Nanocrystalline diamond thin films deposited by 35 kHz Ar-rich plasmas

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Abstract

We give evidence of nanometric size (5–15 nm) crystalline diamonds in carbon thin films obtained at low substrate temperature (15 °C) under the action of low pressure (0.1–0.3 Torr) 35 kHz excited CH4/Ar (80–95%) plasmas. The decrease in Ar concentration was found to lead to higher film hardness while crystalline nanodiamonds are observed in a wide interval (1–3.5 h) of deposition times but only for very high Ar concentration (95%). The polycrystalline nanodiamond grains are found over 10–20% within an amorphous carbon matrix. It is suggested that the distribution of nanodiamond grains might be connected to the nonuniform ion energy distribution in the Ar-rich plasma generated at 35 kHz. Morphological and structural features of the deposited films were also investigated.

Keywords: CVD; Plasma; Diamond films

1. Introduction

Recent results by Gruen and coworkers [1–7] have shown the feasibility of depositing nanocrystalline diamond thin films from microwave (2.45 GHz) C60/H2/Ar [1,2,5] and CH4/H2/Ar [3,4,6,7] plasmas with Ar concentrations up to 97% or even without the addition of molecular hydrogen [1,4,7]. They were also able to establish concrete MW discharge conditions under which structural film changes were observed to lead from microcrystalline to nanocrystalline diamond films [6]. The latter structural changes have been related to a change in the film growth mechanisms and growing precursors, that is, from CH3 in hydrogen-rich growing environments to the dimer C2 as the most probable growth species in low (or null) hydrogen content plasma systems. Further systematic analysis of their films enabled them to conclude that nanocrystalline diamond growth processes [1,2,8] differ from “conventional” hydrogen-based growth mechanisms typically found in diamond thin films obtained from MW-produced CH4/H2 plasmas. All these results, including previous studies reported by Shih et al. [9] and Zhu et al. [10], refer to diamond deposition processes from microwave plasmas produced at high pressures (over 40 Torr) and hot substrates (over 500 °C).

On the other hand, Amaratunga et al. [11] were the first ones reporting the presence of single-crystal nanodiamonds (20–40 nm in diameter) forming a poly-crystalline matrix widely observed almost over the entire surface of their carbon thin films deposited with rf (13.56 MHz)-produced CH4/Ar (≥98%) plas-
mas at low pressures (0.2–0.5 Torr). They even observed smaller crystals (10 nm in diameter) within the amorphous parts of the deposited films. Their films were deposited, in contrast to typical MW-produced diamond and nanodiamond thin films, on substrates kept at low temperature (20 °C).

While nanodiamond thin films obtained under Ar-rich CH₄/Ar plasmas are proved to be obtained at MW (2.45 GHz) and rf (13.56 MHz), their growth mechanisms might somehow differ. As it will be sketched out below, these possible distinct growing mechanisms could be mainly associated to the plasma excitation frequency and substrate temperature.

This work describes the possibility of obtaining nanodiamond thin films from CH₄/Ar-rich plasmas produced at very low excitation frequency (35 kHz) with two (15 and 200 °C) substrate temperatures (Tₛ) and during two deposition times (1 and 3.5 h). The presence of nanodiamond crystals has been associated to a shift of the distribution function of the ions to higher energies as the plasma excitation frequency decreases.

2. Experimental

Film deposition was carried out using a Plasmalab PL-80 reactor operating at 35 kHz. In this system both electrodes are water cooled at ~15 °C and the rf power is coupled to the bottom electrode holding the substrate. Two Ar concentrations (80 and 95%), together with two gas pressures (0.1 and 0.3 Torr) and two deposition times (1 and 3.5 h) were used. The rf power was kept constant at 300 W while the substrate temperature was fixed at 15 and 200 °C, respectively. The substrates used were n-type single-crystal silicon wafers with \{1 0 0\} orientation and 0.3–1.0 cm resistivity. Before deposition, the substrates were cleaned in ultrasonic baths of acetone and ethanol and the samples were pretreated by an Ar plasma for 5 min. Analysis of the deposited films has been performed using atomic force microscopy (AFM) and transmission electron microscopy (TEM). For this purpose, small flakes of the film were scratched using a stainless steel tip and taking them by a standard electron microscope grid. The hardness of the deposited films was measured using nanoindentation techniques. For the measurements presented here, we used a Nano-Indenter II (Nano Instruments Inc.), with a Berkovich pyramid diamond indenter. We have used the ac indentation technique which was first introduced by Oliver and Pharr [12]. This technique allows us to measure continuously the hardness and Young’s modulus of the sample as a function of the indentation depth.

