chemical Engineering, Chonbuk National University, Jeonju 561-576, Korea

*Functional Nano Thin-film Laboratory, Department of Physics, Chonbuk National University, Jeonju 561-576, Korea

**Center for Interdisciplinary Research in Basic Sciences, Jamia Millia, Islamia, Jamia Nagar, New Delhi 110025, India

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Abstract—A comparative study for the nucleation of diamond was carried out using surface treatment like (i) surface scratching with 1 μm diamond paste and (ii) surface etching using chlorine plasma at different RF powers (50, 100 and 150 W). Atomic force microscopic study shows variation in roughness from 31 nm to 110 nm. Scratching results in random scratches, whereas plasma etches a surface uniformly. Scanning electron microscopic observations show well faceted crystallites with a predominance of angular shaped grains corresponding to $\langle 100 \rangle$ and $\langle 110 \rangle$ crystallite surfaces for the scratched as well as plasma etched substrate. Surface etching at 150 W plasma power results in a better growth in comparison with 50 and 100 W plasma powers. Chlorine-radical is found responsible for the changes in the growth morphology. Raman spectroscopy shows a sharp peak at $1,332\text{ cm}^{-1}$ and a peak at $\sim 1,580\text{ cm}^{-1}$ for both samples.

Key words: Diamond Nucleation, Surface Treatment, Plasma Etching, Cl-radical, Scratching

INTRODUCTION

Since the discovery of the chemical vapor deposition as a means for the growth of diamond films, intense efforts have been made to grow ever better quality films. This technique has been proven to be a very versatile tool to synthesize highly oriented diamond thin films, fullerene, and decorated and branched carbon nanotubes in the past. An important step for the nucleation of diamond is the nucleation enhancement by surface pretreatments, which results in the increased nucleation densities and growth rates. The commonly used pretreatment methods are scratching, seeding, electrical biasing, ion implantation, laser irradiation, carburization etc. [1-4]. Amongst all the methods, scratching of the substrate is found most efficient.

The reported nucleation mechanism on non-diamond substrates is as follows: first, an activated species (such as high energy carbon atom or hydrocarbons) is generated due to the plasma (generated locally in the vicinity of heated filament, e.g., due to hydrogen gas) which then migrates on the substrate forming a cluster at a stable site. This process is achieved with much difficulty, since the produced cluster tends to evaporate because of high density hydrogen plasma and higher substrate temperature. To overcome such problems, either the carbon concentration in the raw material is increased or the substrate surface is pre-treated (scratching). The substrates with high carbon affinity can be selected to stabilize the diamond nucleus. Thus the cluster produced is easily transformed into the diamond nucleus by plasma energy [5].

The diamond nucleation mechanism is generally clear; however, the structure of the precursor and the transition mechanism from an amorphous carbon cluster to a diamond nucleation remains unclear in the case of carburized surfaces. A recent approach to enhance

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 [6-10].

Various treatment methods have been tried for the nucleation enhancement of diamond on diamond/non-diamond substrates. Some of these are: surface scratching with abrasives, electrical biasing at the early stage of growth, pulsed-laser irradiation, chemical pretreatment and coating the substrate with thin metal film as a seed layer. In addition, surface scratching with diamond grits and other ceramic powders, coating by carbon nanotubes (CNTs), graphite films or fibers, ion implantation, etc, also encases the nucleation of diamond on such substrates. However, there are certain problems with every treatment, with advantages over other methods, e.g., thin metal film results in poor adhesion and metal contamination (as it melts at the deposition temperature). The crystallinity of the diamond film is greatly affected or found dependent on the carbonaceous phase used while seeding/treatment (e.g., diamond grit, CNTs, surface carburization etc.) [1,10]. Many of these earlier attempts to grow diamond films on non-diamond substrates yielded mostly polycrystalline films consisting of randomly oriented crystals, mixed phases and defects (e.g., secondary nucleation, dislocations, stacking faults etc.). Nucleation density has been increased from less than $10^5/\text{cm}^2$ on untreated substrates up to 10^{10} - $10^{12}/\text{cm}^2$ on scratched or biased substrates [1]. However, scratching on large scale can pose a problem in reproducibility. Here we present a new method of surface treatment for diamond nucleation enhancement, which is found simpler, easier and reproducible for large scale applications.

