Electron microscopic characterization of diamond films grown on Si by bias-controlled chemical vapor deposition

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Diamond films grown by Bias-Controlled Hot Filament Chemical Vapor Deposition (BCCVD) on silicon (Si) substrates were characterized by Transmission Electron Microscopy (TEM). Both plan-view and cross-sectional TEM samples were made from diamond films grown under different biasing conditions. It was found that defect densities in the films were substantially reduced under zero and reverse bias (substrate negative relative to the filament) as compared to forward bias. Furthermore, the diamond/Si interface of the reverse and zero bias films consisted of a single thin interfacial layer whereas multiple interfacial layers existed at the diamond/Si interface of films grown under forward (positive) bias. Tungsten (W) contamination was also found in the interfacial layers of forward bias films. It is concluded that forward biasing in the present condition is not favorable for growing high quality, low defect density, diamond films. The possible mechanisms which induced the microstructural differences under different biasing conditions are discussed.

I. INTRODUCTION

Diamond film and particle synthesis from the vapor phase under low pressure has been demonstrated by at least 10 different methods since it was first achieved at reasonable growth rates in 1981.¹ Currently, intensive research activities around the world are aimed at developing a new era in diamond technology which will fully utilize the unique properties of diamond in applications ranging from coatings for wear resistance and cutting tools to optical windows for visible and infrared (IR) transmission, as well as thin films for high temperature, high power semiconductor devices. A decade of research has now led in the general direction of controlling nucleation, increasing the growth rate, reducing defects, and eliminating graphite codeposition. Uniform, large area deposition, and the ultimate goal of heteroepitaxial growth of single crystal films are also major concerns of the research community.² Unfortunately, little has been known about the mechanisms of diamond nucleation and growth which would be very helpful in achieving these goals.^{3,4} Therefore, any correlation of process parameters to film properties which aids in furthering the understanding of potential nucleation and growth mechanisms is very beneficial in providing efficient guidelines for advancing the diamond technology. The present research correlates biasing conditions in a hot filament chemical vapor deposition system with film quality and defect density. This, in turn, allows speculation of the role of charged species in the mechanism of diamond growth.

Hot filament chemical vapor deposition is one of the most common diamond growth techniques due to

its simplicity and low cost.⁵⁻⁸ A heated filament above the substrate surface is utilized to thermally crack the hydrogen gas into atomic hydrogen. It also activates and dissociates the methane molecules as well as enhances surface processes via thermal excitation and electron bombardment. It has been found that placing a bias between the filament and substrate to enhance electron bombardment of the substrate has increased the nucleation density and growth rates by several times.^{9,10} This clearly implies that charged species, especially electrons, may play a significant role during the diamond growth. However, in this previous work, although growth rates and nucleation density were improved, the quality of the films was not assessed. Therefore, in the present research, a modified hot filament (or filament assisted, thermal filament) chemical vapor deposition (CVD) system is utilized to study the effects of charged species in the growth of diamond. A controlled bias is applied to the substrate and the filament independently; thus, this growth technique has been termed bias controlled CVD (BCCVD).¹¹ Transmission Electron Microscopy (TEM) was then employed to correlate the defect microstructure and the interfacial characteristics with the processing conditions. The defect densities are also compared to the surface morphologies and Raman spectra from the films.

II. EXPERIMENTAL

Diamond films were grown on silicon (001) substrates in a bias controlled hot filament chemical vapor deposition (BCCVD) system. A schematic of the growth system and its current-voltage characteristics

are presented elsewhere.¹¹ A gas mixture of methane and hydrogen in the ratio of 3%, total flow at 100 sccm, and pressure at 3.3 kPa, is introduced above a tungsten filament heated to 1930 °C. The substrate is mounted on a molybdenum holder which is heated to 850 °C by a boron nitride encapsulated heater. With all other growth parameters fixed, the filament bias and substrate bias voltage were varied independently relative to the grounded chamber. However, it was found that the current depended only on the potential difference between the filament and substrate ($\Delta V = V_{\text{substrate}} - V_{\text{filament}}$) without any influence from their position relative to ground. Films were grown under various forward bias (positive ΔV , more positive substrate potential), zero bias ($\Delta V = 0$, no potential difference), and reverse bias (negative ΔV , more negative substrate potential) conditions. TEM studies were conducted on films grown under three representative conditions, namely forward bias of 150 V ($\Delta V = 150$ V), zero bias, and reverse bias of 150 V ($\Delta V = -150$ V).

