The composition, microstructure and mechanical properties of Ni/DLC nanocomposite films by filtered cathodic vacuum arc deposition

Han Zhou¹, Qingyan Hou², Tianqing Xiao³, Yudong Wang⁴, Bin Liao⁵, Xu Zhang^{*}

Abstract

In this paper, Ni/DLC nanocomposite films were deposited on the un-heated silicon (100) by the filtered cathodic vacuum arc deposition (FCVAD) under different CH₄ and C₂H₂ flow rates. The composition, microstructure and mechanical properties of the Ni/DLC films were investigated by scanning electron microscopy (SEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and nanoindentation. The Ni/DLC films typically consisted of nickel nanograins around 11 nm, which were embedded in amorphous carbon matrix with the thickness of 0.35-2.8 nm. The film structure and the mechanical properties are strongly affected by the precursor gas type and flow rate. The porous structure, with the nanopore size equaling to the nickel grain size, can be seen after the etching process of the as-deposited film, providing a possible method for the preparation of nanoporous DLC films. A maximum hardness of 13.2 GPa and 21.64 GPa is achieved for the Ni/DLC films under the CH₄ flow rate of 30 sccm and C₂H₂ flow rate of 40 sccm, respectively, under which the maximum thickness of the amorphous carbon phase is also obtained.

Key words

Nanocomposite films; Filtered arc deposition; CH₄ flow rate; C₂H₂ flow rate

Introduction

Metal containing carbon nanocomposite films (Me/DLC films) [1-6] which include metal or metal carbide phase embedded in amorphous carbon matrix have attracted a significant attention for the past few decades. The association between the carbon matrix and the encapsulated metallic or metal carbide phase not only improve the overall properties of the nanocomposite films [1,7,8], but also reduce the residual stress in the films which is always an obstacle for the preparation of high quality DLC films. As a transition metal, nickel has always been selected for the preparation of Me/DLC films because its catalysis on the DLC phase, which induces the graphitization of the amorphous carbon and the accompanying phase and structure changes, as well as the noticeable properties of the Ni/DLC films. The microstructure evolution and phase transition based on the deposition temperature, the ratio of carbon and nickel content and other deposition parameters have been focused on the Ni/DLC films [2,3,9]. Accordingly, a series of properties such as the electromagnetism, thermostability, biocompatibility and thermistor have also been investigated [10-12].

To acquire the Me/DLC films, a series of method were carried out such as magnetron sputtering [5], microwave plasma-assisted chemical vapor deposition [11], co-sputtering [9,13], hyperthermal ion deposition [14], and cathodic arc deposition [15]. Comparing with other deposition techniques, filtered cathodic vacuum arc deposition (FCVAD) shows significant advantages such as the fast deposition rate, deriving the dense and ultra-hard films by filtering the large and neutral particles and controlling the composition of the films by conveniently adjusting the device parameters, which can be used more widely for industrialization [16]. During the

plasma deposition process, expect for the experiment parameters mentioned above, the ion bombardment, which can be adjusted by tuning the bias voltage, arc voltage and the flow rate of precursor gas, also plays an important role on the microstructure and the phase transition of films by affecting the surface atom mobility and internal stresses, which have been highlighted in [16-18].

Therefore, this paper investigates the effect of CH₄ and C₂H₂ flow rate on the chemical composition, the structure evolution as well as the mechanical properties of the Ni/DLC nanocomposite films by the FCVAD method.

Experimental procedure

The nanocomposite Ni/DLC films were deposited on (100) single crystalline silicon wafers by filtered cathodic vacuum arc system in a CH₄ and C₂H₂ atmosphere respectively. The schematic of the device is shown in Fig.1. A 100 mm in diameter and a purity of 99.99% of Ni cathode was triggered to produce Ni plasma at a constant arc current of 100 A. The Ni plasma was then affected by an electromagnetic field and imported into the vacuum chamber through a 90° bent duct. The base pressure of deposition chamber was adjusted to 3*10⁻³ Pa before the experiment and the substrate bias was -200 V. During the experiment, the gas flow rate was 10, 20, 30 and 40 sccm, respectively. With increasing the gas flow rate, the chamber pressure increased steadily from 1.5*10⁻² Pa at 10 sccm to a maximum of 4.8*10⁻² Pa at 40 sccm and the deposition rate increased correspondingly.

