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# Controllable fabrication of self-organized nano-multilayers in copper–carbon films*

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In order to clarify the influence of methane concentration and deposition time on self-organized nano-multilayers, three serial copper–carbon films have been prepared at various methane concentrations with different deposition times using a facile magnetron sputtering deposition system. The ratios of methane concentration ($CH_4/Ar+CH_4$) used in the experiments are 20%, 40%, and 60%, and the deposition times are 5 minutes, 20 minutes, and 40 minutes, respectively. Despite the difference in the growth conditions, self-organizing multilayered copper–carbon films are prepared at different deposition times by changing methane concentration. The film composition and microstructure are investigated by x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and high-resolution transmission electron microscopy (HRTEM). By comparing the composition and microstructure of three serial films, the optimal growth conditions and compositions for self-organizing nano-multilayers in copper–carbon film are acquired. The results demonstrate that the self-organized nano-multilayered structure prefers to form in two conditions during the deposition process. One is that the methane should be curbed at low concentration for long deposition time, and the other condition is that the methane should be controlled at high concentration for short deposition time. In particular, nano-multilayered structure is self-organized in the copper–carbon film with copper concentration of 10–25 at.%. Furthermore, an interesting microstructure transition phenomenon is observed in copper–carbon films, that is, the nano-multilayered structure is gradually replaced by a nano-composite structure with deposition time and finally covered by amorphous carbon.

**Keywords:** nano-multilayers, self-organized, controllable fabrication, copper–carbon films

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## 1. Introduction

The design and fabrication of nano-multilayered structures provide a great opportunity to significantly enhance materials' properties at the macro-scale.[1,2] In particular, metal–carbon films with a nano-multilayered structure have attracted enormous attention over the past few years due to their extraordinary properties, e.g., low internal stresses, good adhesion to substrate, etc.[3–6] The traditional fabrication process for nano-multilayer film usually requires adjusting a parameter periodically or substrate revolution, which causes intricate operation procedures and limits its industrial applications.[7] In the past few years, a peculiar phenomenon, i.e., self-organized formation of nano-multilayered structure in carbon-based films with the incorporation of some transition metal, has been reported by different groups.[8–13] This self-organized multilayered structure greatly simplifies the fabrication process compared with traditional multilayered film and exhibits enormous potential for industrial applications.[14,15] Therefore, many groups have been devoted to exploring the influence of various deposition parameters, such as different metals,[11] temperature,[10] ion energy,[9] different deposition methods,[16] etc., on self-organizing nano-multilayer structures. It is known that during the magnetron sputtering process, the deposition time plays a significant role in the film thickness, morphology, etc.[17,18] As a major factor in self-organizing multilayered structures, the deposition time can undoubtedly not be ignored. To date, little work has focused on discussing the influence of deposition time on self-organizing nano-multilayer structures at various methane concentrations. Meanwhile, studies on the controllable preparation of self-organized nano-multilayered structure in metal–carbon film are rare.

The self-organizing mechanism of multilayered structure is still under debate. Wu *et al.* took the chemical interaction of carbon and metal into account, discussing the relationship between different metals (such as Ni, Cu, Pt, etc.) and self-organized nano-multilayers.[8] Chen *et al.* considered that the driving force of spontaneously forming multilayered structure was owing to energetic ion bombardment of the growth surface, which results in the phase separation process and finally produces the nano-multilayered structure.[13] It was also reported that the low deposition rate and small grain size of cop-

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per were conducive to the self-organization of multilayers in copper–carbon film from our previous work.[19] Thus, clarifying the influence of deposition time on self-organized nano-multilayers at various methane concentrations is propitious for a comprehensive understanding of the self-organizing mechanism.

Bearing these aspects in mind, our group employed a single copper target and fixed substrates according to a facile reactive magnetron sputtering deposition system to prepare three serial copper–carbon films at different deposition times with various methane concentrations; the deposition times used in the experiment were 5 minutes, 20 minutes, and 40 minutes. Moreover, the microstructure and composition of the films is discussed. By comparing the composition and microstructure of three serial films, we have obtained the optimal growth condition and composition for self-organizing nano-multilayer structure in copper–carbon films, and the preparation of the nano-multilayered structure is expected to be controllable. It possesses potential value for carbon-based film to develop industrial production techniques due to its convenient fabrication process. In addition, we report for the first time a peculiar transition phenomenon in copper–carbon film, that the nano-multilayered structure is gradually replaced by a nanocomposite structure with increasing deposition time and is finally covered by amorphous carbon.

