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H plasma processing triggered phase transformation from DLC to diamond nano-particles ☆

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ABSTRACT

Phase transformation from diamond-like carbon (DLC) films to amorphous carbon (a-C) encapsulated diamond nano-particles (a-DNPs) has been realized by using longtime and low power radio frequency (rf, 40–60 W) H plasma processing at 1000 K. SEM observation showed that a thin film consisted of densely packed nano-particles (NPs) was formed on the surface of DLC films after a longtime H plasma processing. The length of the NPs increased dramatically with the processing time, but the density change was negligible ($\sim3\times10^{11}$ cm^{-2}). Visible and UV Raman revealed that the NPs were consisted of diamond and a-C. XPS showed a processing time dependent content increase of SP^3-hybridized carbon, confirming the growth of diamond during the plasma treatment. Based on previous researches, a core (diamond)-shell (a-C) structure and a two-step transforming model were proposed. We conjecture that the SP^3-hybridized carbon clusters in DLC behave as the seeds for the DNP growth, and the rf H plasma treatment provides an appropriate driving force for the running of this phase transformation.

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1. Introduction

Diamond has shown exceptional potential in electronic applications involving high temperature, high power and high frequency due to its unique physical characteristics like high breakdown voltage and excellent thermal conductivity [1,2], as well as applications like fabricating pressure generator [3], engineering diamond by fabricating superlattices [4], quantum computing [5], and so on. The traditional syntheses of single-crystal or polycrystalline diamond are usually realized by using microwave plasma enhanced chemical vapor deposition (MWPECVD) and in a homoepitaxial way [6,7]. Another method for the synthesis of diamond or diamond nano-particles (DNPs) is phase transformation using plasma or energetic ion irradiation, and researches in this respect have been carried out widely in recent years. M. Zaiser and F. Banhart systematically studied the phase transformation from carbon onion to diamond by using energetic electron irradiation and worked out a corresponding nonequilibrium phase diagram basing on experimental observations and theoretical analyses [8,9]. Similar transformation was studied in the crystallization of Si from amorphous Si by H-mediation [10–12]. Even recently, a report from R.Z. Khaliullin and his coworkers revealed a nucleation mechanism for the direct graphite-to-diamond phase transition [13]. However, phase transformation from diamond-like carbon (DLC) film to diamond has never been reported. In thinking that the DLC is a SP^3-bond abundant material and the SP^3-bond is a fundamental unit in the diamond construction, the phase transformation from DLC to diamond can be catalyzed.

In this work, we report the longtime and low power radio frequency (rf) H plasma processing triggered phase transformation from DLC to diamond. Basing on previous researches, we proposed an amorphous carbon (a-C) encapsulated DNP (a-DNP) growth model.

2. Experimental details

The DLC films were deposited by using a metal vapor vacuum arc (MEVVA) ion source. Single crystal n (100) Si wafers without any pretreatment were utilized as the substrates. The deposition was carried out in a vacuum chamber which was pre-pumped to 5×10^{-4} Pa. The Si substrates were fixated on a rolling stainless specimen holder and exposed to carbon plasma during the DLC deposition. A negative bias of ~150 V was applied on the substrates. The deposition time was about 40 min, during which an approximately 100-nm thick DLC film was deposited.

A capacitively coupled rf system (13.56 MHz) was employed to carry out the phase transformation study, as schematically shown in Fig. 1. The glow discharge was energized by ionizing H$_2$, which was the only gas used in this study. Before the rf H plasma processing, the vacuum chamber was pre-pumped to $\sim8\times10^{-4}$ Pa to eliminate the background impurity. Then the as-prepared DLC films were heated to ~1000 K by an own designed heater at a pressure of ~100 Pa in H$_2$ environment. During the processing, the rf power, the gas flow,
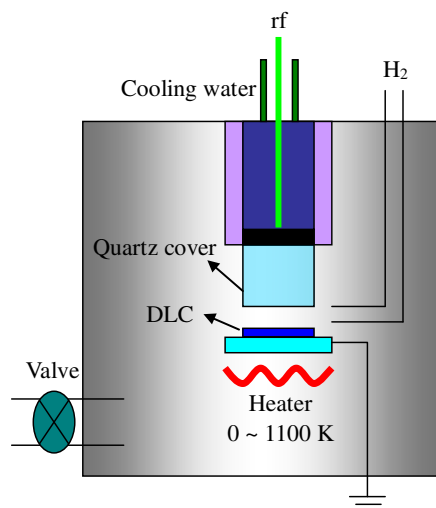

Fig. 1. Schematic scheme of the rf H plasma system used for phase transformation.

the pressure and the temperature were 40–60 W, 2.5 sccm (standard cubic centimeter per minute), 100 Pa and 1000 K, respectively. A morphological evolution with time study was carried out, in which we respectively ceased the plasma processing at 10 h and 30 h.