In each indentation experiment, the indenter was first loaded and unloaded three times in succession at a constant rate of 10% of the peak load to assure that the contact was maintained between the specimen and the indenter. Three hold periods of 50 s were inserted at the maximum depths and another hold period of 100 s was inserted at the minimum of the final unloading. During this last hold period, the displacement of the indenter was carefully monitored to establish the rate of thermal drift in the machine for subsequent correction of the data. Two experiments were carried out for maximum depths of 10, 20 and 30 nm, and 30, 60 and 90 nm, respectively.

3. Results and discussion

The presence of nanocrystalline diamonds (5–15 nm in diameter) forming a polycrystalline array within the amorphous carbon matrix was detected in films prepared with very high (≃95%) Ar concentrations at 1 and 3.5 h deposition times and with low substrate temperature (15 °C). The diamond nanocrystals are surrounded by larger diamond crystals within an amorphous matrix. We see in Fig. 1 a TEM image including the electron diffraction pattern of the surface which shows the presence of very small diamond crystals corresponding to the sample deposited for 3.5 h, 0.3 Torr and Tₛ = 15 °C. The measured lattice plane spacings of the first lines ([1 1 1], [2 2 0] and [3 1 1]) observed in the diffraction pattern are, respectively, 0.205, 0.125 and 0.108 nm, and they are within 1% error of the published values for diamond.

Variation of the pressure to 0.1 Torr (with 95% Ar concentration, 1 or 3.5 h deposition time and Tₛ = 15 °C) also leads to the formation of nanodiamond crystals; however, no diamond crystals were observed when working at Tₛ = 200 °C, 0.3 or 0.1 Torr, 1 h deposition time and 80–95% Ar concentration. On the other hand, regardless the deposition
time, a decrease of the hardness and an increase of the rms (root mean square) surface roughness of the films grown at \( T_s = 15 \) and 200 °C was measured as the pressure decreases (see Table 1). Though only a slight decrease in film hardness is observed with decreasing pressure, a strong increase (from \( \approx 0.2 \) to \( \approx 2 \) nm) in film roughness is measured. The presence of H radicals in the film could explain the low hardness values found for the samples, though no specific analysis of the films was performed.

Fig. 2 shows a three-dimensional AFM image of the film grown for 3.5 h, one of the samples where nanodiamond crystals have been detected by electron diffraction, deposited at 0.3 Torr, \( T_s = 15 \) °C and 95% Ar concentration. The measured growth rate ranges from 0.1 \( \mu \)m/h (\( T_s = 15 \) °C) to 0.2 \( \mu \)m/h (\( T_s = 200 \) °C) and the rms surface roughness is extremely low (just 0.2 nm) in the case of films grown at \( T_s = 15 \) °C for 3.5 h. Such low roughness (very smooth surfaces) and growth rates follow the trend observed by Zhou et al. [6] in MW Ar-rich systems, that is, they exhibit a significant decrease (especially at \( T_s = 15 \) °C) as Ar concentration increases. On the other hand, though nanodiamond crystals are not directly visible in Fig. 2, some repetitive geometrical

![Fig. 1. TEM image (80 kV accelerating voltage) showing nanodiamond crystals, with grain sizes ranging from 5 to 15 nm, observed in a film prepared from a 35 kHz-produced CH\(_4\)/Ar (95%) plasma at 0.3 Torr and 3.5 h deposition time. The inset image shows the electron diffraction pattern corresponding to the film area shown; the rings correspond to the \{1 1 1\}, \{2 2 0\} and \{3 1 1\} lattice spacings of diamond.](image1)

![Fig. 2. Three-dimensional AFM image of the film grown from a 35 kHz excited CH\(_4\)/Ar (95%) plasma at 0.3 Torr, \( T_s = 15 \) °C and 3.5 h deposition time showing an extremely smooth surface.](image2)

