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Ultrasmooth nanocrystalline carbon film induced by low concentration doping: Carbide disorienting graphene nanocrystallite



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ABSTRACT

The fabrication of nanocrystalline films is usually accompanied by undesired surface roughening, which limits their applications in tribology, optics and electronics. Here, we report a technique to reduce the average roughness of graphene nanocrystalline carbon film from 18.3 nm to 0.66 nm by ~5 at.% Ti-doping. The surface of the Ti-doped graphene nanocrystalline carbon film stay ultrasmooth from few nanometer thick up to 1 μ m thick. Based on the nanostructure characterization, the ultrasmooth mechanism is interpreted that Ti-doping leads to the formation of Ti–C bond, and changes the growth of graphene nanocrystallite from preferred vertical-aligned orientation to random orientation. The ultrasmooth mechanism is general, as shown by similar effects with low concentration doping of Si, Al, Cr, Zr and W. This approach paves a way for fabricating ultrasmooth nanocrystalline carbon films without a requirement of ion-impact-induced downhill current, and significantly improving the hardness of the graphene nanocrystalline carbon film.

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1. Introduction

Ultrasmooth surface is a crucial requirement in many application fields of conventional optics, nanophotonic device, magnetic storage technology, semiconductor technology and AFM/STM characterization [1-4]. Since amorphous carbon (a-C) film possesses extreme smoothness and diamond-like properties, it has emerged as an important surface protective coating in widespread applications for decades [5-7]. A specific example is the fabrication of ultrasmooth a-C film, as a key for ultrahigh storage density hard disks [1,8]. Nowadays, with the development of sophisticated devices, demands of multifunctional integrated films have substantially increased. As for a-C film, it is expected to integrate desired properties for specific applications without sacrificing the original features. A feasible way is to embed different nanocrystallites, such as graphene, nanotube, diamond and carbide, into the amorphous carbon matrix [9–17]. The excellent characteristics of the nanocrystallites widen and enhance the properties of the films. For example, amorphous carbon film containing graphene nanocrystallites exhibited great improvements in electrical conductivity

* Corresponding author. E-mail address: dfdiao@szu.edu.cn (D. Diao). [9], magnetic moment [10], photo responsivity [11], electrochemical activity [12], low-friction behavior [13] and triboelectric performance [14]. Diamond nanocrystallites could improve tribological properties of the carbon film with impressively low friction and wear [15,16]. When titanium carbide (TiC) nanocrystallites were embedded in the amorphous carbon matrix, the thermal stability, adhesion strength, corrosion resistance and wear resistance were increased [17,18]. However, the deposition of these kinds of nanocrystalline carbon films were usually accompanied by undesired surface roughening, which hinders the broad applications of the excellent integrated properties.

In general, the roughness of thin films is caused by irregular and stochastic precipitation of depositing particles due to the fluctuation of particle flux (noise) and shadowing effects [19–21]. For achieving ultrasmoothness of a-C film, a key factor is to introduce certain ion-impact-induced downhill currents in the top layer of a growing film, which erodes hills and forms efficient lateral transport process on the film surface [1]. And another important prerequisite is amorphicity. Once nanocrystallites formed in the amorphous carbon matrix at high depositing temperature or at high impact energy, considerable surface roughening occurred accordingly [22–24]. Indeed, the different growth rates between amorphous area and nanocrystalline area on the top surface of a growing film is the main reason for the formation of shadowing









Fig. 1. Schematic setup of a unique hybrid sputtering system for the deposition of doped graphene nanocrystalline carbon film with low-energy electron irradiation. The electron cyclotron resonance (ECR) plasma sputtering and magnetron sputtering can be independently controlled. A positive bias is applied to the substrate for modulating low-energy electron irradiation. (A colour version of this figure can be viewed online.)

effect and surface roughening. It has been reported that ultrasmooth TiC/a-C nanocomposite film could be fabricated by increasing energy flux of ion impingement during pulsed DC sputtering [25,26]. Based on the cross-sectional nanostructure observations, an amorphous front layer of 2 nm covered the nanocomposite film and suppressed the influence of nanocrystallites on the roughness evolution of the nanocomposite films. Therefore, the ultrasmooth mechanism also followed the ion-impact-induced downhill model and subplantation model [27], which is proposed for the formation of sp^3 carbon bonding and tetrahedral a-C film growth. However, it is a special case for obtaining ultrasmooth nanocrystalline carbon films, and less applicable for the deposition technique without sufficient ion-impact-induced downhill current.