Scanning electron microscope (Hitachi S-4800, 10 kV), visible (532 nm) and UV (325 nm) Raman (LobRAM ARAMIS), X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM) were employed to characterize the samples. It should be emphasized that the samples used for the SEM observation were pre-deposited a ultrathin conductive coating to prevent the accumulation of static electric fields at the specimens due to the electron system irradiation required during imaging.

3. Results

3.1. Transformation from DLC to NPs

Fig. 2 shows SEM images of NPs covered DLC after exposing to H plasma for 10 h with an rf power of 40 W. We scratched the DLC during SEM sample preparation in view of a convenient comparison,
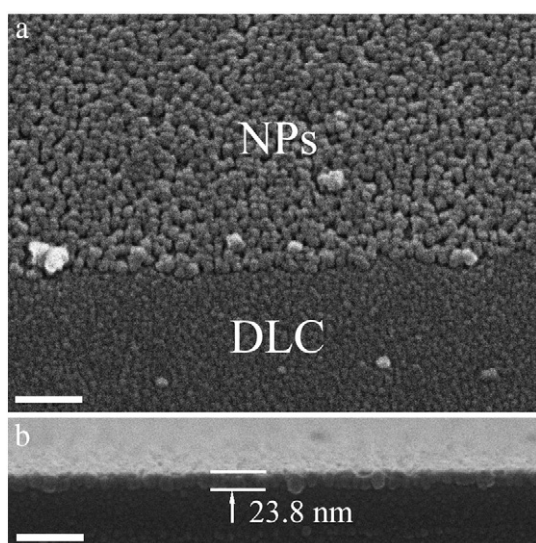
which can be observed in the oblique view shown in Fig. 2(a). Part of the sample is covered by NPs while the rest is DLC. The small-sized nano-particles on the DLC, shown in the lower part of Fig. 2(a), are resulted from the conducting layer that is used to increase the conductivity of the samples. The NPs are densely packed on the surface of the DLC forming a continuous film, and the thickness of which is ~23.8 nm shown in Fig. 2(b). It means that the transformed part of the DLC is quite limited due to the extremely weak ion irradiation in such a low rf power condition. Furthermore, we may find that the irregularly shaped NPs, to some extent, resemble that of a-C.

3.2. Morphological evolution of the NPs with the processing time

Fig. 3 shows a morphological evolution of the DLC with the ever-prolonging H plasma processing time under an rf power of 50 W. Fig. 3(a) shows the surface topography of the original DLC, which is even and uniform with a thickness of ~100 nm. After exposing the DLC to H plasma for 10 h, a rough surface with densely packed NPs is obtained (Fig. 3(b)). The mean diameter, the density and the length of the NPs are ~13 nm, ~3×10^{11} cm^{-2} and ~23.5 nm (inset of Fig. 3(b)), respectively. In comparison with the NPs obtained with an rf power of 40 W discussed previously (~23.8 nm, Fig. 2(b)), the length change of the NPs is negligible. It thus suggests that there must be a certain range of the rf power for this transformation. We tried some other rf powers between 40 and 60 W, and it turned out to be that there was hardly any change in the morphology of the NPs at all, especially the thickness of the NP films. Prolonging the processing time to 30 h, the respective mean diameter and length of the NPs reach ~18 nm and ~47.6 nm, as shown in Fig. 3(c). Compared to the NPs formed in the 10-hour plasma processing, both the mean diameter and the length of the NPs increase dramatically in
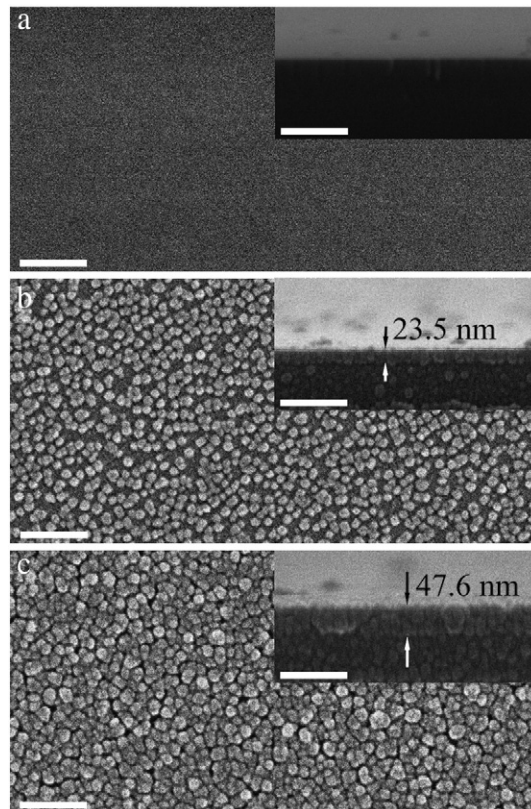