Both plan-view and cross-sectional TEM specimens were prepared with a standard ion-thinning technique. The low ion thinning rate of diamond (~ 0.5 $\mu\text{m/h}$) and the substantial difference between the thinning rate of the diamond films and Si substrates did pose some difficulties in preparing cross-sectional TEM samples. Nevertheless, it was found that dimpling the specimens down to less than 5–10 μm of thickness (the Si appears reddish at this thickness), and then milling with Ar^+ at 6 kV, 10° incidence from both sides until perforation, then continued milling at 5 kV, 5° incidence for another hour gave very satisfactory results. The average ion milling time was approximately 6 h. The only disadvantage of this technique is that the Ar^+ tends to sputter the Mo specimen stage of the ion mill at low incident angles, and this sputtered Mo usually redeposited on the specimen surface, thereby contaminating the specimen and causing some confusion and uncertainty in the interpretation of x-ray microanalysis results. All the samples were examined either on a Hitachi H-800 scanning transmission electron microscope (STEM) operated at 200 kV, or on a Philips EM 430T transmission electron microscope (TEM) operated at 300 kV. High resolution transmission electron microscopy (HRTEM) was performed on a JEOL 200 CX TEM operated at 200 kV. Energy dispersive x-ray spectrometry (EDXS) was conducted on a Kevex ultrathin window x-ray spectrometer which is coupled with a Philips EM 430 TEM.

III. RESULTS

Plan-view TEM was used to investigate the defect type, density, and distribution. Figure 1 shows the plan-view TEM micrographs of diamond films grown under a forward bias of 150 V [Fig. 1(a)], zero bias [Fig. 1(b)], and reverse bias of 150 V [Fig. 1(c)] and the

corresponding surface morphology (scanning electron micrographs) and Raman spectra. For the TEM, all the individual diamond grains were tilted to the diamond $\langle 110 \rangle$ zone axis because defect density comparisons are meaningful only when compared under identical diffraction conditions. It is immediately apparent that a higher defect density is associated with the films grown under forward bias [Fig. 1(a)]. Moreover, this correlates with a degraded Raman spectrum and a poorer surface morphology (i.e., a less faceted surface). The Raman spectra can be seen to degrade in two different ways: an increase in Full Width Half Maximum (FWHM) and an increase in the intensity of the sp^2 bonded carbon peak at ~ 1500 cm^{-1} relative to the sp^3 diamond component at 1332 cm^{-1} . It is plausible that both of these changes are caused by the increased defect density (as opposed to, for example, a grain boundary phase); however, continued research is necessary to confirm such a speculation. The FWHM have been measured at 14.0 cm^{-1} , 5.7 cm^{-1} , and 5.0 cm^{-1} for forward, zero, and reverse bias diamond films, respectively, which is additional evidence of the improved quality of films grown under reverse bias. It has been shown that the FWHM is directly related to the domain size which is required for quantitative analysis of Raman spectra.¹² It was also observed that the domain sizes obtained in this method were smaller than the diamond crystal sizes observed under SEM.¹² Thus, it was speculated that the phonon scattering was confined in the local regions of the diamond crystal by defects. In the present case, using the same method as LeGrice and Nemanich,^{12,13} the domain sizes were calculated to be ~ 51 Å, ~ 114 Å, and ~ 151 Å for forward, zero, and reverse bias films, respectively. Linear analysis was also performed on plan-view TEM micrographs to determine the defect spacing. Fifteen lines were randomly drawn across the micrographs, the number of defects (twins) were counted, and the defect spacing was obtained by dividing the total length of the lines by the total number of defects. The population of defects in forward bias films was so high that defect spacing could not accurately be obtained but appears to be less than 50 Å. The defect spacings in zero bias and reverse bias films were found to be ~ 710 Å and ~ 750 Å, respectively. These values are higher than the domain sizes obtained from the FWHM. However, as shown in Figs. 1(b) and 1(c), the defects are not distributed evenly in the films; thus, the FWHM could be affected by local high defect density regions (such as near the grain boundaries), yielding a smaller domain size. Qualitatively, the defect spacing seems to correspond to the domain size. However, an exact relationship between domain size and defect spacing could not be drawn here, since a larger data base is needed to make this correlation statistically meaningful. Regardless, both parameters indicate the

poor quality of the forward bias films and imply that the reverse bias films may be of slightly higher quality than those grown at zero bias.