The microstructure and chemical compositions of nc-Ni/DLC films were examined by Hitachi S-4800 Scanning Electron Microscope (SEM) and relevant EDS respectively. Grazing angle X-ray diffraction (GAXRD) measurement was selected for characterizing the crystal structure of the films, using Ringaku Dmax 2500 diffract meter with Cu K_{α1} radiation. The incident angle was 1° and the scanning range of 2θ was 10-90°. To obtain the average grain size, Scherrer's formula of

$$d = \frac{k\lambda}{B \cos \theta}$$

was used, where k , B , λ , and θ are the constant of 0.89, full width at half maximum (FWHM)(°), wavelength (nm) and diffraction angle (°), respectively. Raman spectra were acquired with a Jobin-Yvon HR800 monochromator cooled CCD at 7 mW power, and the 532 nm line of Ar-Kr laser was used. The surface chemical states of the films were investigated by X-ray photoelectron spectroscopy (XPS) using Al K_α radiation at 320 W constant powers. To exclude the contaminant on the surface of the films, the Ar⁺ sputtering for 30 s was used on the films. The film thickness was measured by surface morphology instrument with the pattern of Talysurf 5P-120 and the deposition rate was measured accordingly. Nanohardness and modulus of elasticity were measured by Wrexham Micro Materials Ltd. Nano test system equipped with a Berkovich diamond tip applying a constant load of 2 mN and six indentations at different places on the surface were measured. To avoid the influence of the substrate, etch indentation depths were ranged from 5% to 10% of the film thickness.

Moreover, the etching process for the as-deposited films immersed in 3M HCl solution for 24h was employed for a better understanding of the structure composition of the Ni/DLC films. The etched films were rinsed by deionized water to exclude the residues in the films and then dried under 60°C for 10 h.

Fig.1 Schematic diagram of filtered cathodic vacuum arc deposition system

Results and discussion

Composition

Fig.2 The comparison of relative content of nickel and carbon in the films under different CH₄ and C₂H₂ flow rate respectively

The compositions of the as-deposited Ni/DLC nanocomposite films under different CH₄ and C₂H₂ flow rates are shown in Fig. 2. With increasing the C₂H₂ flow rate, the carbon content in the Ni/DLC nanocomposite films increases from 19.5 at. % at 10 sccm to a maximum of 59.9 at. % at 40 sccm while the nickel content decreases from 80.5 at. % at 10 sccm to 50.1 at. % at 40 sccm. As the C₂H₂ flow rate increases, more C₂H₂ gas is ionized, resulting the increasing of the carbon content in the films. However, the change of the composition in the films obtained under the CH₄ gas is much different. Except for the low carbon content of 5 at. % obtained under the flow rate of 10 sccm, the carbon content increases subtly from 21.8 at. % at 20 sccm to 23 at. % at 40 sccm, which means that comparing with the situation with using C₂H₂ as precursor gas, the CH₄ flow rate has a subtle influence on the relative contents of carbon and nickel in the films.

The subtle increasing of the carbon content in the films under a higher CH₄ flow rate

may be explained by following two reasons: firstly, the first ionization energy of CH_4 (about 12.61 eV) is higher than that of C_2H_2 (about 11.56 eV) [19], the CH_4 is harder to be ionized than C_2H_2 during the collision with nickel plasma, therefore a lower portion of ionized CH_4 gas is involved in the following deposition process, as the magnetic filter duct ensures that only the ionized particles are involved in the deposition process to acquire the dense and flat films by filtering the neutral and the large particles. Secondly, the more hydrogen ions involved in the deposition of the films under the CH_4 atmosphere induces a much more drastic etching affection of the carbon atoms in the films [4,7,16].