Fig. 3. Morphological evolution of the DLC with the increasing rf H plasma processing time. SEM top view images of (a) original, (b) 10-hour and (c) 30-hour H plasma processed DLC films, and the insets are the corresponding side views. Other experimental parameters: 50 W, 2.5 sccm, 100 Pa, 1000 K. All the scale bars are 100 nm.

Fig. 2. SEM images of the NPs covered DLC after a 10-hour H plasma processing. (a) Oblique view and (b) side view SEM images. Experimental parameters: 40 W, 2.5 sccm, 100 Pa, 1000 K. Scale bar: 100 nm.

the prolonged 20 h, especially the length that has doubled. However, the density change of the NPs is negligible, suggesting that size-increasing of the NPs is dominative during this 20 h rather than new NP nucleation.

3.3. Raman characterization of the NPs covered DLC

The visible Raman spectra (wavelength: 532 nm) of the original, 10-hour and 30-hour H plasma processed DLC films are shown in Fig. 4(a). Compared to the weak broad single Raman peak of the original DLC film, two Raman peaks centered around 1334 cm^{-1} and 1596 cm^{-1}, which are related to the disordered carbon (D-band) and the graphite carbon (G-band), respectively [14], are observed in that of the H plasma processed DLC films. This is mainly attributed to the increase of SP^3-hybridized carbon after the longtime plasma treatment; but also to the resonance effect of SP^2-hybridized carbon in the visible [15]. We use the intensity ratio of D-band to G-band (I_D/I_G) to evaluate the structural change of the DLC films with the prolonging processing time. I_D/I_G increases from ~0.36 to ~0.58 when the plasma processing time increases from 10 to 30 h, suggesting an increasing disordering of the DLC films. We further employed UV Raman (wavelength: 325 nm) to identify the DLC films, as shown in Fig. 4(b). A peak centered around 1332 cm^{-1}, which is absent in that of the original DLC films and demonstrates the formation of diamond [15,16], is observed in the Raman spectra of the H plasma processed DLC films, indicating that the NPs covered on the DLC films after the longtime H plasma treatment are diamond NPs with amorphous carbon (a-DNPs).

Since we have identified the composition of the NPs, the content change of diamond with the processing time needs to be further studied. In thinking that the diamond is SP^3-hybridized, we can, to some extent, figure out the diamond growth by measuring the content change of the SP^3-hybridized carbon with the prolonging processing time. Fig. 5(a–c) shows the raw and fitted XPS spectra of the original, 10-hour and 30-hour H plasma processed DLC films, respectively. The fitted peaks centered around 284.1 eV, 284.7 eV and 288.0 eV are corresponding with the SP^2-hybridized carbon [17], SP^3-hybridized carbon [18] and organic contaminated carbon [19], respectively. Fig. 5d shows the percentage change of the SP^2- and SP^3-hybridized carbon as a function of the H plasma processing time. It can be observed that the content of SP^3-hybridized carbon increases from 48%

(original) to 55% (10 hrs) and then to 72% (30 h) as processing time prolongs. Combining with the SEM images (Fig. 3) and UV Raman spectra (Fig. 4(b)) shown previously, we can roughly conjecture that the diamond grows as H plasma processing time prolonging.