## 2. Experimental section

### 2.1. Preparation of the film

A facile reactive magnetron sputtering facility (SP-0806SI) equipped with only one single magnetron gun was used to deposit the copper–carbon films on single crystal wafers of (100) silicon substrate; high purity argon (99.99%) and high purity methane (99.99%) were used as a sputtering gas of the copper target (purity 99.9%). The details about the deposition facility and deposition process are described elsewhere.[19] The substrates were cleaned ultrasonically in an acetone bath and dried in air followed by plasma etching with $Ar^+$ ions in a vacuum chamber to remove the native oxide on the substrates' surface. In the initial period of the deposition process, the deposition chamber was firstly pumped to a pressure lower than $6.0 \times 10^{-3}$ Pa, and then fed with an Ar+$CH_4$ gas mixture to a stationary deposition pressure of 1.2 Pa. The ratios of methane concentration ($CH_4$/Ar+$CH_4$) used in the experiment are 20%, 40%, and 60% (sccm/sccm, sccm: standard cubic centimeters per minute) for deposition times of 5 minutes, 20 minutes, and 40 minutes, respectively, and the total flow rate was maintained at 220 sccm. The direct current (DC) powers were 600 W and the substrates were fixed on the sample holder which was 50 mm away from the sputtering target. The substrates were not heated, biased, and rotated during the deposition process under all the conditions. The chamber temperature was approximately maintained at 70 ℃ during all the deposition processes.

### 2.2. Characterization of the films

The fractured cross-section morphology and the thickness of the as-prepared films were observed using an SU8020 field emission scanning electron microscope (FESEM). Thin foils from different films' cross-sections were prepared using a focused ion beam (ion source: gallium liquid metal). A Field Electron and Ion Company (FEI) Tecnai G2TF20FE-TEM high-resolution transmission electron microscope (HRTEM) operating at 200 kV was used to analyze the microstructure of the as-prepared films. The compositions of the copper–carbon films were analyzed using energy dispersive x-ray (EDX) analysis and a Perkin–Elmer PHI-5702 multifunctional x-ray photoelectron spectroscope (XPS); Al-$K\alpha$ was used as the exciting source with the binding energy of Au (1s) as the reference. Moreover, a Rigaku D/max-2500 facility operating with Cu-$K$ radiation was conducted to record the x-ray diffraction (XRD) patterns of the as-prepared copper–carbon films.

## 3. Results and discussion

Figure 1 shows the average deposition rate of copper–carbon films deposited for 5 minutes, 20 minutes, and 40 minutes at various methane concentrations. The deposition rate of films prepared at three deposition times is found to decrease with methane concentration. The thickness of the films deposited for 5 minutes decreases from 782 nm to 210 nm as the methane concentration increases from 20% to 60% (the thicknesses of the as-prepared films are measured by fractured cross-section FESEM morphology). The deposition rate can be calculated to vary from 156.4 nm/min to 42.0 nm/min. The deposition rate of the films deposited for 20 minutes decreases from 85.5 nm/min to 18.5 nm/min as the methane concentration increases from 20% to 60%. And the deposition rate of the films deposited for 40 minutes decreases from 30.6 nm/min to 19.8 nm/min with the methane concentration. During the deposition process, the growth of copper–carbon films is simultaneously attributed to the sputtering copper atoms and the carbon ions decomposed from the methane.[20] Thus, the two dominant factors would determine the overall deposition rate and composition of the as-prepared films. According to a previous study, Wu *et al.* reported that the deposition rate of carbon was found to be much less than that of the metal during the magnetron sputtering process.[8] Therefore, the decline in the deposition rate of the films is mainly attributed to the decrease in the copper sputtering yield. It is known that the target poisoning phenomenon often occurs in reactive sputtered deposition processes and plays an essential role in the sputtering rate.[21,22] The increase in the methane concentration will facilitate the adsorption of carbon ions on the target surface throughout the duration of the poisoning process,[23]

and simultaneously weaken the sputtering yield of the Cu target because of the reduced Ar content, which results in an immediate decrease in the Cu sputtering rate. In spite of the slight increase in the carbon deposition rate because of the increased methane concentration, the total film deposition rate is also reduced obviously caused by the rapid decline in the Cu deposition rate. According to our previous research, a low deposition rate favors forming well-aligned uniformed copper nanocrystalline grains and self-organizing the nano-multilayered structure.[19]

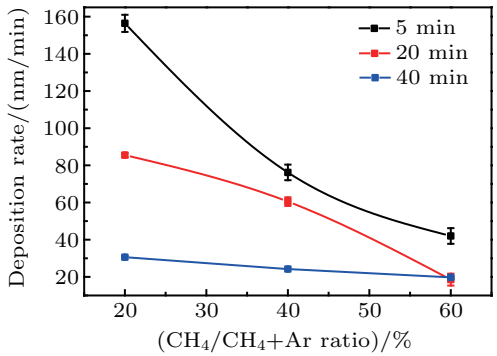



**Fig. 1.** Deposition rate of the copper–carbon films as a function of the $CH_4$ concentration corresponding to 5 minutes, 20 minutes, and 40 minutes deposition times.