Grain structure and chemical bonding

X R D

a n a l y s i s

Fig. 3(a-b) XRD patterns of films deposited under different CH₄ flow rate (a) and C₂H₂ flow rate (b)

To illustrate the evolution of the crystalline structure of the Ni/DLC films, a series of XRD results for the two sets of samples are shown in Fig. 3(a-b). The diffraction pattern of Ni/DLC films in Fig. 3(a) shows the crystalline structure transformation under the different CH₄ flow rate. For the films deposited at 10 sccm, the diffraction peaks of 44.7°, 51.9° and 76.84° are in good accordance with the lattice plane (111), (200) and (220) of fcc Ni (PDF#04-0850) [3,11,20]. With increasing the CH₄ flow rate to 20 sccm, a new peak at 39.1° accords with the lattice plane of (100) of rhomb Ni₃C (PDF#04-0853) appears, indicating the appearance of rhomb Ni₃C and a mixed structure of fcc Ni and rhomb Ni₃C in the films. The broad peak at 44.7° is also assigned to the superposition of diffraction peaks from fcc Ni and rhomb Ni₃C. A further increasing of the CH₄ flow rate leads to the formation of pure rhomb Ni₃C structure in the films, for the peaks at 39.1°, 41.5°, 44.5° and 58.4° corresponds with the plane of (100), (002), (101) and (102) of rhomb Ni₃C, respectively. The increasing intensity and the decreasing width of the peaks under 30 sccm indicate the growth of Ni grains. However, under the different C₂H₂ flow rates the XRD patterns of the films all have the peaks at 39.1°, 41.5°, 44.5° and 58.4° corresponds with the plane of (100), (002), (101) and (102) of rhomb Ni₃C, respectively, as shown in fig. 3(b). The preferred orientation of the peak (101) becomes weak with increasing the C₂H₂ flow rate. The difference of the grain structure evolution under the different gas type can be associated with the relatively low affinity between nickel and carbon atoms. The insufficient carbon atoms under the lower CH₄ flow rates make carbon atoms less possible to be captured by the nickel ad-atoms to be formed as nickel carbide structure.

Raman analysis

Fig. 4(a-b) Raman spectroscopy under different CH₄ flow rate (a) and C₂H₂ flow rate (b)

Table.1 Parameters of Raman spectroscopy under the CH₄ flow rate of 30 sccm and 40 sccm

CH ₄ flow rate/sccm	D peak position/cm ⁻¹	G peak position/cm ⁻¹	FWHM of D peak	FWHM of G peak	I _D /I _G
30	1428.75	1583.49	184.17	65.85	2.2
40	1398.47	1563.2	205.1	91.94	1.47

Table. 2 Parameters of Raman spectroscopy under the C₂H₂ flow rate of 20sccm, 30 sccm and 40 sccm

C ₂ H ₂ flow rate/sccm	D peak position/cm ⁻¹	G peak position/cm ⁻¹	FWHM of D peak	FWHM of G peak	I _D /I _G
20	1398.47	1563.2	205.1	91.94	1.47
30	1428.75	1583.49	184.17	65.85	2.2
40	1428.75	1583.49	184.17	65.85	2.2

20	1385.15	1560.67	126.49	182.48	0.75
30	1386.19	1567.48	120.86	244.46	1.8
40	1387.94	1566.31	120.64	290.97	2.68