It is also observed that the numerous defects emerge from the center of an individual diamond grain grown under forward bias, as shown in Fig. 1(a). Closer

examination shows that those defects are twins and microtwins. Twinning in $\{111\}$ has been known to be the predominant defect in CVD diamond.^{14,15} The grain in Fig. 1(a) is also "multiply twinned" with five-fold symmetry apparent at the center of the grain. Such fivefold multiply twinned particles (MTP) are com-

(a)

FIG. 1. Plan-view TEM micrographs of a single diamond grain grown under (a) forward bias of 150 V, (b) zero bias, (c) reverse bias of 150 V, and corresponding scanning electron micrographs and Raman spectra of diamond films.

(b)

FIG. 1. (continued)

monly seen in plasma enhanced CVD diamond and have been studied thoroughly.^{16,17} No other type of defect was apparent; however, due to the indistinguishable nature of simple stacking faults versus microtwins whose thicknesses are a few tens of Å,¹⁸ some stacking faults may also exist. In the zero and reverse bias films [Figs. 1(b) and 1(c)], the density of defects (i.e., the

number of twin plates) is seen to be reduced significantly. Selected area diffraction (SAD) indicated again that the twinning occurred along {111}. There was no major difference between the defect density of the zero and reverse bias films, although, as stated earlier, spacings were somewhat larger in the reverse bias films. The defects emerge from the center of the diamond

(c)

FIG. 1. (continued)

grain to the grain boundary, but are not distributed evenly.

Cross-sectional TEM (XTEM) micrographs of diamond films grown under a forward bias of 150 V, zero bias, and reverse bias of 150 V are shown in Figs. 2(a), 2(b), and 2(c), respectively. It is noted that in all the

micrographs the defects (dark lines and zones) emerge from the center of the base of each crystal. This is similar to previous observations in diamond films grown by plasma assisted CVD methods.^{19–21} Since the defects are generated because of the growth species sitting in the improper lattice sites during the deposition process,

the defect lines actually reflect the trace of crystal growth.¹⁹ Thus, this implies that each diamond grain is nucleated from the single site from where the defects nucleated and undergoes a three-dimensional growth. The similar growth morphologies in films grown by different techniques suggest that, in some respects, similar growth mechanisms exist regardless of the diamond growth techniques used.

The forward bias films consist of several fan-shaped sectors which are full of defects (dark lines), as shown in Fig. 2(a). The SAD pattern over the entire grain shows a single crystal $\langle 110 \rangle$ spot pattern with intensive twin spots [Fig. 2(a) inset]. This pattern suggests that those fan-shaped sectors (subgrains) are

actually twin-related and the "grains" are due to multiple twinning. This observation correlates very well with SEM observations. In the zero bias films, as shown in Fig. 2(b), only a few dark lines emerging from the center of the grain are present, indicating the defect density has been substantially reduced. Well-defined grain outlines show the (111) plane at the surface which correspond to the highly faceted morphology observed in the SEM. The variation in contrast inside the diamond grain and the SAD pattern confirmed the grain is also multiply twinned but with fewer twin sectors (subgrains). XTEM of the reverse bias diamond films [Fig. 2(c)] also showed a well-faceted crystal surface and a low defect similar to the zero bias films.

FIG. 2. Cross-sectional TEM micrographs showing the growth morphology of diamond crystals grown under (a) forward bias of 150 V, (b) zero bias, and (c) reverse bias of 150 V.