Furthermore, by comparing the deposition rate of copper–carbon films deposited for 5 minutes, 20 minutes, and 40 minutes, the decline in the deposition rate is more obvious with the increase of the methane concentration when the deposition time is short (5 minutes and 20 minutes), especially for the film deposited for 5 minutes. However, when the deposition time is 40 minutes, the difference in deposition rate between various methane concentrations is not apparent, being maintained at 20 nm/min approximately. When the deposition time is 5 minutes and 20 minutes, the great decline in the deposition rate contributed to the target experiencing rapid transition from non-poisoning to poisoning. Under the condition of 40 minutes, the copper sputtering has little influence on the deposition rate of the film due to the severe accumulation of carbon on the Cu target surface, which results in little difference in the deposition rate of the films.

Figure 2 shows the characteristic Cu 2p XPS spectra of the films prepared for 5 minutes, 20 minutes, and 40 minutes at different $CH_4$ concentrations. It can be observed that the intensity of the Cu 2p peak decreases with the methane concentration, demonstrating a decrease of Cu content in the film. All the spectra of the films reveal two peaks corresponding to Cu (2p 1/2) and Cu (2p 3/2) with binding energies at $\sim$ 952.7 eV and $\sim$ 932.8 eV, which suggests that Cu exists in the films in metallic state form and no C–Cu bonding is formed.[24] A small peak at 934.3 eV deconvoluted from the major peak and the peak at 944.4 eV are assigned to CuO due to the fact that the Cu surface is oxidized to Cu (II) in the air as shown in Fig. 2(a).[14,25]

Figure 3 shows the XPS C 1s peaks of the as-prepared copper–carbon films deposited at various methane concentrations with different deposition times. All the spectra of the prepared films reveal only one peak corresponding to C 1s with binding energies at $\sim$ 285 eV, which suggests no C–Cu bonds forming in the films. The C 1s spectra could be deconstructed into three peaks centered at 284.2 eV, 285.2 eV, and 288.5 eV, corresponding to the $sp^2$ hybrid carbon, $sp^3$ hybrid carbon, and C–O bond, respectively; the O signal is due to oxygen contamination in the air.[26]

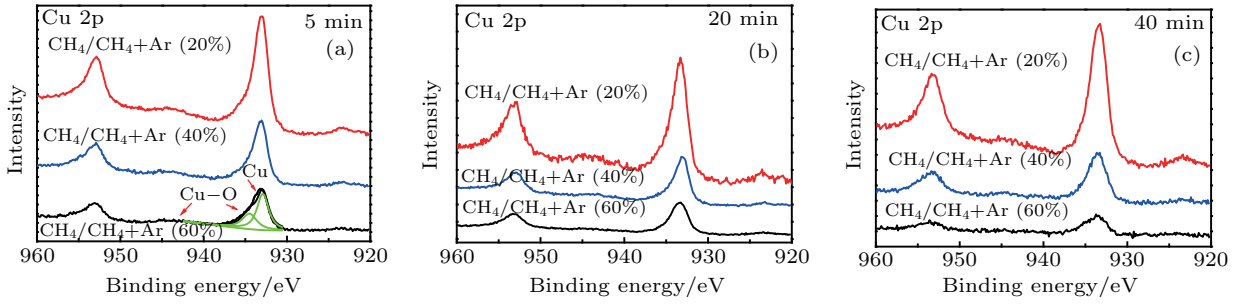



**Fig. 2.** Typical XPS Cu 2p peaks of the films at various $CH_4$ concentrations with the deposition time of (a) 5 minutes, (b) 20 minutes, and (c) 40 minutes.

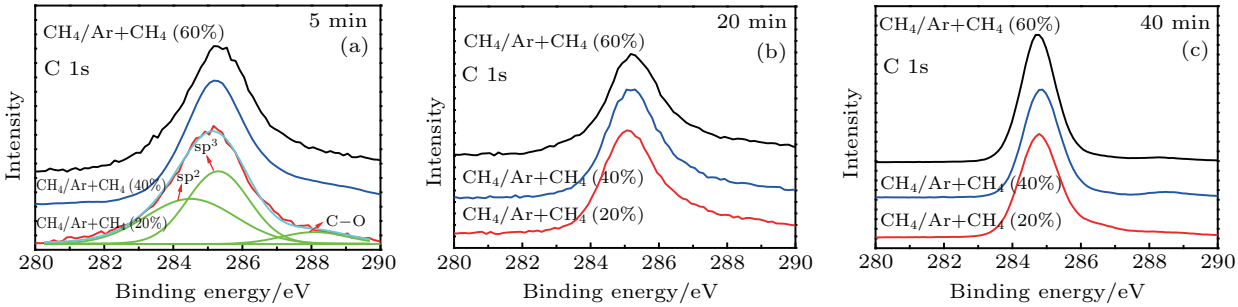



**Fig. 3.** Typical XPS C 1s peak of the films at various $CH_4$ concentrations with the deposition time of (a) 5 minutes, (b) 20 minutes, and (c) 40 minutes.