Fig. 4(a-b) summarizes the Raman spectroscopy of Ni/DLC films under the different CH₄ flow rate and C₂H₂ flow rate. The amorphous carbon peaks could be hardly detected under the low CH₄ flow rate of 10 sccm. With increasing the flow rate, the appearance of D band located around 1350 cm⁻¹ assigned to the disorder-induced band and G band located around 1580 cm⁻¹ assigned to the E_{2g} symmetric vibrational mode of sp² band indicate the existence of amorphous carbon [21,22]. The attendance of O-O peak around 1550 cm⁻¹, which is relevant to the oxygen in the air, implies the low amorphous carbon phase in the films. The subtle increase of the intensity of the amorphous carbon peaks is consistent with the composition result obtained above that the carbon content increases little with increasing the CH₄ flow rate. The Raman peaks of amorphous carbon at 30 and 40 sccm can be fitted with two Gaussian peaks and the corresponding fitting parameters, such as the position and FWHM of D and G peaks, the ratio of I_D and I_G, are shown in table. 1. The I_D/I_G for the films at 30 sccm and 40 sccm is 2.2 and 1.47, respectively. The obtained Raman spectra for Ni/DLC films deposited under different C₂H₂ flow rate are presented in fig. 4(b). The obviously much higher intensities of D and G peaks indicate the more portion of amorphous carbon exists in the films. As shown in table. 2, the blue shift of the position of D and G peaks comparing the ones under CH₄ flow rates indicates the difference of compressive resistance in the films. Considering a lower I_D/I_G indicates a more sp³ content to some extent [20,21], the increasing of I_D/I_G from 0.75 to 2.68 with increasing the C₂H₂ flow rate shows the films are more graphitized under higher C₂H₂ flow rate.

XPS analysis

Fig. 5(a-d) high resolution spectra of the films for C1s under different CH₄ flow rate (a) and different C₂H₂ flow rate (b); the typical Ni2p spectra of the deposited films (c); the typical O1s spectra of the deposited films under C₂H₂ flow rate (d)

The XPS spectra of the Ni/DLC films are presented in Fig. 5. The films were sputtered by Ar⁺ for 30 s to exclude the contamination of C and O in the air. The C1s spectra in the films under the different CH₄ and C₂H₂ flow rate are shown in fig. 5(a) and fig. 5(b), respectively. Except for the spectra of C1s under the CH₄ flow rate of 10 sccm, whose intensity is too low to be fitted, the high resolution of C1s spectra under different CH₄ flow rate can be fitted by three peaks. The peaks around 284.4 eV and 285.3 eV can be labeled as sp²-C bond and sp³-C bond in amorphous carbon phase, respectively [3,23]. Considering the Ni₃C peak which is located at 281.5 eV is absent in our C1s spectra, The peak around 283.5 eV labeled as the Ni-C bond might be explained by two reasons: one is that the Ni-C bond belongs to the nickel carbide phase which exists as a transmission between the encapsulated nickel phase and the surrounded amorphous carbon matrix; the other is that the Ni-C bond corresponds with the interstitial solid solution formed by the random insertion of the carbon ad-atoms in metalized nickel phase [23]. The high portion of the Ni-C peak shows that most of the carbon atoms exist as nickel carbon phase in the films and the concentration of amorphous carbon is relatively low. Moreover, the peaks of C-O bond and C=O bond which should be located at 286.6 eV and 288.3 eV in C1s were too low to be recognized. For the high resolution of C1s under different C₂H₂ flow rate five peaks are fitted, which are shown in fig. 5(b). The peaks at 284.4 eV, 285.3 eV, 283.5 eV is also corresponding with sp²-C bond, sp³-C bond and C-Ni bond, respectively. Moreover, the other two peak located at 286.6 eV and 288.3 eV are labeled as C-O bond and C=O bond. The much more portion of sp²-C and sp³-C indicates the higher amorphous carbon content in the films. The typical Ni2p spectra for the films under CH₄ and C₂H₂ flow rates and the typical O1s for the films under C₂H₂ flow rate are given in Fig. 5(c-d). For the Ni2p shown in fig. 5(c), the peak located at 852.4 eV is assigned to metal Ni but the subtle shift of this peak comparing with that of metal nickel [23] indicates the existence of the nickel carbide phase. Another two peaks located at 854.4 eV and 859 eV are assigned as the oxide of nickel obtained by the contamination in the air [23,25]. Because of the low oxygen content in the films under CH₄ flow rate, only the typical O1s spectrum for the films under different C₂H₂ flow rate is shown in fig. 5(d). As can be seen, three peaks located at 529.6 eV, 531.6 eV and 533.8 eV are attributed to O-C/O=C, NiO and Ni₂O₃ respectively, which have a good coincidence with the peaks of C-O/C=O at 286.6 eV/288.3 eV in C1s and the Ni-O peak at 854.4 eV/859 eV in Ni2p.