4. Discussion

Basing on previous studies carried out by Sun et al. that mainly focused on the phase transformation from carbon nanotubes to diamond nano-whiskers [20–22] and the above Raman and XPS analyses, we propose here a core-shell structure for the a-DNPs: a diamond core encapsulated by a-C. Fig. 6 shows a schematic illustration for the formation of a-DNPs, and the three stages shown in the schemes are corresponding with the respective SEM images in the morphological evolution study discussed previously (Fig. 3). For the original DLC, the surface is smooth but full of nano-scale defects, which mainly arises from the SP^3-hybridized carbon. At the beginning of the H plasma processing, part of the SP^3-hybridized carbon clusters, only an extremely small part (~1 in 10^4–10^6) [23], starts to grow in a diamond way, while the vast majority of these SP^3-bonded clusters were removed due to the atomic thermal motion and the etching effect of H. This H driven phase transformation has been studied widely both in the phase change from graphite to diamond that induced by energetic ions or electrons and in the crystallization of Si in amorphous Si [8–12]. From the point of view of the diversity of Gibbs free energy (ΔG), $\Delta G = G_D - G_G$, where G_D and G_G are the respective Gibbs free energy of the diamond and the graphite during phase transformation, a possible phase transformation from graphite to diamond is that ΔG should be negative. The fact is that ΔG will always be positive if we only take thermal motion of the carbon atoms into consideration, because graphite is more stable than diamond in a pure thermal driving system [9]. However, the introduction of atomic H can revise this phase transformation by inserting into the loosely bound a-C atoms and make the ΔG negative [8–12], leading to the growth of diamond. Diamond growth is achieved at the cost of the surrounding a-C, and that is the origin of the core-shell structure. Basing on previous researches, we conjecture a faceting process occurs during the diamond size-increasing phase, which is determined by the intrinsic property of the diamond [20]. Then, the a-DNP starts to grow in a preferential orientation, corresponding with the prolonged H plasma processing time from 10 h to 30 h, as
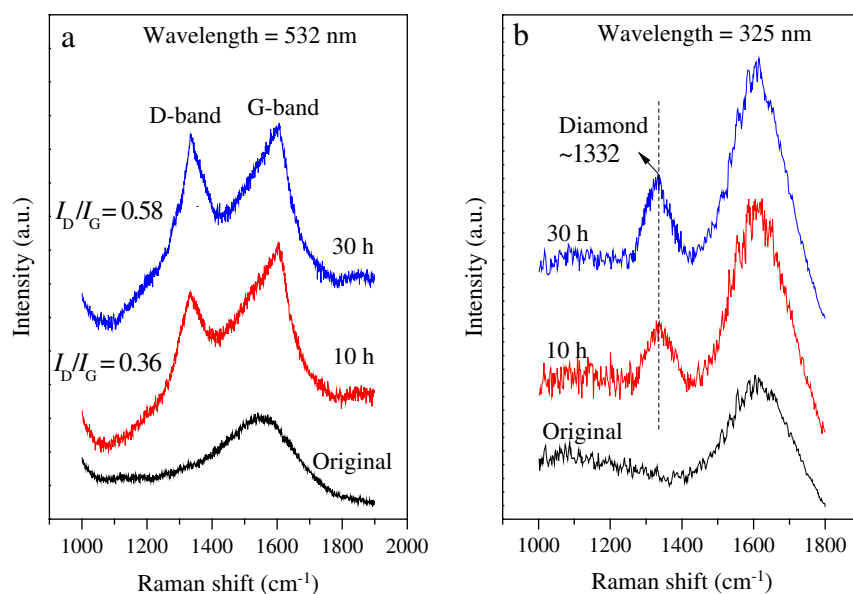

Fig. 4. Raman spectra of the NPs covered DLC films. (a) Visible Raman (wavelength: 532 nm) spectra of the original, 10-hour and 30-hour H plasma processed DLC films. (b) UV Raman (wavelength: 325 nm) spectra of the original, 10-hour and 30-hour H plasma processed DLC films.
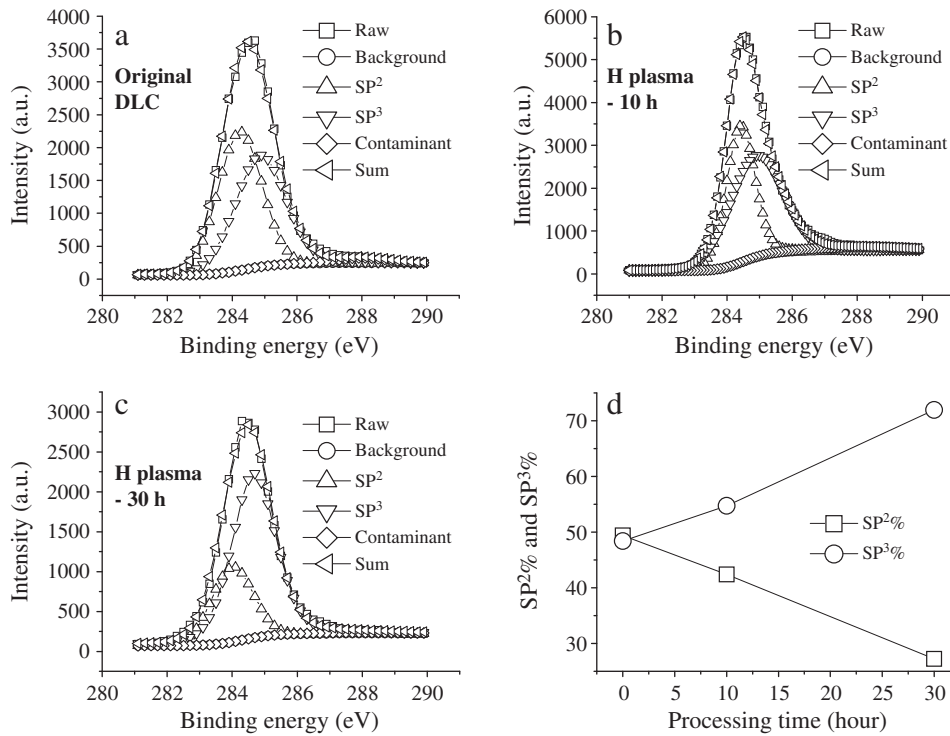
Fig. 5. XPS spectra of (a) original, (b) 10-hour and (c) 30-hour H plasma processed DLC films. (d) Percentage change of the SP^2- and SP^3-hybridized carbon as a function of the H plasma processing time.