The XRD analysis is employed to study the constitution of the as-deposited films seen in Fig. 4. The three strong peaks at $2\theta = 43.3°$, $2\theta = 50.4°$, and $2\theta = 74.1°$ correspond to the (111), (200), and (220) planes of Cu crystallite, respectively. The two peaks at $2\theta = 36.6°$ and $2\theta = 61.8°$ correspond to the (111) and (220) planes of CuO crystallite, respectively.[27] It is found that the crystallinity of the copper–carbon films prepared at different deposition times decreases with the methane concentration, indicating a decrease of the Cu content in the film. In particular, the decline in copper crystallinity is more obvious with the increase of the methane concentration when the deposition times are 5 minutes and 20 minutes. When the deposition time is 40 minutes, the intensity difference between various methane concentrations is not apparent. This variation trend is consistent with Fig. 1.

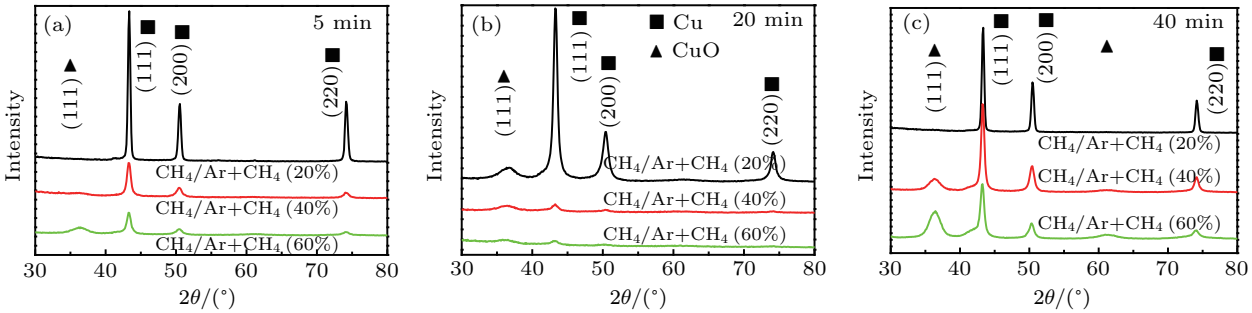



**Fig. 4.** XRD patterns of the films at various $CH_4$ concentrations with the deposition time of (a) 5 minutes, (b) 20 minutes, and (c) 40 minutes.