Grain size and mean phase separation

Fig. 6(a-b) the schematic of the metal nickel phase (a) and the surrounded amorphous carbon matrix (b)

To calculate the thickness of the amorphous carbon phase in the films, the microstructure of films was simplified as the adjacent cubic with gaps equaling to the thickness of amorphous carbon [6,26], and the schematics are shown in fig. 6. Considering the basic repetitive unit, the relationship between nickel phase and amorphous carbon phase can be calculated as follows:

$$\frac{m_{Ni}}{M_{Ni}} = \frac{m_{a-C}}{M_{a-C}}$$

Thus, the thickness of amorphous carbon s can be calculated by the following simplification:

$$\frac{8d^3}{12sd^2 + 4s^2d + s^3} = \frac{\rho_{a-C} M_{Ni} [Ni]\%}{\rho_{Ni} M_{a-C} [a-C]\%}$$

In this formula, V_{Ni} and V_{a-C} are the volume of Ni and amorphous carbon respectively, d is the grain size, ρ_{Ni} stands for the density of mental Ni, taken equal to 8.9 g/cm³, ρ_{a-C} for the density of amorphous carbon, approximates 2.5 g/cm³, M_{Ni} and M_{a-C} are the atomic weight of Ni and a-C, equals to 58.7 amu and 12 amu respectively. [Ni]% and [a-C]% represent the concentration of Ni and a-C.

Fig.7 Grain size and the mean separation of the films under different CH₄ and C₂H₂ flow rate respectively

The grain size derived from the XRD using Scherrer formula and the mean separation which equals to the thickness of amorphous carbon phase are shown in Fig. 7. It should be noted that the grain sizes under the situation are around 11 nm and have a relatively subtle change under either the gas type or the flow rate. The mean

separations calculated by the cubic model are only about 0.345 nm and 1.01 nm at 10 sccm under CH₄ and C₂H₂ flow rate, respectively. With increasing the CH₄ flow rate, the mean separation increases slightly and keeps around 1.56 nm, which has the similar trend with the carbon content in the films in that situation. For the condition under C₂H₂ flow rate, the mean separation keeps increasing and up to a maximum of 2.68 nm under 40 sccm, indicating much more amorphous carbon content in the films.

SEM analysis

Fig. 8(a-b) Cross sectional structure of the as-deposited Ni/DLC films under the CH₄ flow rate(a) and C₂H₂ flow rate(b)

Fig.8 (a-b) shows the cross-sectional structure of the as-deposited Ni/DLC films under different CH₄ and C₂H₂ flow rate, respectively. Under the relatively low CH₄ flow rate of 10 sccm, the sufficient nickel content of about 95 at. % in the film induces a typical metal morphology of the cross section, which is shown in fig.8 (a). A further increasing of the CH₄ flow rate has little effect on the carbon content but induces a structure evolution of the films with the cross structure transforming from

spherical to columnar. Under the CH₄ flow rate of 20 sccm, the cross-sectional structure of the film exhibits spherical structure, indicating the surface diffusivity induced repeat nucleation dominates during the deposition process. With farther increasing the CH₄ flow rate, the morphology turns to an elongated one and eventually to columnar, whose length was almost comparable with the thickness of film under 40sccm. However, for the films under different C₂H₂ flow rate which is shown in fig. 8(b), the structure evolution occurs from the columnar to dense spherical structure with the C₂H₂ flow rate keeps increasing, which is totally opposite

to the one under CH₄ flow rate.