Recently, a kind of graphene nanocrystallite embedded carbon film was deposited under low-energy (0-300 eV) electron irradiation in an electron cyclotron resonance (ECR) plasma sputtering system [9]. During the deposition, a positive bias voltage was applied to the substrate, which helps to attract electrons and repulse ions in the plasma, forming electron irradiation on the film surface. The electron irradiation energy and density dominated the formation of graphene nanocrystallites in the film. However, inevitable rough surface were observed due to the growth of nanocrystallites and the lack of ion irradiation on the surface. According to the ion-impact-induced downhill model, the growth of graphene nanocrystallite and ultrasmooth surface seem to be incompatible as fire and water. Aiming at this situation, a compromise proposal is to alternately employ the electron irradiation and ion irradiation during the fabrication of smooth nanocrystalline film. For instance, electron/ion alternative irradiation for multilayer carbon film fabrication [28], ion etching after growth of nanocrystalline carbon film [29], low-energy electron irradiation induced top-surface nanocrystallization of a-C film [30]. Nevertheless, all of these methods need several strict processes and have a limitation on the thickness (<10 nm) of single nanocrystalline layer for guaranteeing ultrasmoothness with an average roughness on the order of 0.1 nm.

In this paper, a general low concentration doping method is

demonstrated to be effective for fabricating ultrasmooth graphene nanocrystalline carbon (GNC) films from few nanometer thick up to 1 μ m thick without a requirement of ion-impact-induced downhill current. We showed that the ultrasmoothing effect depends on the bonding between the doping element and carbon, which changes the growth of graphene nanocrystalline from preferred vertical-aligned orientation to random orientation. More interestingly, the doping also significantly improved the hardness of the GNC film, which is beneficial for achieving good potential integrated performance in application.

2. Experimental details

2.1. Film fabrication

Pure and doped GNC films were deposited on silicon substrates (p-type <100>) with low-energy electron irradiation using a multifunctional ECR plasma sputtering system, as shown schematically in Fig. 1. The system possesses a unique hybrid sputtering function with ECR plasma sputtering and magnetron sputtering. The ECR plasma sputtering was used for depositing GNC film with low-energy electron irradiation. The magnetron sputtering independently controlled the doping parameters during the GNC film deposition. The background pressure of the vacuum chamber was 8×10^{-5} Pa, and argon was inflated keeping the working pressure at 1×10^{-1} Pa. Mirror-confinement magnetic field was formed with magnetic coils. And the ECR plasma was generated by introducing microwave (2.45 GHz, 500 W) through a quartz window. Before deposition, Si substrate was cleaned by argon ion sputtering for 3 min. Then, argon ions sputtered the ECR carbon target with a bias voltage of -500 V to provide carbon atoms for the film growth. During the film deposition, low-energy electron irradiation on the film was realized by applying a positive bias voltage of +80 V to the substrate. The electron irradiation energy was ~80 eV and electron irradiation density was 66.2 mA/cm². The detailed formation principle of low-energy electron irradiation was reported in our previous works [9,31]. Different elements doping of Ti, Si, Al, Cr, Zr,



Fig. 2. Surface morphologies by SEM and AFM for (a) 150 nm pure GNC film and (b) 150 nm Ti-doped GNC film. *R*_a is the average roughness. (c) Roughness and Ti/C atomic ratio of 150 nm pure GNC film and 150 nm Ti-doped GNC films with different Ti target currents. (d) Roughness evolutions of pure GNC film and Ti-doped GNC film (Ti target current: 0.7 A) with film thickness. (A colour version of this figure can be viewed online.)

W and Cu were realized by changing magnetron sputtering targets. Magnetron target currents were set as 0.1 A, 0.3 A, 0.5 A and 0.7 A to obtain different doping concentrations. The film thickness was controlled by the deposition time. The film growth rate ranging from 5 to 6 nm/min according to different doping parameters.

2.2. Characterization

The surface morphology of film was measured by atomic force microscopy (AFM, BRUKER, Innova) in a tapping mode. Silicon tip with curvature radius of 4 nm was used, and the images were obtained with a scan size of 5 μ m \times 5 μ m and a scan frequency of 0.8 Hz. The chemical composition of film was analyzed using an AXIS ultra DLD multifunctional XPS with a monochromatic Al K α X-ray source.