XTEM was also used to reveal differences in the characteristics of the diamond/Si interface under different biasing conditions. All the specimens were tilted to the Si [110] pole for edge-on viewing. Figures 3(a)–3(c) reveal the diamond/Si interfacial area and the corresponding electron diffraction patterns under different biasing conditions. It is obvious that in the forward bias condition, the interface consists of multiple structures over rather extended regions (~ 200 Å), as shown in Fig. 3(a). It appears that a region of foreign particles is deposited first, followed by a thin layer of film, and finally another region of apparent particulates before the growth of the diamond. In contrast, XTEM micrographs in Figs. 3(b) and 3(c) showed that only a single thin interfacial layer is present in films grown under zero bias and a reverse bias of 150 V. Its thickness varies between 20 Å and 40 Å, depending on surface roughness. The diffraction patterns also confirm that multiple phases exist in the forward bias film, while only Si and diamond (pointed by arrows) spots are observed in the zero and reverse bias films. These interfacial structures have been investigated further by

HRTEM. Figure 4 shows an HRTEM micrograph of a reverse bias film; the atomic fringes of Si and lattice fringes of diamond are clearly seen. No attempts were made to determine the exact atomic positions at the interface as this involves detailed defocusing experiments and extensive image simulations which are beyond the scope of the present manuscript. However, the lattice spacing of the interfacial layer is very close to Si and it is closely aligned with the Si substrate. In addition, no diffraction spots appear in the SAD pattern other than spots from Si and diamond (Fig. 4). It can be speculated that this interfacial layer might be Si damaged during substrate pretreatment (scratching), and then recrystallized in the initial stages of diamond growth when the substrate temperature is raised. However, more detailed HRTEM is needed to confirm this theory.

Energy dispersive x-ray spectrometry (EDXS) was used to characterize the chemistry of the interfacial layers of all the films studied in the TEM. An electron probe with a diameter of ~ 100 Å is focused onto the diamond/Si interface and x-ray spectra were collected

FIG. 3. Cross-sectional TEM micrographs and corresponding SAD patterns showing diamond/Si interfacial structure of diamond films grown under (a) forward bias of 150 V, (b) zero bias, and (c) reverse bias of 150 V. (d) Indexing of SAD pattern of forward bias film [shown in (a)] reveals multiple phases in the interfacial region.

(c)

FIG. 3. (continued)

(d)

for 300 s. These spectra indicated the presence of Si, molybdenum (Mo), and tungsten (W) in forward bias interfacial layers, as shown in Fig. 5, while only Si and Mo show up in the spectra collected from interfacial layers formed under reverse bias and zero bias. It is believed that the Si is from the substrate and that the Mo

is a contaminant from sample preparation (ion milling). Mo is found in all TEM samples prepared with the technique described in the experimental section, but is not observed in samples prior to ion milling. Hole count spectra (i.e., spectra taken while the electron beam was focused through the hole in the TEM sample) were also

FIG. 4. High resolution TEM micrograph showing the detailed diamond interfacial structure of reverse bias films.

taken and showed only traces of Si. This verifies that the data collected were not an artifact of extraneous signals from beyond the sample. Spectra were also collected inside the Si and diamond near the interface area; no W was found in either of those spectra within the detectability limit of this technique (~ 0.1 wt. %). Therefore, the possibilities of this W contamination from the microscope or sample preparation were care-

FIG. 5. Energy dispersive x-ray spectrum taken from interfacial area of 150 V forward biased films showing the presence of tungsten (W, $L_{\alpha 1} = 8.396$ KeV, $L_{\beta 1} = 9.67$ KeV).

fully eliminated. Consequently, the source of this W contaminant is believed to be the tungsten filament used inside the growth chamber, probably caused by the dc plasma created via forward biasing. This biasing attracts positive species to the filament, which sputter W into the gas which then redeposits on the substrate. Additionally, from electron microdiffraction results, it appears that no tungsten carbide phases exist at these tungsten contaminated interfacial layers within the detectability of the microscope. However, diffraction spots with their lattice spacing very close to elemental tungsten and tungsten silicide (W_5Si_3) were observed [Fig. 3(d), SAD pattern indexing].