Fig. 9(a-b) Cross sectional structure of the Ni/DLC films at the flow rate of 20sccm after the etching process under CH₄ flow rate (a) and C₂H₂ flow rate (b)

For a further understanding of the phase type of the films, the as-deposited films under the flow rate of 20 sccm were etched by 3M HCl solution and the corresponding cross sectional images are shown in fig. 9(a-b). For the cross-sectional structure of the etched film obtained under 20sccm of CH₄ flow rate, which is shown in fig. 9(a), nanopores can be clearly seen after the etching process and the size of the pores is about 10 nm, equaling to the grain size obtained by the XRD results. Moreover, only 20 at. % of the Ni atoms is left in the etched film, which is much lower than the original Ni content about 79 at. % in the deposited film, indicating a large part of Ni atoms was etched during the etching process. For the etched film under the same C₂H₂ flow rate shown in fig. 9(b), the cross-sectional structure with finer grains comparing with the un-etched columnar grains indicates the thorough penetration of the film and the etching process had an obvious affection on the grain boundary. Considering high overpotential of the oxidation for nickel carbide as compared with metal nickel in the acid solutions [27], the nickel carbide could hardly be etched in HCl solutions. Thus, the nanopores obtained after the etching process under the CH₄ flow rate of 20 sccm might be explained by the dissolution of fcc nickel phase, which also confirms the coexistence of the fcc Ni and nickel carbide phase in the film under the CH₄ flow rate of 20sccm.

As the results obtained above, the etching process might provide an available

method for the identification of the phase structure in the Ni/DLC films and the possibility for the preparation of the nanoporous carbon thin films.

Mechanical properties

Fig. 10 The nanohardness of the films under different CH₄ and C₂H₂ flow rate

According to the nano indentation test, the hardness of the as-deposited Ni/DLC films under different CH₄ and C₂H₂ flow rate are plotted in Fig. 10. At the CH₄ flow rate of 10 sccm, the hardness of the film is only about 7.3 GPa, which is only a little higher than the pure Ni film of 6 GPa [28], this result is of good consistence with the result discussed above that the film is dominant by metal nickel phase at the CH₄ flow rate of 10 sccm. With increasing the CH₄ flow rate, the hardness of the films changes subtle and has a maximum of 13.2 GPa at 30 sccm, at which the mean separation has a maximum of 1.43 nm. The hardness of the Ni/DLC nanocomposite films deposited under the C₂H₂ gas is higher than the ones under CH₄ flow rate. With increasing the C₂H₂ flow rate the hardness has a maximum of 21.64 GPa at 40 sccm at which the max mean separation of 2.68 nm is also obtained. The hardness of nanocomposite films is the integrated results of the carbon content, the grain size and category in the matrix and the sp³ content in carbon matrix [28], the maximum of hardness obtained under the flow rate at which the mean separation has a maximum obtained in the both situation indicates the affection of second-phase strengthen mechanism by the introduction of the carbon phases in the films, which is always associated with the ion bombardment during the films deposition.

Conclusions

Ni/DLC films deposited under room temperature by the FCVAD technique with using CH₄ and C₂H₂ as the precursor gas have been investigated by the means of XRD, SEM, Raman and XPS. The nanostructure and the mechanical properties of the films under the different situation are strongly affected by the gas flow rate and type.

With increasing the CH₄ flow rate, the grain type from pure fcc Ni, through coexisting rhomb Ni₃C and fcc Ni, to a pure rhomb Ni₃C phase and a film structure evolution from spherical to columnar is occurred with increasing the CH₄ flow rate while the relative content of carbon and nickel atoms change little as the flow rate exceeds 20 sccm. For the Ni/DLC films under C₂H₂ flow rate, the grain type keeps constant in a relatively large carbon content scale from 19.5 at. % to 59.9 at. %, offering a possibility for the preparation of films with stable grain type under broader

tuning parameters. The grain sizes are all around 11 nm under the different gas type and flow rate. The maximum hardness of the film about 13.2 GPa and 21.64 GPa are obtained under the CH₄ flow rate of 30 sccm and C₂H₂ flow rate of 40 sccm respectively, at which the maximum of mean separation of 1.43 nm and 2.68 nm is also obtained, indicating the hardness reinforcement mechanism of the Ni/DLC films compared with pure Ni films induced by effective load transfer of the second phase. Moreover, during the etching process of the as-deposited films, the existence of nanopores whose size is almost consistent with the grain size of the nickel phase makes porous DLC films possible by the simple etching process of the Ni/DLC films.

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