The nanostructures of the carbon films were analyzed with a Raman spectroscopy (HORIBA, HR-Resolution; wavelength of 532 nm) and a Cs-corrected transmission electron microscopy (TEM, FEI, Titan 3 Themis G2). The TEM was operated at 80 kV to avoid possible damages or recrystallization caused by electron irradiation, and the point to point resolution is 0.08 nm. The plan view TEM specimens were prepared by scratching the film surface with a diamond pencil, then transferring the flakes onto a copper micro grid. The cross-sectional TEM specimens were cut from the films and progressively thinned to about 100 nm thick by using a focused ion beam (FIB, FEI, Scios). A Pt protective layer was deposited on the top of the specimen and the final polishing was done with a beam current of only 27 pA to avoid possible damages (including ion doping) or thermal recrystallization caused by ion bombardments. The FIB was also employed as a scanning electron microscope (SEM) to observe the surface morphology of the films.

The electrical conductivity of film was measured by a four-point probe (RTS-8) at room temperature. The nanoindentation tests of films were performed with a nanoindenter (Hysitron, TI-950). A Berkovich diamond indenter with tip radius of 100 nm was used and the maximum load for indentation was 200 μ N. A pre-test on

quartz standard sample was done to calibrate the equipment. The tests were operated in a clean room with a temperature of 24 °C and a relative humidity of 45–50%.

3. Results and discussion

3.1. Surface morphology of Ti-doped GNC film

Fig. 2a-b shows the scanning electron microscope (SEM) and atomic force microscope (AFM) images of the surface morphology of a 150 nm pure GNC film and a 150 nm Ti-doped GNC film. It can be seen that the pure GNC film is very rough with many large hills on the surface. The average roughness (R_a) is 18.3 nm. In contrast, Ti-doped GNC film appears to be ultra-smooth with R_a of 0.66 nm, which is approximately two orders of magnitude less than that of the pure GNC film. The height histograms of the two AFM images are shown in Figs. S1a-b (See Supplementary data). The height histogram provides a measure of the maximum peak-to-valley height difference and the deviation from the average height. The height histogram of pure GNC film has a broad distribution, with an average value of 128.9 nm and the maximum value of 171.6 nm. The Ti-doped GNC film has a narrow distribution, with an average value of 7.9 nm and the maximum value of 12.1 nm. These reveal that the Ti doping can reduce the surface roughness of the pure GNC film by orders of magnitude.

To systematically investigate the effect of Ti doping on the surface morphology, Ti-doped GNC films with different Ti/C atomic ratios and film thicknesses were fabricated by varying the Ti target current and the deposition time. Ti/C atomic ratio of the films were evaluated by X-ray photoelectron spectra (XPS). The details of XPS survey spectra and C 1 s XPS spectra are shown in Figs. S2–S3 (See Supplementary data). Fig. 2c shows the Ti/C atomic ratio and the roughness of 150 nm pure GNC film and 150 nm Ti-doped GNC films. The Ti/C atomic ratio increased almost linearly with the Ti target current. For the film fabricated with Ti target current of 0.7 A, the Ti/C atomic ratio is 0.05. So the concentration of Ti in the film is ~5 at.%. The roughness sharply decreased from 18.3 nm to 4.96 nm with the Ti target current of 0.1 A, and further decreased to lower than 1 nm with increasing the Ti target current to 0.5 A. Fig. 2d shows the roughness evolutions of the pure GNC film and Ti-doped GNC film (Ti target current: 0.7 A) with film thickness. The corresponding AFM images of the pure GNC films and Ti-doped GNC films with different film thicknesses are shown in Fig. S4 (See Supplementary data). For the pure GNC film, the surface roughness increased remarkably from 0.17 nm at film thickness of 5 nm-18.3 nm at film thickness of 150 nm, then saturated with further increasing of film thickness, indicating the surface roughening with the growth of graphene nanocrystallites in the film. For the Ti-doped GNC film, the surface roughness little increased from 0.15 nm at film thickness of 5 nm-1.15 nm at film thickness of 1 μ m, revealing the surface nearly stayed ultrasmooth from few nanometer thick up to 1 µm thick. These results demonstrate that low concentration Ti-doping significantly reduced the roughness of GNC film.

