Preparation and structural properties of thin carbon films by very-high-frequency magnetron sputtering*

Ming-Wei Gao(高明伟)[1], Chao Ye(叶超)[1,2,†], Xiang-Ying Wang(王响英)[3], Yi-Song He(何一松)[1], Jia-Min Guo(郭佳敏)[1], and Pei-Fang Yang(杨培芳)[1]

[1] *College of Physics, Optoelectronics and Energy, Soochow University, Suzhou* 215006, *China*
[2] *Key Laboratory of Thin Films of Jiangsu Province, Soochow University, Suzhou* 215006, *China*
[3] *Medical College, Soochow University, Suzhou* 215123, *China*

(Received 25 January 2016; revised manuscript received 7 March 2016; published online 1 June 2016)

Growth and structural properties of thin a-C films prepared by the 60 MHz very-high-frequency (VHF) magnetron sputtering were investigated. The energy and flux of ions impinging the substrate were also analyzed. It is found that the thin a-C films prepared by the 60 MHz sputtering have a lower growth rate, a smooth surface, and more sp^3 contents. These features are related to the higher ion energy and the lower ions flux onto the substrate. Therefore, the 60 MHz VHF sputtering is more suitable for the preparation of thin a-C film with more sp^3 contents.

Keywords: carbon thin films, very-high-frequency sputtering, structural properties

PACS: 52.80.Pi, 81.15.Cd, 68.55.–a **DOI:** 10.1088/1674-1056/25/7/075202

1. Introduction

Amorphous carbon (a-C) and diamond-like carbon (DLC) films have attracted a great deal of attention for a long time because of their unique properties, such as high hardness, low friction, high wear resistance, chemical inertness, low magnetic susceptibility, and large optical band gap.[1–11] These properties are critical to many applications, such as magnetic storage devices and microelectromechanical systems. Recently, the thin (< 30 nm)[1] and ultrathin (< 2 nm)[2] a-C films are of particular interest as protective overcoats in several leading technologies. For this application, the a-C films with high hardness, low friction, and very thin thickness are needed. Because the mechanical properties depend on the stronger σ bonds in the films,[5] the sp^3 contents in the a-C films should be increased as high as possible.

To synthesize thin a-C films, several deposition methods can be used, including (low pressure) radio frequency (RF) sputtering,[1,3–5] filtered cathodic vacuum arc (FCVA),[5] and pulsed DC sputtering.[2] By these methods, it is found that the ion bombardment energy is a key factor affecting the sp^3 contents and the films roughness of a-C films.[4] Thus, in order to increase the sp^3 contents in the a-C films and improve the film hardness and roughness, the ion energy should be effectively increased, usually to 20–30 eV,[2] by applied substrate bias or using FCVA.[2,4] However, because of the higher deposition rate (at least 10 nm/min) in the RF sputtering and FCVA technology,[5] for the ultrathin a-C film deposition, the deposition time must be very short (0.2–0.4 min),[4,5] which makes the control of film thickness very difficult. Recent works on the magnetron sputtering driven by some special frequency (2 MHz, 13.56 MHz, 27.12 MHz, and 60 MHz) showed that the driving frequency can effectively influence the energy and flux of ions impinging the substrate, and the 60 MHz magnetron sputtering has a feature of a lower deposition rate and higher ion energy.[12,13] This feature makes the 60 MHz magnetron sputtering more suitable for the preparation of thin a-C film as protective overcoat application. However, the investigation on this method is seldomly reported. Therefore, in this work, the 60 MHz very-high-frequency (VHF) magnetron sputtering is developed to deposit the thin a-C films. The growth and structure properties of the thin a-C films are investigated, and the possible relationship between the growth and structure of thin a-C films and the plasma properties are discussed.

2. Experimental details

In the experiment, the a-C thin films were deposited on n-type (100) silicon wafers and NaCl wafers by an unbalanced planar magnetron sputtering.[12,14,15] The reactor was a cylindrical vacuum chamber made of stainless steel, had a diameter of 350 mm and a height of 300 mm, in which the circular 99.999% pure (5 N) carbon target with a diameter of 50 mm, mounted on the water-cooled copper surface, was placed at the top of the chamber, and the stainless steel substrate holder with a diameter of 100 mm was set at the bottom, about 70 mm away from the target surface. The wall of the reactor was electrically grounded, but the substrate holder was electrically floated. The sputtering target was biased with a VHF voltage of 60 MHz through the corresponding matching box. As a comparison, the a-C thin films were also deposited

