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Citation: AIP Advances 1, 042117 (2011); doi: 10.1063/1.3656241
View online: http://dx.doi.org/10.1063/1.3656241
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Mechanisms of suppressing secondary nucleation for low-power and low-temperature microwave plasma self-bias-enhanced growth of diamond films in argon diluted methane

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(Received 5 July 2011; accepted 15 September 2011; published online 17 October 2011)

We report on mechanisms for suppressing diamond secondary nucleation in microwave plasma self-bias-enhanced growth (SBEG) of diamond films in methane diluted by argon. High-density plasma at a small distance from the substrate induces a floating potential which promotes high-flux, low-energy ion bombardment on diamond growing surfaces along with an equal flux of electrons. Increased atomic hydrogen generated by electron impact dissociation of methane and low-energy ion bombardment help remove hydrocarbon coatings on diamond grains in favor of continuous grain growth and, therefore, the suppression of secondary diamond nucleation. Energetic meta-stable excited argon, abundant C2 dimers, and enhanced effective surface temperature due to low-energy ion bombardment further promote the diamond grain growth resulting in the deposition of a diamond film with columnar diamond grains of much larger grain sizes and a much lower density of grain boundaries than ultrananocrystalline diamond (UNCD) films grown under similar conditions without optimized plasma-substrate interactions. SEM, XRD, PL, and Raman scattering help confirm the deposition of diamond films with columnar grains.

I. INTRODUCTION

Chemically vapor deposited (CVD) diamond possesses many excellent properties for practical applications. Among diamond CVD processes, microwave plasma enhanced chemical vapor deposition (MPECVD) in methane diluted by argon with neither hydrogen nor oxygen additives has attracted a lot of attention due to its capability of low-power and low-temperature deposition of ultra smooth, ultra-nano-crystalline diamond (UNCD) films with diamond grains of 3-5nm, in comparison with microcrystalline diamond films deposited by hydrogen-rich plasma. High concentration of C2 dimers is generated when the gas pressure increases to 100 Torr and above. The high C2 concentration and low atomic hydrogen concentration lead to the coating on diamond growing surfaces with non-diamond carbons and hydrocarbons which block the further growth of crystalline diamond grains and provide favorable conditions for secondary nucleation of diamond.

The lower ionization potential for argon than hydrogen and the additional dissociation energy for molecular hydrogen require lower microwave power for generation and sustaining argon-rich plasma than hydrogen-rich plasma. Besides, heat released due to abstraction of atomic hydrogen on diamond surface by atomic hydrogen further adds to the thermal loading of the substrate. As a result, it is favorable for low-power and low-temperature MPECVD of diamond films.
However, secondary nucleation results in grain boundaries with undesirable non-diamond carbons and hydrocarbons, which hinder the high thermal conductivity of high-quality diamond films. UNCD deposited by microwave plasma in methane diluted by argon has been reported to exhibit two orders of magnitude lower thermal conductivity than that of high-quality natural diamond due to mainly high-density grain boundaries. Therefore, for applications demanding high thermal conductivity and low-temperature deposition, novel mechanisms for microwave plasma CVD in methane diluted by argon for reducing the density of grain boundaries and increasing the quality of diamond grains are desired.

Bombardment of substrates by energetic ions induced by externally applied bias voltage of the diamond growing surfaces has been reported to result in enhanced secondary nucleation of diamond nuclei in favor of the deposition of UNCD films. Deposition of diamond films by hydrogen containing argon-rich methane plasma with mixed microcrystalline and nanocrystalline domains has also previously been reported. In our prior work, 5% hydrogen was added to the gas mixture of 1% methane and 94% argon in order to increase the supply of atomic hydrogen for the suppression of secondary nucleation of diamond. Simultaneous deposition of both large-grain microcrystalline and small-grain nanocrystalline diamond on different parts of a silicon substrate has been demonstrated by plasma generated by 1kW, 2.45GHz microwave power at 170 Torr gas pressure and at the 800-900°C substrate temperature. In that case, only the central part of the substrate is in direct contact with the CVD processing plasma. This area is, therefore, subjected to physical and chemical interactions with the diamond CVD plasma differently from the remaining substrate, which is at a varied distance from the plasma. Although the macroscopic diamond CVD conditions, such as gas pressure, composition, flow rates, average substrate temperature, applied microwave power, etc. are the same, a diamond film containing different sized diamond grains ranging from UNCD to microcrystalline diamond is deposited. The result demonstrated that physical and chemical interactions between the substrate and the plasma are as important as the macroscopic CVD processing parameters. Due to the non-uniform nature of the small plasma ball generated in hydrogen-containing plasma at a high gas pressure of 170 Torr, it was not clear which physical and/or chemical interactions are the most important for determining the rate of secondary nucleation and the growth of large diamond grains.