3.2. Mechanism for ultrasmooth surface of doped GNC film

In order to reveal the ultrasmooth mechanism by low concentration Ti-doping, the nanostructures of the pure GNC film and Tidoped GNC film (Ti target current: 0.7 A) were observed and analyzed with a Cs-corrected TEM and a Raman spectroscopy using a 532 nm laser for excitation. The results are shown in Fig. 3. For the GNC film, the plan view TEM image in Fig. 3a clearly shows a nanocrystalline structure with randomly oriented nanocrystallites embedded in the amorphous carbon matrix. The interplanar spacing of the nanocrystallites is approximately 0.34 nm, matches the interplanar spacing of graphene sheets. The corresponding Raman spectrum exhibits three sharp bands of D band. G band and 2D band respectively around 1340, 1590 and 2700 cm^{-1} , which also confirms the existence of graphene nanocrystallites [32,33]. From the cross-sectional view TEM images (Fig. 3b), it can be seen that the film surface is undulant and the embedded graphene nanocrystallites are kind of vertical-aligned to the substrate. The adjacent graphene nanocrystallites are separated by amorphous carbon or defect structure. The nanocrystallite size is about 1-10 nm. Fig. 3c shows a schematic cross-sectional image of the pure GNC film. Graphene nanocrystallites prefer to vertical growth in the film. The edges of growing nanocrystallites are more active to bond with adatoms than the adjacent amorphous structures [31], resulting in different growth rate and rough surface.

For the Ti-doped GNC film, ~5 at.% Ti-doping induced the formation of TiC nanocrystallites, as marked with the white circles in Fig. 3d—e. The TiC nanocrystallites of about 2—5 nm are homogeneously embedded in the film with random orientation. The spacing of the lattice fringes in one direction is 0.22 nm, close to the d value of the TiC (200) plane. In addition, the Ti-doping also affected the growth



Fig. 3. (a) Plan view and (b) cross-sectional view TEM images of pure GNC film. The inserted Raman spectra also indicating the existence of graphene nanocrystallites. (c) Schematic cross-sectional image of the pure GNC film. (d) Plan view and (e) Cross-sectional view TEM images of Ti-doped GNC film (Ti target current: 0.7 A). (f) Schematic cross-sectional image of Ti-doped GNC film. (g–j) Cross-sectional view EDS results of Ti-doped GNC film. The bright field STEM image, Ti, C element distributions and their composite are presented. (A colour version of this figure can be viewed online.)



Fig. 4. (a) Roughness versus I_D/I_G of pure GNC film and different element doped GNC films. SEM images and Raman spectra of (b) Al-doped GNC film and (c) Si-doped GNC film (Doping target current: 0.7 A). (d) SEM and AFM images of Cu-doped GNC film (Cu target current: 0.3 A). (e) Plan view TEM images and Raman spectrum of Cu-doped GNC film. (A colour version of this figure can be viewed online.)

of graphene nanocrystallites in the film. Compared with Fig. 3a-b, it can be found that the size of graphene nanocrystallites decreased. And the orientation of the graphene nanocrystallites in the crosssectional view changed from vertical align to random. The peak intensity ratio of I_D/I_G of Raman spectrum was obtained by fitting the D band and G band with a Lorentzian line and a Breit-Fano-Wagner (BFW) line (See Fig. S5 in the Supplementary data), respectively. According to the three-stage amorphization proposed by Ferrari and Robertson [34], the pure GNC film and Ti-doped GNC films are in stage 2 ranging from amorphous carbon type to nanocrystalline type. The nanocrystallite size is proportional to the I_D/I_G. With the Ti-doping, the ratio of I_D/I_G and the relative intensity of 2D band decreased (Fig. 3d), which proves the decrease of graphene nanocrystallite size as well. From the TEM images (Fig. 3d-e), it also can be observed that the graphene and TiC nanocrystallites cross-linked or interlocked with each other. Fig. 3g-j shows the cross-sectional view energy dispersion spectrum (EDS) results of Ti-doped GNC film. The brightfield scanning transmission electron microscopy (STEM) image and the EDS elemental maps of Ti and C, more clearly verify the cross-link relationship between of graphene and TiC nanocrystallites. In view of this, it is reasonable to deduce that the formation of Ti-C bonds (or TiC nanocrystallite) at edges of graphene sheets changed the orientation and size of graphene nanocrystallite, and consequently induced the ultrasmooth surface of the Ti-doped GNC film. Fig. 3f shows a schematic cross-sectional image of the Ti-doped GNC film. During film growth, the addition of Ti atoms can bond strongly with carbon to form Ti-C bonds [35], which is confirmed by XPS in Fig. S3b (See Supplementary data). The edges of graphene sheets have higher energy and are the preferred sites for nucleation of TiC nanocrystallite [36]. Thus, the growth of graphene nanocrystallite was interrupted, or the incorporation of Ti triggered the curving of graphene sheet and orientation transformation of graphene nanocrystallites. In this process, electron irradiation transferred sufficient energy to adatom through inelastic collision [9,31], guaranteeing the adatom possesses high mobility and effective lateral transport ability. In addition, the TiC nanocrystallites in the film can also act as a good catalytic for formation of sp^2 clustering (graphene sheets) [37]. Therefore, the Tidoping breaks the oriented growth of graphene nanocrystallite, curbs the enlarging of the graphene nanocrystallite size, and subsequently eliminates the heterogeneous growth on the top surface of a growing film.