*Project supported by the National Natural Science Foundation of China (Grant No. 11275136).
†Corresponding author. E-mail: cye@suda.edu.cn
© 2016 Chinese Physical Society and IOP Publishing Ltd

using a 13.56 MHz RF magnetron sputtering. The input power applied to the sputtering target was varied from 100 W to 250 W. The device was pumped down to a base pressure less than 5×10^{-4} Pa before each deposition, with a 600 l/s turbo-molecular pump backed up with a mechanical pump. Argon with a fixed flow rate of 30 sccm was used as the discharge gas and the operating pressure was maintained at 4.7–5.0 Pa. The target was pre-sputtered in Ar for 10 min prior to each run. The deposition time was fixed at 30 min.

The surface morphology of a-C thin films was measured using a Bruker Dimension Icon atomic force microscopy (AFM) with semicontact operating mode. The Raman spectra of the a-C thin films were recorded with a JY HR800 Raman spectrometer in the Raman shift range of 1200–1700 cm^{-1} with a resolution of 1 cm^{-1}. The laser excitation line was 514 nm and a laser power was 5 mW. The bond configurations of a-C thin films were characterized by a Bruker VERTEX80 Fourier transform infrared (FTIR) instrument operating in the wavenumber range of 600–4000 cm^{-1} with a resolution of 0.2 cm^{-1}. The film thickness and optical property were measured by using J.A.Woollam M-2000D spectroscopic ellipsometry (SE). For the AFM, Raman, and SE characterizations, the a-C thin films deposited on the Si wafer substrates were used, while for the FTIR characterization, the a-C thin films deposited on the NaCl wafer substrates were used. In order to understand the possible reason for the growth of a-C thin films, the energy and flux of ions impinging the substrate were measured at the substrate using the Semion HV-2500 retarding field energy analyzer (RFEA).

3. Results and discussion

3.1. Growth rate of a-C films

Using spectroscopic ellipsometry, the thicknesses of a-C films were measured, which are in the range of 12.7–28.9 nm (60 MHz sputtering) and 13.7–45.6 nm (13.56 MHz sputtering), respectively, increasing with the sputtering power (from 100 W to 250 W). Because the thicknesses of a-C films deposited by the 60 MHz VHF sputtering are thinner than 30 nm, they are thin a-C films, not ultrathin a-C films. According to the film thickness, the growth rates of a-C films are calculated, which are in the range of 0.42–0.97 nm/min (60 MHz sputtering) and 0.46–1.52 nm/min (13.56 MHz sputtering), respectively, as shown in Fig. 1. It can be seen that a low growth rate of 0.42 nm/min can be achieved using the 60 MHz VHF sputtering. Thus, if the deposition time is decreased to about 5 min, the film thickness can be reduced to ~ 2 nm. This growth rate is largely lower than that of ultrathin a-C films synthesized by RF low-pressure sputtering (11.6 nm/min)[4] and FCVA (12 nm/min).[5] Therefore, the low growth rate of 60 MHz VHF sputtering makes it easy to control the film thickness, not as in the RF low-pressure sputtering and FCVA, the deposition time must be exactly controlled to 0.4 min[4] or 12–30 s.[5]

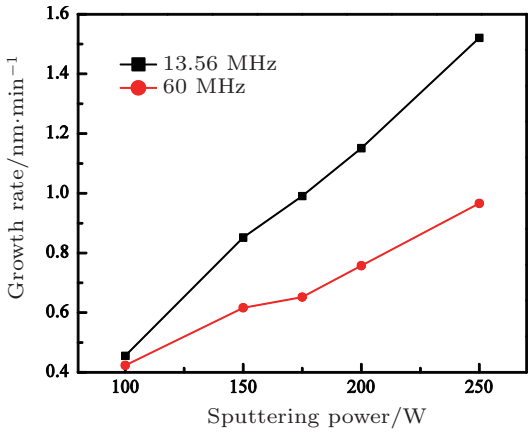


Fig. 1. (color online) The variation of growth rate with the sputtering power.