Table 1

<table>
<thead>
<tr>
<th>Ar (%)</th>
<th>( T_s ) (°C)</th>
<th>( p ) (Torr)</th>
<th>DT (h)</th>
<th>( R ) (nm)</th>
<th>( H ) (GPa)</th>
<th>FT (μm)</th>
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</thead>
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<tr>
<td>80</td>
<td>15</td>
<td>0.1</td>
<td>1, 3.5</td>
<td>2.0, 1.4</td>
<td>13.0</td>
<td>0.1, 0.35</td>
</tr>
<tr>
<td>80</td>
<td>15</td>
<td>0.3</td>
<td>1, 3.5</td>
<td>0.8, 0.5</td>
<td>13.5</td>
<td>0.1, 0.35</td>
</tr>
<tr>
<td>95*</td>
<td>15</td>
<td>0.1</td>
<td>1, 3.5</td>
<td>1.8, 1.2</td>
<td>8.8</td>
<td>0.1, 0.35</td>
</tr>
<tr>
<td>95*</td>
<td>15</td>
<td>0.3</td>
<td>1, 3.5</td>
<td>0.6, 0.2</td>
<td>9.2</td>
<td>0.1, 0.35</td>
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<tr>
<td>80</td>
<td>200</td>
<td>0.1</td>
<td>1</td>
<td>1.4</td>
<td>13.8</td>
<td>0.2</td>
</tr>
<tr>
<td>80</td>
<td>200</td>
<td>0.3</td>
<td>1</td>
<td>1.0</td>
<td>15.0</td>
<td>0.2</td>
</tr>
<tr>
<td>95</td>
<td>200</td>
<td>0.1</td>
<td>1</td>
<td>1.2</td>
<td>10.7</td>
<td>0.2</td>
</tr>
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<td>200</td>
<td>0.3</td>
<td>1</td>
<td>0.8</td>
<td>12.0</td>
<td>0.2</td>
</tr>
</tbody>
</table>

* Nanocrystals observed.
patterns, i.e. angular structures, can be distinguished allowing one to localise the nanodiamonds crystals detected in the electron diffraction pattern of the 3.5 h, \( T_s \simeq 15^\circ C \) sample.

Nanodiamond crystals of different sizes, ranging from 5 to 15 nm, were found within an amorphous carbon matrix. While both Amaratunga’s and Gruen’s nanodiamond crystals, obtained at 13.56 MHz and 2.45 GHz, respectively, were seen over their entire film surface [11], our nanodiamond crystals are not uniformly distributed and they are found, by direct observation using TEM at low magnification, to cover between 10 and 20% of the deposited film surface. Such distinct distribution might be explained in terms of the combined effect associated to the substrate temperature and the ion energy distributions corresponding to the different plasma excitation frequencies (2.45 GHz, 13.56 MHz and 35 kHz) of the various systems used by different research groups. Moreover, as suggested above, the discharge excitation frequency and substrate temperature might control the film growing mechanisms.

Following both the experimental results and theoretical predictions by Aisenberg and Chabot [13] and Lifshitz et al. [14], respectively; Amaratunga et al. [11] explain their uniform nanodiamond crystal distribution, grown from a 13.56 MHz excited CH\(_4\)/Ar plasma on a low temperature (20 \({}^\circ\)C) substrate, by the impact of Ar\(^+\) energetic ions coming from the plasma. According to Lifshitz et al. [14], diamond film nucleation is especially aided at certain (optimum) ion energies that were specifically tuned in Amaratunga’s experiment [11].

As we shall see below, we have associated the scarce amount of nanodiamonds observed in our films grown for 1 and 3.5 h to the fact that most of the ions impacting the substrate have energies out of the 50–200 eV (optimum) range at 15 \({}^\circ\)C [14]. However, the nonuniform diamond crystal distribution found in our 35 kHz Ar-rich experiment might be connected to the form of the ion energy distribution near the substrate. According to well-known concepts [15] on the plasma sheath ion dynamics and its dependence on the plasma excitation frequency, the maximum kinetic energy (neglecting excitation and ionisation processes in the sheath) of an ion reaching a surface depends on whether it moves across the sheath slowly (high frequency) or quickly (low frequency) relative to the oscillating plasma potential \( V_p(t) \) [15]. The most important effect of changing the excitation frequency is that the voltages (at constant pressure and rf power) in the plasma increase as the frequency is decreased [16]. Therefore, ion bombardment energies are greater at low frequency.