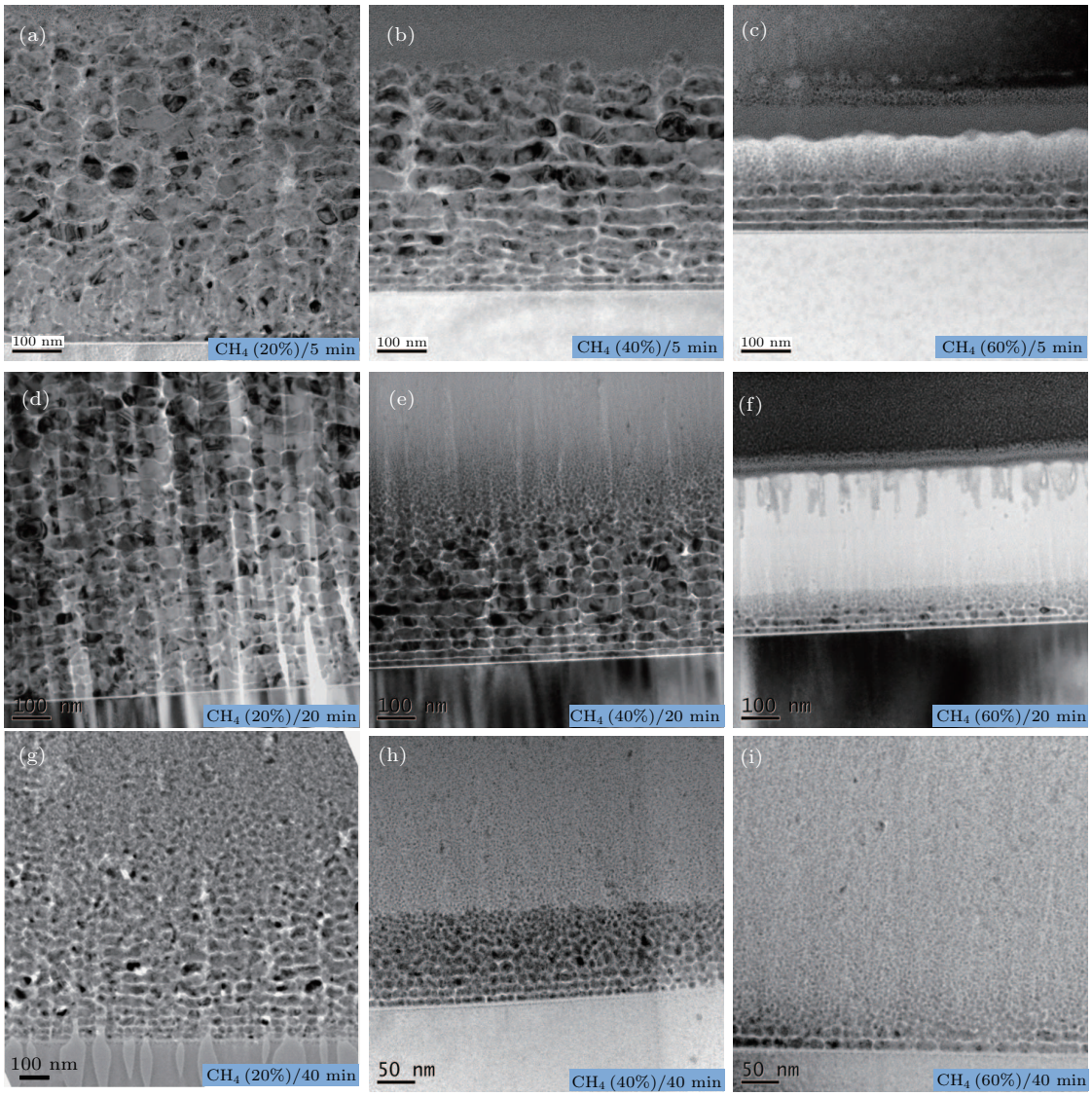



**Fig. 5.** TEM cross-sectional images of the films at various $CH_4$ concentrations with the deposition time of 5 minutes, 20 minutes, and 40 minutes.

Figure 5 shows the transmission electron microscopy (TEM) cross-sectional images of the films deposited for 5 minutes, 20 minutes, and 40 minutes at various methane concentrations. It is found that the dark regions are polycrystalline Cu and the bright regions are amorphous carbon in all TEM graphics of the films due to the difference in chemical contrast between light and heavy elements.[11] When the deposition time is maintained at 5 minutes and the methane concentration is 20%, the film mainly consists of large, separated, and irregular copper grains because of the excessive sputtering yield of the Cu target,[24] and the carbon content in the film is extremely low as shown in Fig. 5(a). As the methane concentration increases to 40%, some copper grains gradually convert into small and uniform nanocrystalline structure, and these nanocrystalline grains align parallel, forming a copper-rich layer structure. Meanwhile, the carbon in the film becomes a long strip-like structure, which suggests that the multilayered structure starts to form in the film, as shown in Fig. 5(b). The uniform nano-multilayers are formed in the film deposited at 60% methane concentration; the bright layers and the dark layers are carbon-rich layers and copper-rich layers, respectively, as shown in Fig. 5(c); the multilayer structure only consists of a few layers and degrades fast. When the deposition time is 20 minutes, the film prepared at 20% methane concentration also consists of discontinuous and large copper clusters due to the fast deposition rate, as shown in Fig. 5(d). As the methane concentration increases to 40% and 60%, uniform nano-multilayers are formed in the films, as shown in Figs. 5(e) and 5(f). However, when the deposition time is 40 minutes, it is obvious that the multilayers are formed in the film with a methane concentration of 20%, as shown in Fig. 5(g). When the methane concentration is 40%, the copper grains become detached and the multilayered structures in the film have been found to start vanishing, as shown in Fig. 5(h). When the methane concentration increases to 60%, the nano-multilayered structure has been found to disappear after forming four layers, as shown in Fig. 5(i). It is definitely concluded that nano-multilayer structure can be formed in the copper–carbon films by controlling the methane concentration and deposition time according to Figs. 5(c), 5(e), 5(f), and 5(g). It can be defined that two growth conditions are suitable for the formation of self-organized nano-multilayers in copper–carbon films. One is that the methane should be curbed at low concentration for long deposition time; the other is that the methane should be controlled at high concentration for short deposition time. Because the specimens are not rotated and other deposition parameters are constant during the film preparation process, the special nano-multilayered structures are prepared in the copper–carbon films via a self-organization mechanism.

The compositions of the resulting carbon–copper thin films are analyzed in an energy dispersive x-ray analysis. Figure 6 shows the average copper concentration and the size of copper grains in the copper–carbon films deposited for 5 minutes, 20 minutes, and 40 minutes under various methane concentrations. It can be seen from Fig. 6(a) that the copper concentration of the copper–carbon films is found to decrease from 75 at.% to 25 at.% as the methane concentration increases from 20% to 60% at the 5 minutes deposition time. When the deposition time is 20 minutes, the copper concentration of the films decreases from 50 at.% to 5 at.% with the methane concentration. And the copper content of films deposited for 40 minutes decreases from 25 at.% to 5 at.%. The copper concentrations of the copper–carbon films deposited for times of 5 minutes and 20 minutes are obviously more than that of those deposited for 40 minutes at the same methane concentration. It also proves that the effect of the methane concentration is more obvious on the copper sputtering yield for short deposition time as compared with long deposition time. Interestingly, it is observed that the copper content of the films deposited at the two optimal growth conditions has a limitation of around 10–25 at.%, as shown in Fig. 6(a). The obvious nano-multilayered structure cannot spontaneously form in the copper–carbon film when the copper content exceeds this range. The size of copper grains in the as-prepared copper–carbon films is also measured from the corresponding TEM pictures. The films with self-organized multilayered structure exhibit small and uniform copper nanocrystalline grains, as shown in Figs. 6(a) and 5. Moreover, small and uniform copper nanocrystalline grains are advantageous for forming