In the present work, a comparative study is carried out using (i) inductively coupled plasma generation of Cl_2 gas to produce Cl radicals for Si wafer etching at various RF powers (50-150 W) and (ii) Si surface scratching with 1 μm diamond paste. Morphological and structural data were obtained by scanning electron microscopy (SEM). Surface states were analyzed by X-ray photoelectron spec-

[†]To whom correspondence should be addressed.

E-mail: hsshin@chonbuk.ac.kr

troscopy (XPS) and elemental analysis by Raman spectroscopy.

EXPERIMENTAL

Diamond films were deposited by using hot filament CVD (HFCVD) method as reported earlier [3]. The polished side of p-type Si (100) wafers of size 15 mm×7 mm was used for the diamond deposition. The substrates were degreased in boiling alcohol (isopropyl alcohol) and acetone for 10 min and then dried by using N₂ gas. The substrates (with treated surface) were loaded onto a sample holder and the assembly was then transferred to a high-vacuum reaction chamber. The substrate was aligned at the center of the reaction chamber, just above the filament. The filament (15 mm long and 5 mm cross sectional dia.) was horizontally installed at the center of the chamber perpendicular to the gas flow direction. Distance between the substrate and filament was kept as ~5 mm.

Silicon surface was dry etched with Cl radicals generated with a planar type Vacuum science inductive coupled plasma system (VSICP-

1250A, 13.56 MHz) in a reactive ion-etching mode. The RF power applied to the wafer platen (chuck) induced the positive ions in the plasma onto the wafer platen. RF power was varied from 50 to 150 W to obtain various surface roughness levels. The ion energy was kept constant by a fix excitation frequency of 13.5 MHz. Si surface topology and roughness were examined and estimated by contact-mode atomic force microscopy (AFM).

Surface scratching was carried out manually with 1 µm diamond paste. For scratching, a small quantity of commercially available diamond paste (Stuers, DP-Paste, M, 1 µm, mono-crystalline diamond, Denmark) was put on the cut Si wafer and was rubbed over the surface with soft polishing paper for few minutes. Care was taken to rub in one direction to achieve nearly aligned scratches. The substrates were then degreased and cleaned with alcohol and acetone.

A mixture of high purity H₂ (99.999%), CH₄ (99.95%) gases was flown in from the bottom side of the chamber and their flow rate was controlled by using mass flow controllers (MFC). The reaction gases, which consisted of 1 vol% of CH₄, and 100 vol% of H₂,