Besides, effects of low self-bias voltage generated by microwave plasma floating potential on diamond MPECVD in argon diluted methane without hydrogen additives at high gas pressures have not been reported. In this work, investigation is focused on optimizing the distance between the substrate and a high-density microwave plasma disk generated in mixtures of methane and argon. Instead of the commonly expected enhancement in secondary nucleation of diamond, suppressing of secondary diamond nucleation is pursued while retaining the advantages of low-power and low-temperature MPECVD in argon diluted methane without hydrogen or oxygen additives.

II. EXPERIMENTAL

MPECVD of diamond is carried out in a 1.5kW 2.45GHz SEKI reactor with a quartz bell jar. Clean silicon substrates are pre-seeded with detonation diamond nanoparticles by immersion under ultrasonic agitation in a DMSO solution with 5-10 nm nanodiamond suspension diluted by ethanol at varied ratios. Plasma disk with strong green color emission of about 3cm thick and 7cm in diameter is generated by 400 W microwave power in a gas mixture of 1.6% methane and 98.4% argon with a total gas flow rate of 25 sccm at 110 Torr gas pressure. This applied microwave power (400W) for argon diluted methane plasma without hydrogen additives is much lower than what was applied (1kW) in the prior work for argon-rich plasma with 5% hydrogen additive for depositing diamond films with mixed phases of nanocrystalline and microcrystalline diamonds. A schematic diagram in Fig. 1 depicts the relative positions of the substrate with respect to plasma as well as the impingement by positively charged ions, negatively charged electrons, and neutral particles including reactive radicals and energetic and excited atoms and molecules. Fig. 1(b) depicts the experimental setup when the substrate is immersed in plasma. In Fig. 1(c), plasma is floating at a distance from the substrate.

To optimize the distance of plasma from the substrate, plasma is first generated at a low gas pressure around 1 Torr and by low-power microwave around 200 W to ensure that the generated
FIG. 1. Schematic diagrams representing microwave plasma enhanced CVD of diamond: (a) impingement of positive ions, electrons, and neutral particles from plasma on the diamond growing surfaces; (b) a substrate surrounded and covered by the plasma; (c) a CVD plasma floating at a distance from the substrate.
plasma is neither touching the substrate nor stuck to the top interior surface of the quartz bell jar. The low-power and low-pressure plasma floats above the substrate and produces a floating potential between the plasma and the substrate. The gas pressure and microwave power are then increased gradually to reach the pre-set steady-state diamond CVD conditions. The distance between the plasma and the substrate decreases with increasing gas pressure and microwave power while keeping a constant flow rate ratio of methane to argon. The distance between the plasma and the substrate can be further varied by adjusting the height of the substrate holder inside the microwave cavity.

The distance between the bright plasma and the substrate is estimated to be about 5 mm by visual observation. Due to the higher mobility of electrons than positive ions, more electrons are lost from the plasma than ions and, therefore, the plasma is slightly positively charged with respect to the surrounding surfaces. Between the bright plasma and the substrate, there exists a boundary layer, across which a floating potential is established between the plasma and the substrate in such a way that there is no net charge flow, i.e. a balance between the flux of positively charged ions and the flux of negatively charged plasma species, mainly electrons. This floating potential accelerates positive ions while decelerates electrons from the plasma towards the substrate.