In fact, from the Raman spectra of the pure GNC films with different film thicknesses (See Fig. S6a in the Supplementary data), it can be found that the size of graphene nanocrystallite grew up gradually with the film thickness increased from 5 nm to 150 nm, then stayed steady. This tendency is in accordance with the surface roughness evolution (see Fig. 2d) and vertical growth of graphene nanocrystallite. After doping Ti into the films, the vertical growth of graphene nanocrystallite is suppressed, and the nanocrystallite size reaches its maximum value with the film thickness of 50 nm, which is deduced from the Raman spectra of the Ti-doped GNC films with different film thicknesses (Fig. S6b). Therefore, the ultrasmooth of the Ti-doped GNC film is closely related to the transformation of growth pattern of graphene nanocrystallite.

To further explore the doping-induced ultrasmooth mechanism, different dopants of Si, Al, Cr, Zr, W and Cu were employed, and their effects on the surface morphologies and nanostructures of the films were investigated. Among them, Cr, Zr, W and Ti are strong-carbide-forming metals [35,38], as indicated in Fig. 1. Si is a strong-carbide-forming semimetal. Al is a weak-carbide-forming metal. While Cu is a non-carbide-forming metal [35,39]. The doping target current, roughness (R_a) and I_D/I_G of doped GNC films with different dopants are summarized in Table S1 (See Supplementary data). For the dopants of Si, Al, Cr, Ti, Zr, and W, the roughness (R_a) and I_D/I_G of the



Fig. 5. (a) Electrical conductivity versus doping target current of pure GNC film and different element doped GNC films. (b) Hardness versus I_D/I_G of pure GNC film and different element doped GNC films. (A colour version of this figure can be viewed online.)

doped GNC films almost decreased with the increasing of doping target current. Nearly all of the dopants are useful for achieving ultrasmooth surface. In order to more clearly uncover the relationship between the roughness and nanostructure, the surface roughness versus I_D/I_G of pure GNC film and different element doped GNC films are shown in Fig. 4a. Obviously, the roughness decreased with the decreasing value of I_D/I_G . And when the I_D/I_G decreased to a range of 0.8–0.93 by doping, ultrasmooth surface can be obtained. The I_D/I_C is proportional to the size of graphene nanocrystallite in the film, and also suggests the effect extent of element doping on the growth of graphene nanocrystallite. Therefore, the optimum In/Ic range demonstrates that the way for doping induced ultrasmooth surface is through changing the growth pattern of graphene nanocrystallite, rather than making the nanostructure non-crystallization. And the element doping induced ultrasmooth mechanism is quite general. The element is not only limited to Ti and strong-carbide-forming metals, but also extents to weak-carbide-forming metal (Al) and strong-carbide-forming semimetal (Si). The ultrasmooth surfaces of Al-doped GNC film and Si-doped GNC film are shown in Fig. 4b-c, respectively. For the corresponding Raman spectra, the coupling shapes of D band and G band indicate that the growth pattern of graphene nanocrystallite was affected obviously by Al or Si doping. It should be noted that Al is a weak-carbide-forming metal and forms no typical carbide with the NaCl structure [38,40]. So the formation of carbide nanocrystallite in the GNC film is not a requirement for achieving of ultrasmooth surface. The essential requirement is more like to be the bonding ability between the doping element and carbon.