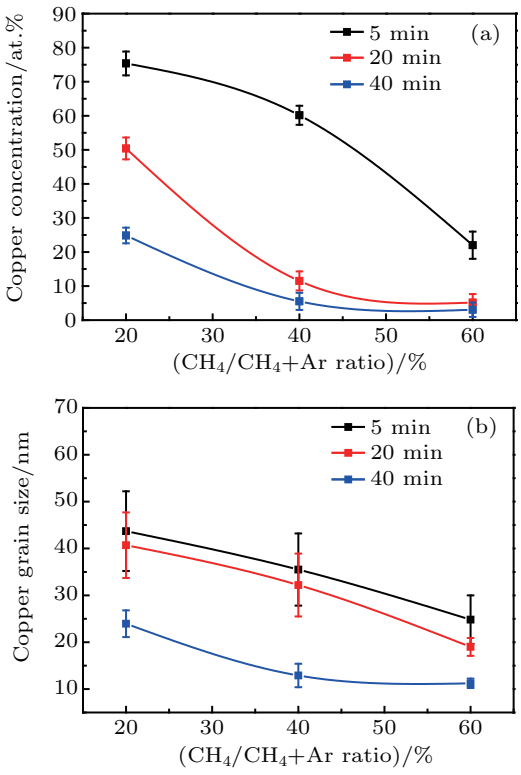



**Fig. 6.** (a) Copper concentration and (b) copper-layer thickness of the copper–carbon films deposited for 5 minutes, 20 minutes, and 40 minutes under various methane concentrations.

multilayered structure in the copper–carbon film according to our previous study.[19] When the deposition time is 5 minutes and the methane concentration is 20%, the copper concentration is too high to self-organize the nano-multilayers in the films, and high methane concentration is required to weaken the sputtering yield of the copper target. Similarly, at the deposition time of 20 minutes, the copper concentration is so high that nano-multilayers could not form spontaneously in the films at the low methane concentration (20%), and high methane concentration is required to make the copper target poisonous and decrease the deposition rate and copper grain size; therefore, the multilayers are only found to self-assemble in the films with methane concentrations of 40% and 60%. In contrast, when the deposition time is 40 minutes, a number of carbon ions would adsorb on the target surface if the methane is fixed at a high concentration. Thus, the copper sputtering yield is seriously affected and the copper concentration is so low that nano-multilayers could not form spontaneously in the films. In order to weaken the target poisoning effect, the methane must be curbed at low concentration. The results demonstrate that the self-organized nano-multilayered structure has a preference for forming in the copper–carbon films with the copper concentration of about 10–25 at.%. To some extent, we could determine whether the multilayers are formed in the copper–carbon films by analyzing the copper concentration (10–25 at.%). The copper concentration of copper–carbon film can be controlled by regulating the methane concentration and deposition time to the appropriate values, which facilitates the formation of nano-multilayered structure.

Interestingly, a peculiar microstructure transition phenomenon has been found in the copper–carbon films with deposition time according to the TEM pictures. Figure 7 shows the TEM micrographs and the corresponding selected area electron diffraction (SAED) patterns of the copper–carbon film at various positions. By analyzing the TEM morphology of the film prepared at 20% methane concentration and 40 minute deposition time, the nano-multilayered structure is formed near the substrate surface, and the monolayer thickness of the film is about 15 nm, as shown in Fig. 7(a). Furthermore, the sharp crystalline diffraction rings are observed in Fig. 7(d), indicating the existence of polycrystalline phases that are identified to be the (111) and (220) reflections of the cubic (face-centered cubic (FCC)) Cu structure.[28,29] The CuO (111) and (220) diffraction rings are also observed in the figure due to the fact that the Cu surface is oxidized in the air. In the middle of the film, the microstructure of the film mainly consists of copper nano-clusters embedded in the amorphous carbon network, as shown in Fig. 7(b). The corresponding SAED also reveals a diffuse halo without any observable diffraction rings, indicating that Cu exists as amorphous embedment as shown in Fig. 7(e), and the nano-multilayered structure of the film starts to be replaced by the nano-composite structure at this position. On the top of the film, the microstructure of the film experiences the transition again, and the corresponding SAED (Fig. 7(f)) shows a broad and diffuse diffraction halo, pointing out a typical amorphous feature, which implies that the composite structure is covered by typical amorphous carbon, as shown in Fig. 7(c).[29,30] Similar microstructure transitions are also observed in the films prepared at 40% methane concentration with 20 minute deposition time, and 60% methane concentration with 5 minute deposition time, as shown in Figs. 8 and 9. A series of microstructure transitions are attributed to the adsorption of carbon on the copper target: a large number of carbon ions decomposed from the methane would accumulate on the surface of the copper target with deposition time during the deposition process, which gradually weakens the sputtering yield of the copper target. The accumulation of carbon ions breaks the growth of multilayered structure in the as-deposited film because it is difficult for the Cu atoms to be sputtered out from the target, resulting in the nano-multilayered structure gradually transforming into a nano-composite structure. When the copper target surface is entirely covered by the carbon ions with deposition time, it is possible to sputter copper from a poisoned target, but the quantity of copper ions is low in plasma. Therefore, the carbon layer growth dominates the film growth in this period, and finally the amorphous carbon layer is synthesized on the top of the film.

