

Effects of cobalt and cobalt oxide buffer layers on nucleation and growth of hot filament chemical vapor deposition diamond films on silicon (100)

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Abstract—An initial study on the nucleation and growth of diamond, using hot filament chemical vapor deposition (HFCVD) technique, was carried out on Co and CoO thin buffer layers on non-carbon substrates (Si (100)), and the results were compared with conventional scratching method. The substrate temperature during the growth was maintained at 750 ± 50 °C. A mixture of CH₄ and H₂ (1 : 100 volume %) was used for deposition. The total pressure during the two hour deposition was 30 ± 2 Torr. X-ray photoelectron spectroscopy (XPS) study showed the diamond nucleation at different time periods on the Co and CoO seed layers. It is observed that Co helps in nucleation of diamond even though it is known to degrade the quality of diamond film on W-C substrate. The reason for improvement in our study is attributed to (i) the low content of Co (~0.01%) compared to W-C substrate (~5-6%), (ii) formation of CoSi₂ phase at elevated temperature, which might work as nucleation sites for diamond. SEM analysis reveals a change in the morphology of diamond film grown on cobalt oxide and a significant reduction in the size of densely packed crystallites. Raman spectroscopic analysis further suggests an improvement in the quality of the film grown on CoO buffer layer.

Keywords: Hot Filament Chemical Vapor Deposition (HFCVD), CVD Diamond, Cobalt, Cobalt Oxide, Filament-substrate Distance

INTRODUCTION

Diamond can be synthesized by various methods reported widely in the literature [1-8]. The morphology of synthetic diamonds is a function of the growth temperature; for a given pressure, cubic diamonds are found at the lower temperature limit for synthesis, whereas octahedral diamonds are produced at temperatures near the high temperature limit. Many substances can be used, but those that allow the largest single crystal diamonds to grow are generally transition metals, particularly those with incomplete d-shells [9,10]. Amongst these, nickel, cobalt, iron and manganese are the most promising. Substrate pretreatments like scratching and biasing, seeding, buffer layers have been widely investigated [11-25]. However, the lattice mismatch between the substrate and the film, dominance of the secondary nucleation and the lack of layer-by-layer growth have generally resulted in the polycrystalline diamond films on non-diamond substrates. Lawson et al. [26] showed that cobalt is also able to form optically active centers in the diamond lattice. Diamonds grown using a cobalt catalyst exhibit a characteristic photoluminescence (PL) band with zero-phonon line (ZPL) at 1.989 eV.

Recently, cobalt has been detected by x-ray fluorescence spectroscopy in HTHP diamond grown using a pure cobalt catalyst [27]. The concentration of cobalt in such samples was found to be an

order of magnitude less than the concentration of nickel present in samples grown using a pure nickel catalyst. The cobalt was shown to have a clear preference for incorporation in the (111) growth sectors, but it is not clear whether the cobalt is in the form of micro inclusions or is really atomically bound to the diamond lattice. The effect of cobalt presence in the cemented carbide substrate degrades the quality of diamond as the catalytic effect of cobalt causes transformation of diamond to graphite and poor film adhesion. It is worth noticing that the percentage of cobalt in cemented carbide substrates is quite high, ~5-6%. The nucleation and the adhesion of diamond film on such substrates can be improved by Co leaching in HNO₃ solution, in-situ plasma decarburization and/or Co etching. In this paper, an attempt is made to understand the nucleation of diamond on non-cemented carbide substrate (scratched Si (100)) with thin buffer layers of cobalt and cobalt oxide. The structure of the HFCVD grown diamond films was characterized by scanning electron microscopy (SEM), energy dispersive analysis of X-rays (EDAX), X-ray photoelectron spectroscopy (XPS) and Raman confocal spectroscopy (Nanofinder 30).

EXPERIMENTATION

All the experimental conditions were similar to our work reported elsewhere [28]. A physical vapor deposition setup with $\sim 10^{-6}$ Torr base pressure was used to carry out cobalt and cobalt oxide film deposition. High purity cobalt (99.9%) flakes from aldrich were evaporated from a tungsten filament. Cobalt films were then heated