Besides heating by the plasma, no other heating sources are applied to the substrate. The temperature of the substrate holder is monitored continuously by a thermocouple sensor inserted into a hole drilled into the back side of the substrate holder. A dual-color optical pyrometer (Williamson, Inc. USA) with minimum interference from the process plasma is used to look through the quartz bell jar at the front surface of the substrate. The temperature measured by the thermocouple is 50-80°C lower than what is measured by the pyrometer. The substrate temperature measured by the pyrometer for the substrate under 400W microwave plasma is 480-530°C. With a high flux of low-energy ions bombarding the diamond growing surfaces, the effective surface temperature is expected to be higher than the average temperature measured by the pyrometer. The bulk temperature of the substrate is expected to be slightly lower than the measured temperature by the pyrometer because the only source of heating for the substrate is from the plasma above the surface of the substrate.

III. RESULTS AND DISCUSSION

Optical emission spectra (OES) measured from the CVD plasma display strong emission signals from $C_2$ along with very weak signals from atomic hydrogen and hydrocarbons. As shown in Fig. 2(a), very small amounts of atomic hydrogen and CH$_x$ radicals originating from the dissociation of methane are detected by OES. The relative emission intensities from $C_2$, atomic hydrogen and CH radicals do not necessarily represent the actual concentrations of these species near the diamond growing surfaces because of the integration of emission from the plasma depending on the position, direction, and solid angle of light collection. Nevertheless, OES for the plasma is similar to that for the microwave plasma for UNCD. The macroscopic experimental parameters for this work are practically the same as what are being used for depositing UNCD. It is worth mentioning that high intensity $C_2$ emission is not unique for UNCD deposition in argon diluted methane. It has also been observed in high-power-density hydrogen-rich MPECVD methane plasma for high-rate growth of diamond.17

A light collecting optical fiber is inserted inside a small tube of about 2-3 mm in diameter and 50 mm in length to guide the solid angle of light collection. By moving the light collecting tube and optical fiber downwards close to the plasma-substrate boundary where a dimmer plasma sheath can be seen visually, the intensity of the optical emission peak from atomic hydrogen increases as shown in Fig. 2(b). This indicates that a higher concentration of atomic hydrogen is generated near the substrate surface. Because of the small distance of about 5mm between the plasma and the substrate and the limited spatial resolution of the light collecting optics, the increased optical emission (Hα) is a collective signal from the lower boundary of the bright plasma, the plasma sheath, and near the diamond growing surfaces. The increase in measured emission intensity does indicate the increase in atomic hydrogen concentration near the diamond growing surface from regions farther from the substrate.
FIG. 2. (a) Optical emission spectrum of diamond CVD plasma which is excited by 400W microwave at 2.45 GHz in 1.6% methane gas diluted by argon gas with a total flow rate of 25 sccm at 110 Torr gas pressure. (b) Comparison of H$\alpha$ optical emission peaks measured from the center part of the plasma (lower intensity) with that from the region between the plasma and the substrate (higher intensity).

Shown by the SEM micrograph in Fig. 3(a) is a diamond film grown by MPECVD under the above mentioned experimental conditions without hydrogen additives. Instead of growing UNCD, a well faceted microcrystalline diamond film with columnar-shape diamond grains has been deposited by microwave plasma in methane diluted by argon. A cross-sectional view of the diamond film is shown by the SEM micrograph in Fig. 3(b). It clearly shows that secondary nucleation of diamond has been suppressed and continuously columnar growth of diamond grains forms large diamond...
FIG. 3. SEM photographs of a microwave plasma CVD microcrystalline diamond film: (a) top view and (b) cross-sectional view. Scale bars are 100 nm.

Grains. These diamond grains are predominantly (111) oriented diamond crystals as shown by the XRD spectrum in Fig. 4.

The diamond film grown for 4 hours is mirror-like visually with an average growth rate of 120-150 nm/h. Raman scattering excited by 532-nm light (Fig. 5(a)) exhibits a clear and sharp peak at 1333 cm\(^{-1}\) which is characteristic of crystalline diamond. The Raman band around 1140 cm\(^{-1}\) is due to the bonding of atomic hydrogen in grain boundaries known as trans-poly-acetylene (TPA). The weak Raman signal indicates reduced grain boundaries and fewer hydrocarbons in the grain boundaries.