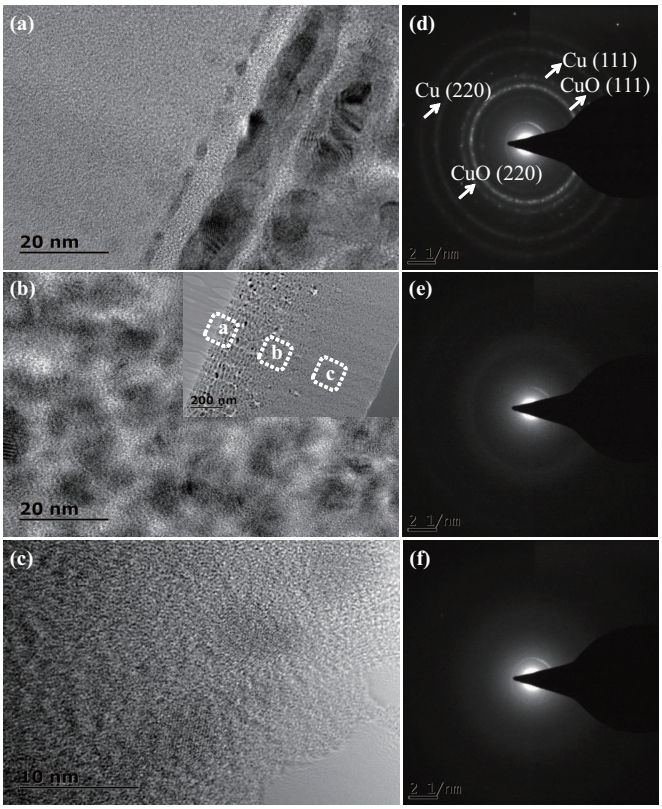



**Fig. 7.** TEM micrographs and corresponding SAED patterns of the copper–carbon film at various positions; the film is prepared at 20% methane concentration and 40 minutes deposition.

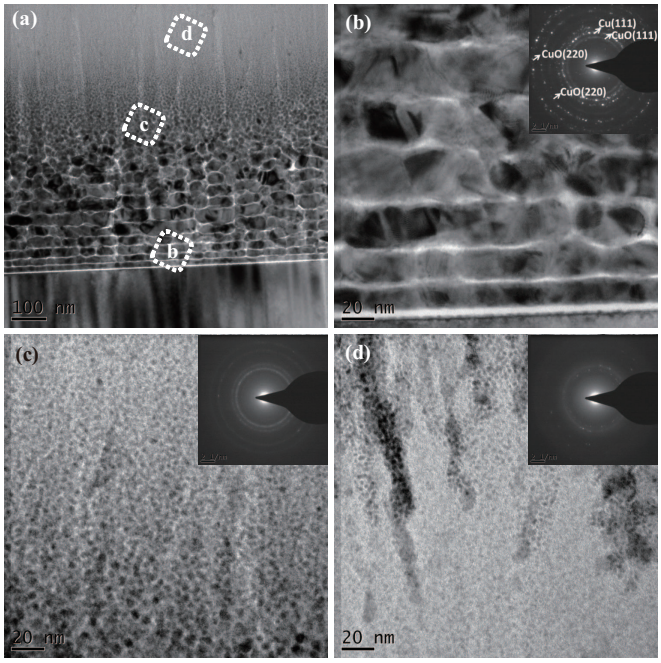



**Fig. 8.** TEM micrographs and corresponding SAED patterns of the copper–carbon film at various positions; the film is prepared at 40% methane concentration and 20 minutes deposition.