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to a substrate temperature of $\sim 300^\circ\text{C}$ in oxygen atmosphere for four hours. Thickness measurement using the stylus technique showed that the film thickness was about $\sim 50 \pm 2$ nm. Cobalt and cobalt oxide coated Si substrates were directly transferred in HFCVD setup, described in detail in an earlier publication [28]. The system was evacuated to a base pressure $\sim 10^{-7}$ Torr. A tungsten filament was positioned at ~ 5 mm distance from the substrate and heated to $2,150 \pm 50^\circ\text{C}$ as measured using an optical pyrometer Minolta TR-630, Japan. This raised the temperature of the substrate to $\sim 700 \pm 50^\circ\text{C}$ as measured using a K-type thermocouple pressed against the backside of the substrate. A gas mixture of H_2 (99.999%) and CH_4 (99.5%) in 100 : 1 proportion was introduced in the deposition chamber at a flow rate of 100 sccm, so that the pressure inside the chamber rose to 30 ± 2 Torr. The deposition was carried out for 120 minutes. Nano-finder30, Tokyo Instruments, with excitation wavelength of 488 nm was employed to analyze the Raman spectra at different places on the diamond films grown on cobalt and cobalt oxide overlayers on scratched Si (100). Scanning electron microscopy with energy dispersive analysis of x-rays (EDAX) attachment (ISM-6400, JEOL-Japan) was used to investigate the morphology and elemental composition of the samples. X-ray photoelectron spectroscopy (XPS) measurements on the diamond films were carried out using S-Probe ESCA Model 2803.

RESULTS AND DISCUSSION

The morphology of the diamond films grown on scratched silicon, with Co and CoO buffer layers can be seen from the SEM images (with same magnification) shown in Fig. 1a, b & c, respectively.

Scratching on Si grows diamond of well reported morphology with diamond crystal predominant facet of (111) orientation (Fig. 1a). The diamond crystal grew with similar morphology to scratched silicon over a Co buffer layer, with smaller crystallite size (Fig. 1b). The diamond film morphology changes, with CoO buffer layer, from rectangular plate to square shaped crystals (Fig. 1c) with predominant (100) orientation. The crystal size decreases further ($\sim 0.5 \mu\text{m}$). The crystallites appear densely packed with small voids. Secondary nucleation can also be seen.

It is widely known that diamond nucleation depends significantly on the surface conditions and pretreatment procedures. Nucleation on non-carbon substrates can be initiated by creating a particular site via scratching with diamond powder, electrical biasing, pre-deposited graphitic carbon etc. Donnet et al. [27] reported that the choice of substrate plays a critical role for nucleation of diamond over W-Co substrate. At higher substrate temperatures, the mobility of Co increases and a large number of cobalt particles with a ball shape are formed on the substrate surface in the first instance; these cobalt atoms interact with carbon adatoms leading to saturated Co-C and hence diamond nucleation. In the present work, we did not observe any cobalt on the surface of Si. This could be due to the very low percentage of the Co ($\sim 0.01\%$ of Si) compared to W-C substrates and the inter-diffusion of Co to Si at elevated temperature leading to formation of CoSi_2 phase. This might create the nucleation sites for the diamond growth. It is reported by Donnet et al. [27] that around Co particles many defects are created due to ball formation causing the accumulation of large number of carbon compounds. This provides an excellent nucleation site for diamond, with possible secondary nucleation at such sites.