If the excitation frequency is high enough that the ions need many rf cycles to cross the sheath, the ions will arrive at the surface with an energy determined by the time average of \( V_p(t) \), i.e. \( \overline{V_p} \), and most of the ions will have this energy leading to an almost monoenergetic ion energy distribution. If, on the contrary, the transit time is much shorter (low frequency) than the period of the rf excitation voltage the ion energies will reflect the temporal oscillations of \( V_p(t) \) and their maximum energy will be \( e(V_p)_{\text{max}} \); however, only some few ions will have such energy. Thus, the ion energy distribution at low plasma excitation frequencies is much broader (nonuniform) than at high frequencies (\( \geq 13.56 \) MHz) and it may reach much higher energies [16].

The plasma excitation frequency also determines the electric behaviour of the sheaths. In general, at high frequencies the sheaths tend to act capacitively while they behave resistively in the low frequency range [16]. When the rf power is capacitively coupled to the excitation electrode and one works at high excitation frequencies (\( \geq 13.56 \) MHz), the capacitive sheath approximation [17] yields a time average plasma potential \( \overline{V_p} \) given by [18]

\[
\overline{V_p} = \frac{1}{2} (V_{RF} + V_{DC})
\]

(1)

where \( V_{DC} \) is the promoted dc self-bias voltage and the voltage on the excitation electrode is \( V(t) = V_{DC} + V_{RF} \sin \omega t \). The resistive sheath approximation [16] provides another appropriate expression for low frequency excited capacitive coupled systems.

On the other hand, measurements of dc self-bias voltage \( (V_{dc}) \) as a function of \( V_{RF} \) in a capacitively coupled Ar plasma [16] excited at different frequencies show that, the higher the excitation frequency the closer \( V_{dc} \) is to \( V_{RF} \) at 13.56 MHz, \( V_{dc} \simeq 0.95V_{RF} \), while at 105 kHz it goes down to \( V_{dc} \simeq 0.80V_{RF} \) and to even lower values at 35 kHz. Moreover, experimental results by Köhler et al. [16] show that the maximum ion energy measured in an rf excited Ar plasma (at 0.02 Torr and \( V_{RF} + V_{DC} = 100 \) V) grows by more than a factor of 3 with decreasing excitation frequency from 13.56 MHz to 35 kHz.
Consequently, what we learn from the previous discussion is that low frequency systems can easily lead to higher maximum ion energies than 13.56 MHz or 2.45 GHz plasma reactors; however, the promoted dc self-bias is less controllable than in high frequency systems. These concepts help to understand the synthesis of polycrystalline diamond and nanodiamond thin films recently achieved at our laboratory from 35 kHz excited CH₄/Ar-rich plasmas. In addition, we believe that, though nanodiamond thin films have been obtained both with rf Ar-rich, at low (35 kHz) and high (13.56 MHz) frequencies, and MW Ar-rich (2.45 GHz) plasma reactors, the growing mechanisms and species involved may be different. It seems that physical mechanisms (the so-called subplantation process firstly proposed by Lifshitz et al. [14] involving the action of C⁺ and Ar⁺ ions on the substrate) are significantly important in rf systems working at low substrate temperatures, while a chemical growing process (the C₂ deposition mechanism firstly proposed by Gruen et al. [1,3]) seems to be more relevant in MW Ar-rich systems at high substrate temperatures (over 500 °C).

4. Summary and conclusions

We have observed nonuniform distribution of nanodiamond crystals in thin films grown on low temperature substrates (15 °C) from decomposition of CH₄/Ar-rich plasmas generated at 35 kHz. The concentration of the diamond nanocrystals on the samples is low, i.e. about 10–20% of the amorphous carbon matrix and, consequently, the film hardness is also low (up to 15 GPa, depending on the deposition conditions). Whereas the scarce amount of nanodiamonds detected in our films is associated to the low energy (i.e. out of the energy range predicted by Lifshitz et al. [14]) of the ions impacting the growing film, the nonuniformity of the nanodiamond crystal distribution is assumed to be due to the 35 kHz nonuniform ion energy distribution near the substrate.

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