shown in Fig. 3(c), and we consider this one dimension growth of a-DNPs to a size effect at the tip of the particles that makes the tips more reactive and so enhances the phase transformation [24]. To sum up, both the diamond nuclei and the amorphous shell are important for the phase transformation from DLC to a-DNPs, the existed SP^3-hybridized clusters in the DLC just facilitate this process.

In addition, an appropriate rf power is important in this phase transformation study. We tried some other rf powers, such as 10–30 W or more than 70 W, and found that a low rf power (<30 W) could not trigger the phase transformation even with a longer processing time. We consider that the H in this low-power condition may not have enough energy to insert into the SP^3-hybridized carbon clusters and mediate a regular running of the phase transformation [8–12]. However, high rf powers (>70 W) are not feasible, either. In this condition, the energetic H has enough power to insert and mediate the phase transformation, but simultaneously, H etching and atomic knock-on sputtering becomes severe, leading to a fast consumption of

the a-C or even the nucleated DNPs, resulting in DLC thinning rather than phase transformation from DLC to diamond. The contradiction between the energy that needs for phase transformation and the energy for weakening H etching and sputtering determines that this phase transformation in our study can only be advanced slowly, and that's why we take an extremely long time to achieve it. In fact, we also found that DLC changed little when the processing time was less than 5 h.

5. Conclusion

Phase transformation from DLC to a-DNPs was realized by using longtime and low-power (40–60 W) rf H plasma processing. SEM observation showed that NPs were formed on the surface of DLC films with a high density of ~3×10^{11} cm^{-2} after a longtime H plasma processing. The length of the NPs increased dramatically with the processing time, but the density change was negligible. Visible and UV Raman spectra confirmed that the NPs were consisted of diamond and a-C, and XPS analyses showed that the diamond grows with the processing time. Basing on previous researches, we proposed a core-shell structure and two-step (diamond nucleation and one dimension growth) transforming model for the a-DNPs and pointed out that both the SP^3-hybridized carbon clusters and the surrounding a-C were indispensable for this DLC-DNP phase transformation.

Fig. 6. Schematic illustration of the phase transformation from DLC to a-DNPs.

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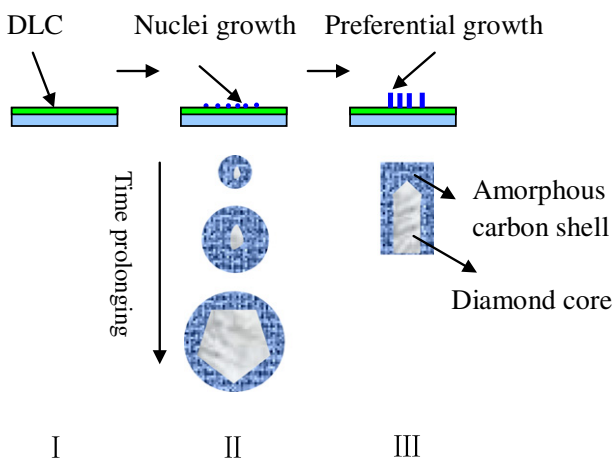
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