The UV Raman spectrum excited by 325-nm light (Fig. 5(b)) reveals a strong diamond peak at 1337 cm\(^{-1}\) and a small G-band around 1590 cm\(^{-1}\) indicating that the deposited diamond film contains
a high fraction of diamond crystals with sp3 bonding with a small fraction of graphitic carbons with
sp2 bonding.18, 19 The shift of the diamond peak from 1332 cm⁻¹ to 1337 cm⁻¹ indicates that residual
compressive stress exists in the deposited diamond film presumably due to the nature of competitive
columnar growth of diamond grains and possibly the high-flux and low-energy ion bombardment
during diamond growth.

Raman scattering excited by 633-nm light shows a strong Raman peak at 2250 cm⁻¹ with
FWHM of 134 cm⁻¹ corresponding to the 1.68 eV photoluminescence from silicon-vacancy and/or
the GR1 color center.20–22 Silicon may come from ion bombardment and plasma etching of the
silicon substrate and the quartz bell jar. Ion bombardment on the diamond growing surface and
the crystal growth of diamond grains at a relatively low temperature than the typical substrate
temperature of 800- 900°C for diamond CVD by hydrogen-rich plasma might have contributed to
the high concentration of vacancies in the diamond grains of the deposited diamond film.

As a comparison, an UNCD film is shown in Fig. 6(a). It is deposited under the same macroscopic
experimental conditions as those for the microcrystalline diamond film shown in Fig. 3. In this case,
the diamond seeded substrate is raised higher to be covered by plasma. The inset in Fig. 6(a)
shows an enlarged micrograph of the diamond films with ridge shaped diamond clusters which are
characteristic of UNCD. The UV Raman spectrum for the UNCD shown in Fig. 6(b) exhibits strong
Raman signals corresponding to the diamond peak at 1335 cm⁻¹, the G-band for graphitic carbons at
1575 cm⁻¹, and a peak at 1165 cm⁻¹ due to hydrogen in the grain boundaries also known as trans-poly-
acetylene (TPA). The much stronger signals for the G-band and the TPA peak for the UNCD shown in
Fig. 6(b) than the corresponding UV Raman signals for microcrystalline diamond shown in Fig. 5(b)
clearly demonstrate that SBEG has a significant effect on the reduction of graphitic carbons and
hydrocarbon species in the deposited diamond films. Without bombardment by a high-flux, low-
energy ions, hydrocarbon radicals might stick to the diamond growing surfaces easily at low substrate
temperatures with very low concentration of atomic hydrogen. The hydrocarbon retards the growth
of diamond grains and promotes secondary nucleation of diamond.

FIG. 4. XRD pattern of the microcrystalline diamond film shown in Fig. 3 which is grown by microwave plasma in methane
diluted by argon without hydrogen additives.
Based on experimental data, floating plasma at a distance of about 5mm above a substrate plays a major role in the suppression of secondary nucleation of diamond and the subsequent growth of microcrystalline diamond films. The plasma without hydrogen additive is fine tuned to become disk shaped and floats at a small distance from the substrate. Therefore, unlike the prior work, where diamond films with grains ranging from nanodiamond to microcrystalline diamonds are deposited in different parts of the same substrate, a uniform microcrystalline diamond film has been deposited on the substrate in this work. Keeping a small distance between the bright high-pressure (about 100 Torr) plasma and the substrate is, therefore, beneficial for the plasma floating potential to play an essential role in manipulating the physical and chemical interactions between the plasma and the diamond growing surfaces.

FIG. 5. Raman spectra excited by (a) 532 nm, (b) 325 nm and (c) 633 nm light for the microcrystalline diamond film shown in Fig. 3.
FIG. 6. (a) SEM micrographs of an ultra-nano-crystalline diamond film deposited under similar experimental parameters as that for the microcrystalline diamond film shown in Fig. 3 without optimized plasma-substrate interactions. The scale bars are 1 μm and 100 nm for the main micrograph and the inset, respectively. (b) UV Raman spectrum excited by 325-nm light for the UNCD shown in (a).