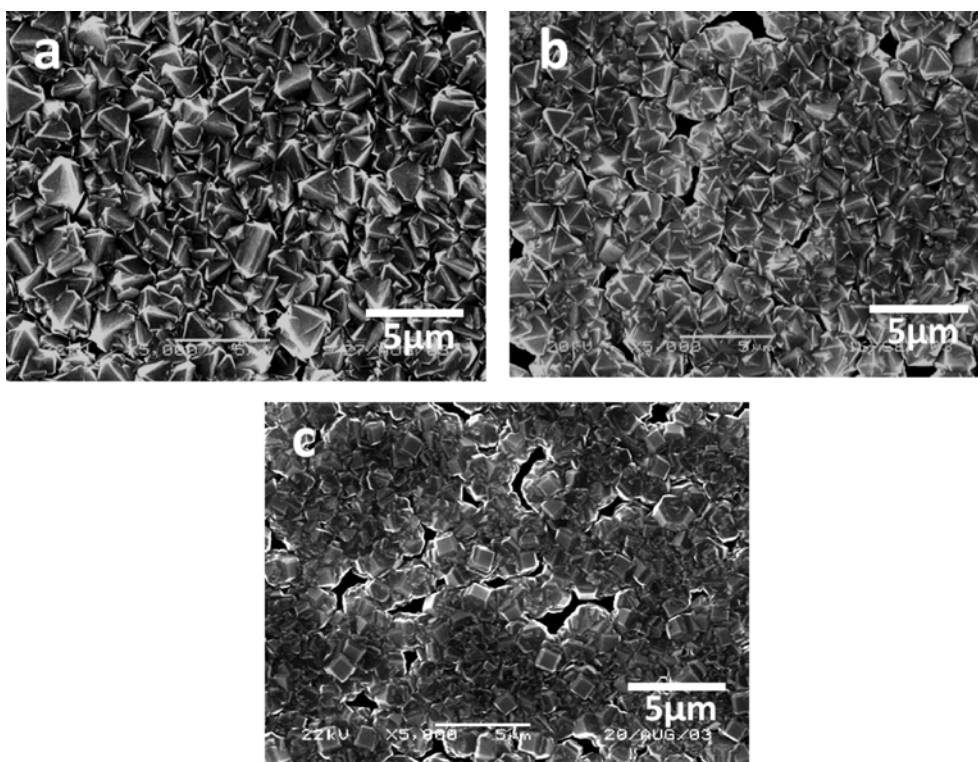


Fig. 1. SEM images of (a) diamond film grown on scratched Si (100) surface, (b) diamond film grown on cobalt overlayered scratched Si (100) surface and (c) diamond film grown on cobalt oxide overlayered scratched Si (100) surface.

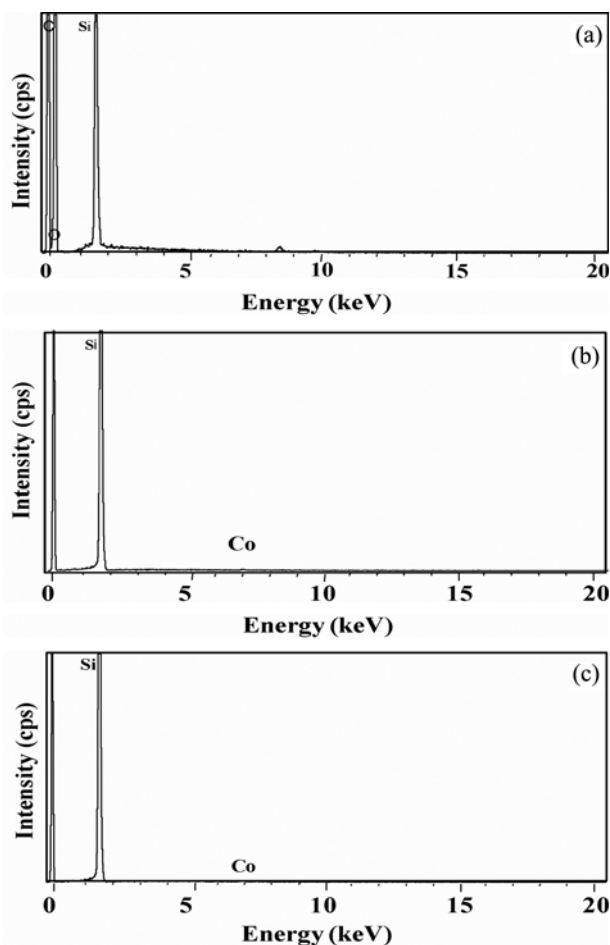


Fig. 2. EDAX spectra of (a) diamond film grown on scratched Si (100) surface, (b) diamond film grown on cobalt overlayers on scratched Si (100) surface and (c) diamond film grown on cobalt oxide overlayers on scratched Si (100) surface.

From the EDAX study of diamond film on scratched silicon, Co and CoO buffer layers in Fig. 2(a), (b) & (c), three major peaks Si,

O, and C are found. In case of Co buffer layer, a small peak of Co can be seen, which indicates that Co did not react completely with Si. It seems to be displaced while diamond growth occurs as reported by Donnet et al. [27]. Highly magnified images are required to study whether the Co has moved to the surface of the grown film. The cross sectional study of the film may highlight the location of Co. This needs further investigation.