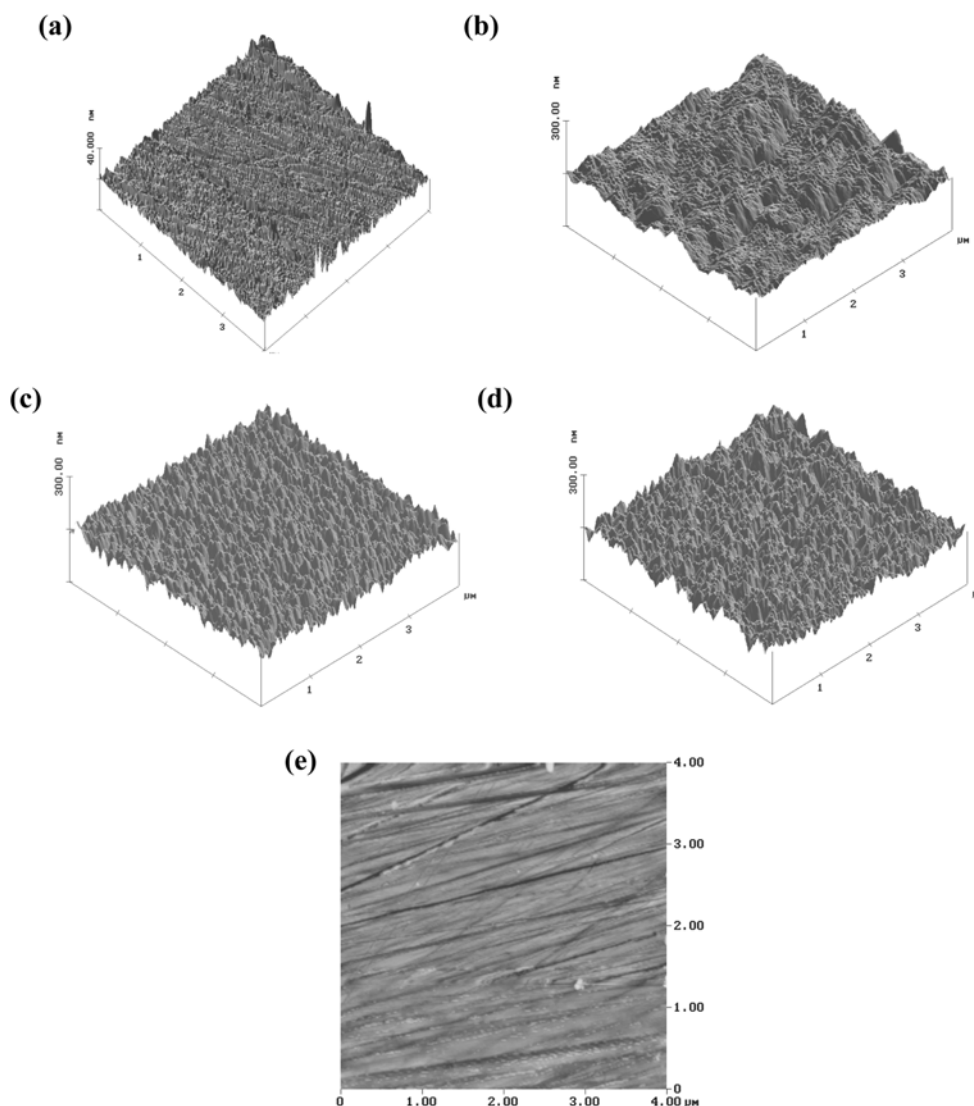


Fig. 1. 3D AFM images of the substrate treated with plasma powers of (a) surface scratched with 1 µm diamond paste, (b) 50 W, (c) 100 W, (d) 150 W, and (e) Planar view of the scratched surface.

were supplied in a total flow rate of 100 sccm. The total gas pressure inside the reaction chamber was kept constant as 30 ± 2 Torr, throughout the deposition process. The deposition was carried out at the substrate temperature of $\sim 900^\circ\text{C}$ and the filament temperature was maintained at $2,400^\circ\text{C}$. The filament temperature was measured by optical pyrometer (Minolta TR-630, Japan), while the substrate temperature was measured by thermocouple, which was adjusted to touch the substrate from backside. The deposition was carried out for two hours.

The morphological observations of the grown film were carried out by using a scanning electron microscope (SEM, JSM-6400, JEOL, Japan). For structural analysis X-ray photoelectron spectroscopy (XPS, 20 KV/15 mA, AIK α , VG Microtech Ltd., U.K.) and Micro Raman spectroscopy with He-Ne laser ($\lambda=632.8$ nm, Renishaw) were used.

RESULTS AND DISCUSSION

The variation in surface roughness when treated with Cl_2 -plasma and diamond scratching can be seen in the AFM images. Fig. 1(a) shows the 3D AFM image of the scratched surface while Figs. 1(b)-(d) show the 3D-images of the surface treated with 50, 100 and 150 W of RF power, respectively. The roughness value varies from 31 nm to 110 nm with different techniques. Scratching results in random (Fig. 1(e), planar view) scratches and a surface roughness value of ~ 31 nm, whereas plasma etches surface uniformly with a little variation in roughness values (90 to 110 nm) with increasing RF

power from 50 to 150 W.