The plasma density near the diamond growing surfaces also plays an important role. Because of the electromagnetic screening effect due to plasma oscillation, 2.45 GHz microwave is absorbed only by the outer-shell of the plasma. High-density plasma is generated in the outer-shell and diffuses into the inner core of the plasma. Therefore, for a plasma at 100 Torr or higher, the outer shell of the diamond CVD plasma is of a higher plasma density than the inner core of the plasma. When plasma is in direct contact with a substrate which is placed on a metallic substrate holder, microwave power is screened by the plasma and can not reach in full power the plasma covered central substrate area.

The substrate in direct contact with the plasma is, therefore, subjected to plasma of a lower density.
than that of the outer-shell plasma. It is desirable for the diamond growing surface to be near the high-density outer-shell plasma. This can be achieved by placing the substrate facing a high-density outer-shell of plasma instead of immersing the substrate inside the plasma. Keeping the plasma at a small distance from the substrate to allow the high-density plasma to be near the substrate and the desirable physical and chemical interactions between the high-density plasma and the substrate is therefore an essential requirement for the effective suppression of secondary diamond nucleation and the promotion of crystalline growth of diamond grains.

Considering the high gas pressure of 110 Torr, and the low applied microwave power of 400W, the floating potential of the microwave plasma is expected to be lower than 20-30 V. Bombardment of the diamond growing surface with low energy ions does not cause carbon-carbon bond breaking but instead raises the effective surface temperature on the diamond growing surfaces and promotes the crystal growth of diamond grains. The low-energy and high-flux ion bombardment might also have resulted in the formation of vacancies in diamond grains as indicated by the strong 1.68eV photoluminescence peak due to silicon-vacancy color center in Fig. 5(c). These low-energy ions can not cause bias enhanced secondary nucleation because they are not energetic enough to break diamond bonds in growing diamond surfaces. The extensive ion bombardment might also contribute to the observed residual compressive stress in the diamond film as indicated by the shift of diamond Raman peak to a higher wavenumber.

The energy of electrons impinging on the substrate depends on the actual high energy tail of the electron energy distribution in the high-density outer-shell of the diamond CVD plasma facing the substrate. Some energetic electrons can overcome the floating potential and reach the substrate. Energetic excited argon atoms and energetic electrons might contribute to the dissociation of methane to produce atomic hydrogen and CHx radicals near the diamond growing surfaces. Increased concentration of atomic hydrogen supplied from the near-by high-density plasma and those generated locally near the substrate surface is detected by optical emission spectra when the light collecting optical fiber is aimed at the plasma-substrate boundary. The higher atomic hydrogen concentration is believed to have contributed to the suppression of secondary diamond nucleation and the promotion of the growth of diamond grains.

IV. CONCLUSIONS

Suppression of secondary diamond nucleation in low-power (400W) and low-substrate temperature (480-530°C) microwave plasma (2.45GHz) enhanced deposition of diamond films in 1.6% methane and 98.4% argon at 110 Torr gas pressure with neither hydrogen nor oxygen additives has been demonstrated. Optimized physical and chemical interactions between the plasma and the substrate are necessary for the suppression of secondary nucleation and the promotion of the growth of diamond grains. By optimizing the relative positions of the plasma and the substrate, continuous columnar growth of diamond grains instead of UNCD is achieved. The novel mechanisms of suppressing secondary nucleation by microwave plasma self-bias-enhanced growth (SBEG) of diamond films in argon diluted methane is expected to find a broad range of practical applications which require low-power, low-temperature microwave plasma deposition of diamond films with outstanding properties of diamond including excellent thermal conductivity and chemical inertness.

ACKNOWLEDGMENT

This work is partially supported by NSC in Taiwan under the following grant number 99-2120-M-006-004, 99-2911-I-006-504, 100-2221-E-006-169-MY3, and 100-2120-M-006-001.