In Fig. 3(a) & (b), an attempt is made to understand what happens to Co and CoO during the early nucleation of diamond by studying the samples with X-ray photoelectron spectroscopy. For this study, two types of samples are used: (a) Co deposited on Si and then exposed to diamond growth for 5, 10, 20, 30 and 120 minutes (b) CoO deposited on Si and then exposed to diamond growth for 5, 10, 20, 30 and 120 minutes. The corresponding wide scan spectra are shown in Fig. 3(a) & (b), respectively. In general, peaks related to Co 3p at 59.3 eV, Co 2p_{3/2} at 780.5 eV, Si 2s at 152.6 eV, Si 2p_{3/2} at 101.8 eV, C 1s at 284.6 eV and O 1s at 532.7 eV are observed with varying peak intensities depending on the diamond growth time. For both the samples (type (a) and (b), (Fig. 3(a) & (b)), an intense O 1s peak indicates that the substrate is partially oxidized due to ambient exposure after Co-deposition. With increasing diamond exposure time, the O 1s peak intensity decreased, while the C 1s peak intensity increased, indicating increase in growth of the diamond phase. When diamond was grown for 120 min, the Co and Si peaks disappeared, which clearly indicates that the substrate is fully coated with diamond. A systematic increase in C 1s peak and reduction in O 1s peak intensities clearly indicates increasing nucleation and growth of diamond with increasing exposure time.

In our work a difference in the diamond growth by Co and CoO buffer layers can be observed in the peak intensities of O 1s and C 1s peaks. A CoO buffer layer resulted in higher C 1s peak intensity than a Co buffer layer, indicating that the formation of an intermediate phase (CoSi₂), which can enhance the nucleation of diamond much easier using CoO, due to reduction of CoO in the presence of H₂ and CH₄ ambient.

In Fig. 4, the Raman Spectra, at different places on the diamond films were acquired using Nanofinder 30 (Tokyo Instruments, $\lambda =$

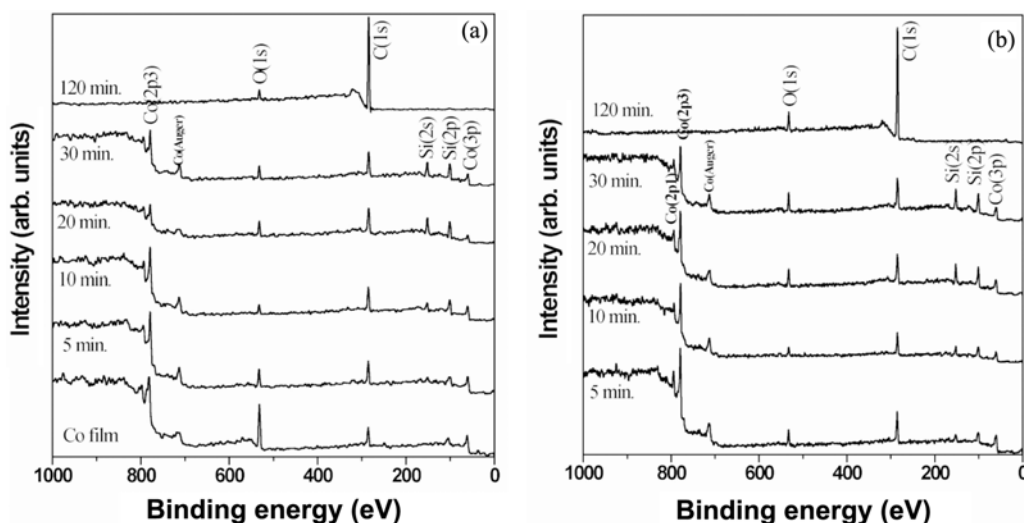


Fig. 3. Wide scan XPS spectra of (a) cobalt deposited on Si and then exposure to diamond growth for 5, 10, 20, 30 and 120 min, and (b) cobalt oxide deposited on Si and then exposure to diamond growth for 5, 10, 20, 30 and 120 min.