The changes in the film morphology, grain alignment, nucleation density, crystal structure with treatment are clearly evident from the SEM images shown in Fig. 2. Fig. 2(a) shows the SEM images of the film grown on scratched substrate and Figs. 2(b)-(d) show the variation in the film morphology of the surface treated with 50 W, 100 W and 150 W RF power. It is realized that the scratching with diamond paste results in a crystallized well faced diamond crystal, which is well reported, with a predominance of angular shaped grains corresponding to the $\langle 100 \rangle$ and $\langle 110 \rangle$ crystallite surfaces.

The morphology of the films grown on plasma etched surfaces changes from amorphous or mixed phase to crystalline phase with the increasing RF power. Mixed carbon and diamond phases are observed for the films grown on surface treated with 50 W and 100 W plasma etched substrates. The crystallites are of cauliflower shape with carbonaceous particles (Fig. 2(c) and (d)). Well faceted crystallites are observed for the film grown on surface treated with 150 W plasma (Fig. 2(d)) with similar crystal structure and alignment to that of the film grown on the scratched substrate. Better crystal structure and growth rate are observed for the films grown on surface treated with 150 W RF power plasma in comparison with surface treated at 50 and 100 W RF power plasma. This may be due to the enhanced topographical irregularities induced by surface etching due to Cl radicals necessary for the fixation of nucleation sites. The grain size in both the cases (Fig. 2(a) and (d)) appears almost the same ($\sim 2 \mu\text{m}$) with slight changes in the distribution of the grains.

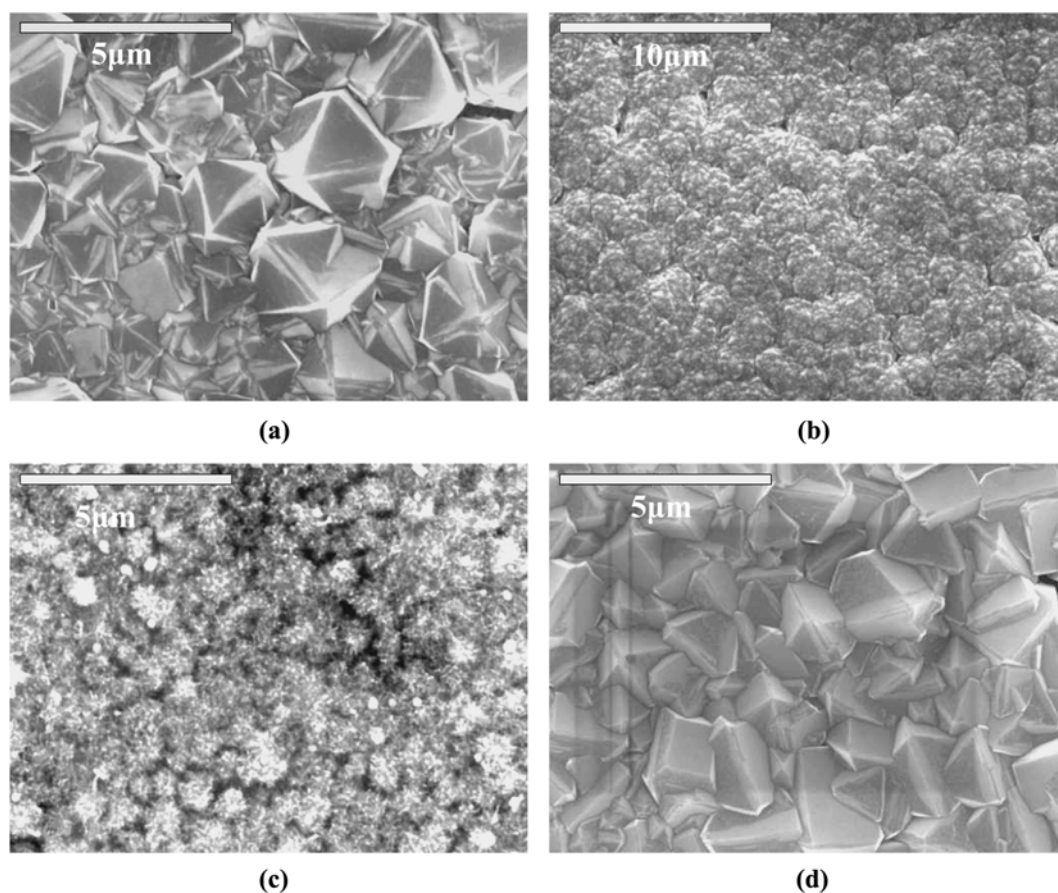


Fig. 2. SEM images of the film grown on (a) scratched substrate, (b) surface etched at 50 W, (c) 100 W and (d) 150 W plasma powers.