To verify the essential requirement for ultrasmooth surface, copper is also employed to dope the GNC film, since it has the lowest affinity to carbon and does not form any carbide phases [35,39]. The doping target current, roughness (R_a) and I_D/I_G of Cudoped GNC films are summarized in Table S2 (See Supplementary data). And from the SEM and AFM images (Fig. 4d), it can be seen that the surface of Cu-doped GNC film is very rough with an average roughness (R_a) of 40.8 nm, which is even higher than that of the pure GNC film. The plan view TEM images in Fig. 4e show that 5-10 nm copper nanocrystallites form in the film. The spacing of the lattice fringes in one direction is calculated to be 0.21 nm, close to the d value of the Cu (111) plane. The Raman spectrum of the Cudoped GNC film is similar to that of the pure GNC film, which indicates that the growth of graphene nanocrystallite is nearly less interrupted by Cu doping, i.e. the growths of graphene nanocrystallite and Cu nanocrystallite in the film are almost independent. Therefore, the Cu doping aggravates the surface roughening, instead. Based on the above experiments and analyses, it can be concluded that the doping induced ultrasmooth surface of GNC film is depended on whether the doping element can bond with carbon to form any carbide (metallic carbide forming elements: Ti, Cr, Zr, W; saline carbide forming element: Al; covalent carbide forming element: Si).

3.3. Electrical and mechanical properties of nanocrystalline carbon films

Fig. 5a shows the electrical conductivity versus target current of pure GNC film and different element doped GNC films. The electrical conductivity of the pure GNC film is 103 S/cm, which is smaller than that of graphite measured along the *c* plane $(1.9 \times 10^4 \text{ S/cm})$ but lager than that measured perpendicular to the *c* plane (1 S/cm) [41]. After doping with different elements, the film conductivity varies within an order of magnitude, indicating that the film maintains good electrical conductivity. It is easy to image the increase of film conductivity with metal doping. For the film doped with semimetal Si, the conductivity decreased slightly with the increasing of target current. The good electrical conductivity of the doped films also supported that the doping mainly changed the growth pattern of graphene nanocrystallite rather than destroys the graphene sheet.

The hardnesses of the pure GNC film and different doped films were evaluated by a nanoindenter, and the results are summarized in Fig. 5b. The hardness of pure GNC film was significantly improved from 2.04 GPa to 6-7 GPa by element doping, and increased lineally with the decreasing value of I_D/I_G. Combined with Fig. 4a, it can be found that high hardness and ultrasmooth surface can be obtained simultaneously with an optimum I_D/I_G range, i.e. an optimum doping parameter range. The hardness of doped GNC films showed a tendency to approach the hardness of diamond like carbon (DLC) film [6,42], which is beneficial for achieving good service life in electrical, magnetic and optical applications. The enhancement of hardness can be interpreted that the effectual doping induced more cross-links between nanocrystallites in the film (see Fig. 3), lowering the negative effect of weak van der Waals force between graphene sheets on the hardness. While the ineffectual doping of Cu led to disastrously decrease of hardness, which can be obviously distinguished from the typical load-displacement curves of pure GNC film, Ti-doped and Cu-doped GNC films in Fig. S7 (See Supplementary data). The hardness is 0.54 GPa for the Cu-doped GNC film with a doping target current of 0.3 A.

Based on the above experiments and analyses, the ultrasmooth surface and abundant graphene nanocrystallites demonstrate that the doped GNC films are hopeful to be explored in a wide range of applications, and the additional functions of the films can be customized based on the doped elements. The high hardness and good electrical conductivity of the doped films are also beneficial for realizing potential integrated performance in application.

4. Conclusions

In summary, we proposed an approach to fabricate ultrasmooth graphene nanocrystalline carbon films by low concentration doping. The surface of doped GNC film remained ultrasmooth from few nanometer thick up to 1 μ m thick. The doping induced ultrasmooth mechanism is general and interpreted that doping element led to the formation of carbide, and changed the growth of graphene nanocrystallite from preferred vertical-aligned orientation to random orientation. The efficacy of this approach is depended on whether the doping element can bond with carbon to form any carbide (metallic carbide, saline carbide, or covalent carbide). This approach provides not only a way for fabricating ultrasmooth nanocrystalline carbon films without a requirement of ion-impact-induced downhill current, but also a new type of multifunction integrated graphene-like film with wide application prospects.

CRediT author statement

Cheng Chen: Conceptualization, Investigation, Validation, Data Curation, Writing - Original Draft.

Xue Fan: Investigation, Writing - Review & Editing.

Dongfeng Diao: Conceptualization, Supervision, Methodology, Writing - Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbon.2019.11.090.

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