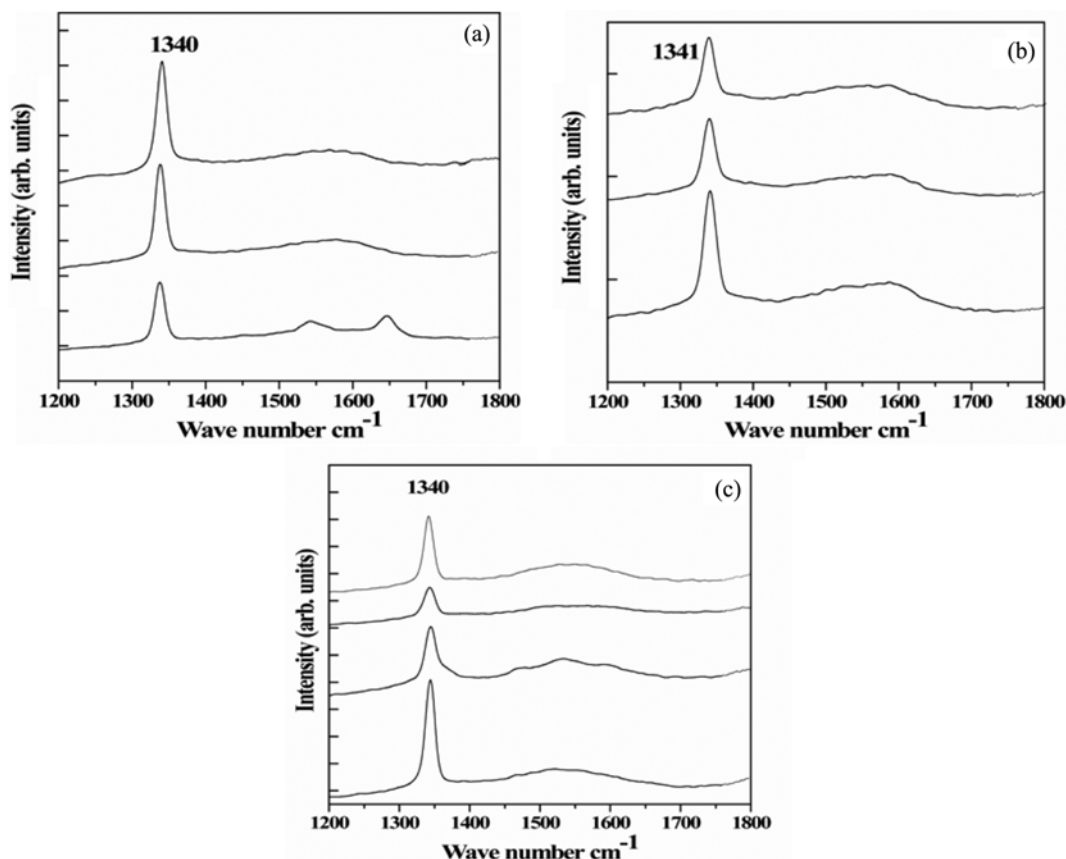


Fig. 4. Raman spectra of (a) diamond film grown on scratched Si (100) surface, (b) diamond film grown on cobalt overlayered scratched Si (100) surface and (c) diamond film grown on cobalt oxide overlayered scratched Si (100) surface.

448 nm, 5 second exposure time) and presented in Fig 2(a)-(c) for scratched Si, Co and CoO overlayers, respectively. Bands at $1,340\text{ cm}^{-1}$ and suppressed D and G bands were observed, which confirm the presence of diamond and non-diamond components in the grown films. The peak due to diamond is detected at $1,340\text{ cm}^{-1}$ for (a) and (c), while (b) shows at $1,341\text{ cm}^{-1}$ with suppressed D and G bands around $1,450\text{ cm}^{-1}$ to $1,600\text{ cm}^{-1}$ [29,30]. This indicates that the grown diamond films possess non diamond components with sp^2 and sp^3 bonding. The stress in the grown diamond films might be due to the displacement of the cobalt during growth. The volume of the dispersed cobalt might also be responsible for the voids in the film. In Fig. 4(b), appearance of the broad peak around $1,600\text{ cm}^{-1}$ shows that the quality of the film is not high. The FWHM of diamond peak for CoO buffer layer is less than the other two cases, indicating that the quality of the film can be better on a CoO buffer layer, as seen in the SEM images (Fig. 1(c)). The Raman spectroscopic results support the XPS observations (Fig. 3(b)). Hence, the quality of diamond film on CoO buffer layered surface is better than scratched Si (100) and Co buffer layered scratched Si (100) surfaces.

CONCLUSION

This study presents the effect of Co and CoO buffer layers deposited on non-carbon substrate (Si) on the nucleation and growth of diamond using HFCVD technique. SEM analysis depicted a change in the morphology of the diamond films overlayered with cobalt

oxide from rectangular plate to square shaped crystals with predominant (100) orientation and a further decrease in crystal size. Moreover, the crystallites appear densely packed with small voids. Raman spectroscopic results support the data obtained by XPS analysis, indicating that grown films are carbon. Furthermore, Raman spectroscopic study also suggested that the grown diamond films possess non diamond components with sp^2 and sp^3 bonding. In conclusion, our study reveals that the quality of diamond films grown on CoO buffer layered surface is better than scratched Si (100) and Co buffer layered scratched Si (100) surfaces. However, a detailed study is required to further understand the role of the CoO in the nucleation of diamond.

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