IV. DISCUSSION

From the present results, it has been shown that biasing affects film microstructures. Thus, charged species (ions and electrons) under different biasing conditions have strong influences on the diamond growth mechanism(s). To elucidate the roles of charged species in affecting diamond growth, the possible sources of such species have to be discussed. Generally, in the current system, there are three possible sources for charged species: (1) thermionic emission of electrons from the filament, (2) surface ionization of the gas atoms or molecules when they impinge onto the heated filament and substrate holder surfaces, and (3) impact ionization when particles (electron, ion, or neutral atoms) collide with each other and kinetic energy is exchanged. From a comparison of the experimental I-V characteristics with theoretical calculations of current expected from these mechanisms, it can be concluded that the possible dominant conduction mechanisms (charged species generated current conduction) are impact ionization for the reverse bias condition, while thermionic emission and impact ionization are the dominant mechanisms under forward bias conditions.²² The major charged species on the growth surface under forward bias are believed to be electrons, while under reverse bias the major charged species on the growth surface are positive ions. However, since not any single mechanism can explain the current phenomena clearly by itself, it is very possible that two or even three of the mechanisms occur at the same time. The quantitative participation of each mechanism in the growth is not known and would be very difficult to verify experimentally. Please refer to Ref. 22 for more detailed discussions of these mechanisms.

Since no gas phase analysis was performed in the present system, it would be premature to speculate as to what type of ions is actually present. However, Celii *et al.*²³ and Harris and Weiner²⁴ have measured the stable gas phase species present in the hot filament assisted CVD system with similar gas inputs (hydrogen and methane). Celii *et al.*²³ concluded that methyl

(CH₃), acetylene (C₂H₂), and ethylene (C₂H₄) were detected above the growing surface, while Harris and Weiner²⁴ concluded that diamond growth occurs mainly from reactions involving acetylene, ethylene, methane, and/or methyl radicals. It could be envisioned that similar species exist in the present system, and the possible ionization processes of these species are likely to be important. However, continued research is necessary for a thorough understanding of this speculation and is beyond the scope of the current research.

Under forward bias conditions, the substrate is positive relative to the filament, and the electrons are the dominant charged species near the growth surface. It was observed that higher currents were generated under forward bias than in reverse bias with the same voltage.²² This implies that a higher flux of charged species (electrons) impinges onto the substrate surface under forward bias conditions. Since the electrons strike the surface with a finite energy caused by the potential difference between the filament and substrate, they could very possibly damage the growth surface and alter the surface energy. In this regard, it is worthwhile to point out that hydrogen desorbs from the diamond surface at approximately 900 °C, causing surface reconstruction.^{25,26} This reconstruction creates π , double bonded surface states which are not conducive to the growth of high quality diamond. The current growth temperature (850 °C) is very close to this transformation temperature, presumably to allow activation of the surface hydrogen for enhanced exchange with the incoming carbon while at the same time avoiding reconstruction. Thus, the additional energy supplied by the incident electrons attracted to the surface by the forward biasing may be sufficient to desorb the hydrogen, causing local regions of surface reconstruction or 'defective bonding', leading to line and planar defects. This is even more plausible when one considers that a twin boundary requires only a 60° rotation of the surface bonding [assuming growth takes place on the diamond (111) plane]. It is a relatively low energy modification of the original surface and thus could be considered to be caused easily by an incident flux of electrons. This is supported by the prevalence of twins in these films. On the other hand, the lower flux of charged ions under reverse bias (as observed by the much lower currents) will not cause as much surface modification and thus results in fewer twins.

V. CONCLUSIONS

In summary, the defect density of diamond films grown under forward bias conditions was much higher than those of zero bias and reverse bias. This increased defect density correlated with an increase in the FWHM of the Raman diamond line as well as an increase in the sp^2/sp^3 peak intensity ratio. Furthermore,

the interfacial area of the forward bias films was found to be contaminated with tungsten. It was also found that the microstructures of the films grown under zero and reverse bias are very similar, although the defect density and Raman FWHM imply that the reverse bias films may be somewhat better quality. It should be noted that recent results currently in preparation for publication also indicate reduced contamination in the reverse bias films, not observable in TEM. From these results, it is clear that the biasing condition, which influences the role of charged species in the growth of diamond, affects the defect density and the nature of the diamond/substrate interface. Under forward bias which creates a dc plasma, more electrons and other negatively charged radicals are attracted by the more positive substrate. Those negative species might either bombard the substrate surface, creating surface damage and/or changing the nature of the hydrogen desorption reaction which occurs during diamond growth, or they may interact with hydrogen and methane in the gas phase. Moreover, the tungsten filament used in the growth chamber is eroded by the dc plasma and creates a large population of W in the gas phase which later redeposits on the surface of the substrate. In all these cases, the surface energy and/or chemistry (surface or gas phase) were altered, creating conditions which are not favorable for high quality, low defect density diamond growth on Si.

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