Plasma etching results in a uniform growth, whereas surface scratching results in a distributed grain growth. This shows that nucleation enhancement in both the cases is similar except for a slight variation in the uniformity and particle distribution.

SEM results clearly indicated that Cl-radical is responsible for the changes in the growth morphology. With increasing plasma power, Cl-radical concentration increases and hence there is increased reactivity at the wafer surface, increasing active surface sites for the nucleation. When these surfaces are exposed to the HFCVD process, the atomic hydrogen created at the filament reacts with Cl-radicals and probably results in halogenated surface reaction, accelerating the creation of active surface sites for diamond nucleation. It is possible that chlorine atoms may desorb surface bound hydrogen and may adsorb at the diamond surface resulting in the formation of a weak C-Cl bonding.

Micro Raman spectroscopic study supports the SEM results with peaks related to diamond and non-diamond phase. Figs. 3(a)-(d) show the spectra of the film grown with surface treatment by scratching and different RF powers of plasma. In all the cases, two peaks are observed corresponding to diamond (D-band, $\sim 1,332\text{ cm}^{-1}$) and non-diamond phase (G-band, $\sim 1,580\text{ cm}^{-1}$). In case of scratched surface, a peak corresponding to silicon ($\sim 949\text{ cm}^{-1}$) can be seen in

the Raman spectrum (Fig. 3(a)), which indicates that a certain part of the substrates remained uncoated and the grains are not distributed uniformly. Similar results are obtained for the films grown on 50 W and 100 W RF power plasma etched substrates (Figs. 3(c) & (d)). The intensity of the peak related to diamond phase in all the cases is stronger than that of the non-diamond phase. Even though the SEM images show the faceted or crystalline growth, there exists an amorphous or non-diamond phase, probably due to the technique limitation, as SEM can just show the morphology based on the electron reflection, whereas Raman reveals information based on the phonon scattering and not the topological information.

Wide scan XPS spectrum (Fig. 4) of the substrate just before deposition shows the peaks corresponding to Si_{2p} , Si_{2s} , C_{1s} , O_{1s} and O Auger. Core level C_{1s} XPS spectra of the scratched and 150 W RF power plasma etched substrate are shown in Fig. 4(b), where C_{1s} peak is found centered at 284.7 and 285.7 eV, respectively. The shift in the peak position indicates the difference in the carbon phase of the grown film [11,12].

An attempt is made to fit core level C_{1s} XPS curves for these two samples by using a Shirley-type base line with mixed Gaussian (30%) and Lorentzian (70%) profile and controlled FWHM. The entire curve fitting was carried out with chi-squared value less than 2 eV,