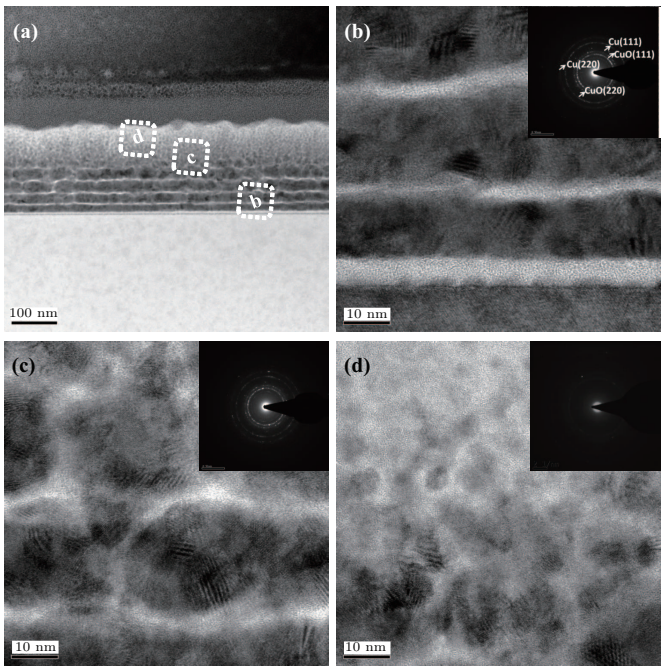



**Fig. 9.** TEM micrographs and corresponding SAED patterns of the copper–carbon film at various positions; the film is prepared at 60% methane concentration and 5 min deposition time.

The optimal growth conditions and composition for self-organizing nano-multilayers in the copper–carbon films are acquired by comparing the composition and microstructure of the three serial films. We superficially describe the optimal growth conditions by the black line in our experimental conditions, as shown in Fig. 10. The copper target maintains good sputtering efficiency with low methane concentration over short deposition time. The methane should be regulated at high concentration to avoid too high a copper concentration in the film to form multilayers; excessive copper causes the film to consist of discontinuous and large copper clusters instead of a multilayered structure. Moreover, the films deposited at high methane concentration possess uniform copper grains and low deposition rate when the deposition time is short, and these uniform grains align parallel to the surface, giving rise to copper-rich layers. Furthermore, low deposition rate is advantageous for the carbon ions and particles to have enough time to synthesize the carbon layer on the top of the copper-rich layer. The sputtering efficiency of the copper target is weakened under the conditions of high methane concentration and long deposition time since a number of carbon ions would be adsorbed on the target surface. When the deposition time is long, methane should be curbed at a low concentration to avoid too many carbon ions being adsorbed on the target, which prevents copper from being sputtered out from the target. Multilayered structure cannot be formed in the film in the absence of copper. Meanwhile, self-organized nano-multilayered structure prefers to form in the films with a copper concentration of 10–25 at.%.

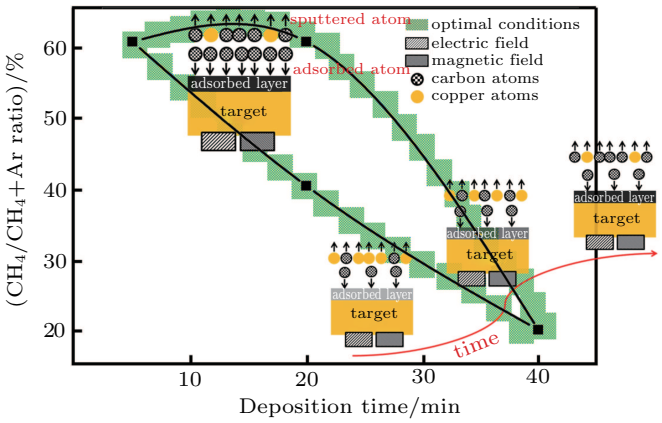



**Fig. 10.** Schematic diagrams of optimal growth conditions for self-organizing nano-multilayered structure in copper–carbon film.

## 4. Conclusion

By comparing the microstructure and composition of copper–carbon films deposited at various methane concentrations with different deposition times, the optimal growth conditions and composition for self-organizing nano-multilayers in copper–carbon films are obtained. Here, it is observed that the nano-multilayered structure is spontaneously formed under two growth conditions. One is that the methane should be curbed at low concentration for long deposition time, and the other condition is that the methane should be controlled at high concentration for short deposition time. It is also demonstrated that the self-organized nano-multilayered structure prefers to form in the films with a copper concentration of around 10–25 at.%. We superficially describe the optimal growth conditions for self-organizing nano-multilayers by schematic diagrams in our experimental conditions. Furthermore, we re-

port for the first time a peculiar microstructure transition phenomenon in copper–carbon film, where the nano-multilayered structure is gradually replaced by the nano-composite structure with deposition time, and finally covered by the amorphous carbon. The self-organized nano-multilayered structure possesses potential value for carbon-based films in the development of industrial production techniques due to its convenient fabrication process.

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