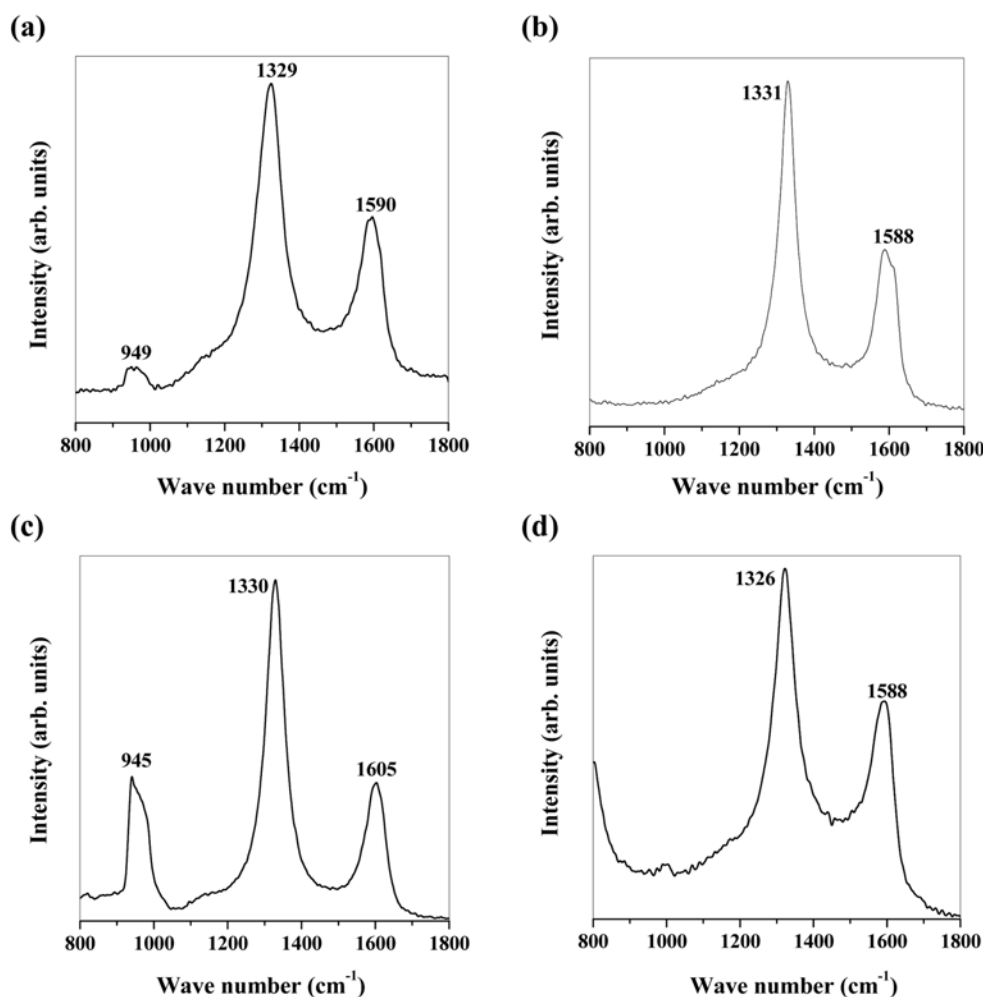


Fig. 3. Micro-Raman spectra of the film grown at substrate (a) surface scratched with diamond paste, (b) surface etched at 50W plasma power, (c) 100 W and (d) 150 W plasma power.

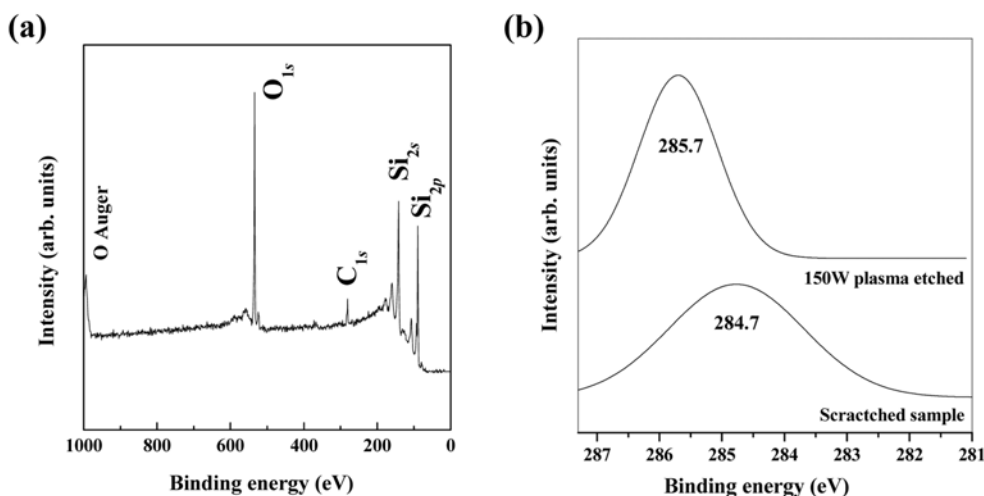


Fig. 4. XPS spectrum of (a) clean substrate just before deposition and (b) core level spectra of the scratched and plasma etched surface (at 150 W plasma power).

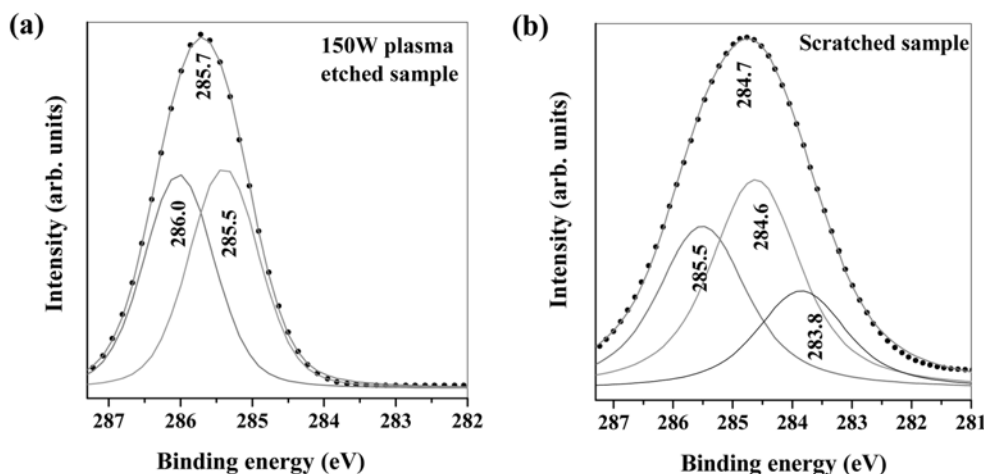


Fig. 5. Curve fitting for core level C_{1s} spectra of the films grown at (a) 150 W plasma etched surface and (b) scratched surface. The scattered data is the experimental data and solid lines are results of curve fitting.

which is reported to be a good value for best fitting [11,12]. The corresponding spectra are shown in Figs. 5(a) and (b) (plasma etched and scratched substrate), respectively. It is noticed that the entire spectrum of the plasma etched sample is shifted towards higher energy side by about 1.2 eV (with reference to C_{1s} peak at 284.5 eV). The fitting data revealed that the C_{1s} peak convoluted two sub-peaks at 286 eV and 285.5 eV. The peak at 285.5 eV is correlated to C-Cl bonding and the peak at 286 eV correlated to the C-C bonding [12]. In case of the film grown on scratched substrate, the peak is found convoluted of three sub-peaks at 285.5 eV, 284.6 eV and 283.8 eV. The peak at 284.6 eV is correlated to C-C bonding, whereas the peaks at 285.5 eV and 283.8 eV to carbide phase, indicating a mixed carbon and graphite phase [11,12] analogous to Raman spectroscopic observations.

CONCLUSION

From this comparative study of the nucleation of diamond on a pre-treated surface, it is realized that surface scratching and the plas-

ma surface etching (at 150 W) give similar results. The roughness value is found to vary from 31 nm to 110 nm with different treatments. Scratching results in a random scratch, whereas plasma etches surface uniformly. Scratching as well as plasma etching results in well faceted crystallites with a predominance of angular shaped grains corresponding to <100> and <110> crystallite surface as observed from SEM images. Surface etching with 150W plasma results in better growth in comparison with surface treated at 50 and 100 W plasma. Raman spectroscopy shows a sharp peak at 1,332 cm⁻¹ and a peak at ~1,580 cm⁻¹ in both the cases. It can be concluded that the plasma etching method has advantages over scratching method due to the process flexibilities such as large area and uniform etching per process/time. Plasma surface treatment process can be easily industrialized for diamond nucleation/growth. A detailed study is required to utilize this process for the growth of diamond.

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