3.2. Surface morphology of a-C films

The surface morphologies of a-C films were analyzed using the AFM technique. Figure 2 shows the 2D AFM amplitude error images of a-C films in a representative area of 2 μm × 2 μm. For the a-C films deposited using 60 MHz VHF sputtering, as the film thickness is as thin as 12.7 nm (deposited at 100 W), the film shows a very flat and smooth surface, as shown in Fig. 2(a). As the film thickness increases to 18.5 nm (deposited at 150 W) and 28.9 nm (deposited at 250 W), the film also shows a very flat and smooth surface, as shown in Figs. 2(b) and 2(c). However, for the a-C films deposited using 13.56 MHz RF sputtering, the surface morphologies are different. The films are composed of a smooth base film and some small carbon grains (indicated by arrows). This surface morphology can also be seen in the amorphous hydrogenated carbon (a-C:H) films via an industrial process, and the formation of carbon grains is thought to relate to the higher deposition rate.[8] As the film thickness is as thin as 13.7 nm (deposited at 100 W), many small carbon grains on the smooth base film can be found, as shown in the Fig. 2(d). As the film thickness increases to 25.6 nm (deposited at 150 W), the size of carbon grains increases and the density of carbon grains decreases, but the surface of the base film is still smooth, as shown in Fig. 2(e). As the film thickness increases to 45.6 nm (deposited at 250 W), the size of carbon grains does not change and the low density of carbon grains remains, but the surface of base film becomes rough, as shown in Fig. 2(f).

From the AFM images, using NanoScope analysis software, the average mean roughness R_a was calculated. The variation of R_a with the sputtering power is shown in Fig. 3. It can be seen that R_a is in the range of 0.94–2.79 nm (60 MHz sputtering) and 2.12–6.07 nm (13.56 MHz sputtering), respectively. Because the surface morphologies of the films deposited at 60 MHz are almost the same, R_a only increases

slightly with the sputtering power. However, for the films deposited at 13.56 MHz sputtering, the variations of both carbon grain size and base film roughness lead to the large variation of R_a with sputtering power. Although R_a of a-C thin film prepared by 13.56 MHz sputtering at 150 W is close to that of 60 MHz, the surface morphologies of these two films are different. Therefore, the a-C films prepared by 60 MHz VHF sputtering have more of a flat and smooth surface.

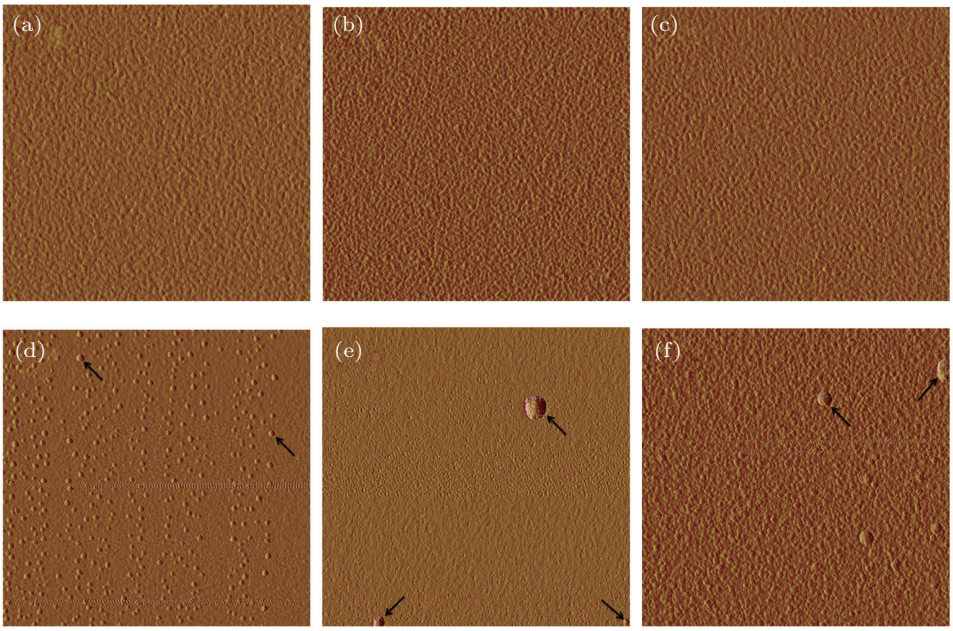


Fig. 2. (color online) 2D AFM amplitude error images of a-C films deposited at (a) 60 MHz, 100 W; (b) 60 MHz, 150 W; (c) 60 MHz, 250 W; (d) 13.56 MHz, 100 W; (e) 13.56 MHz, 150 W; and (f) 13.56 MHz, 250 W.

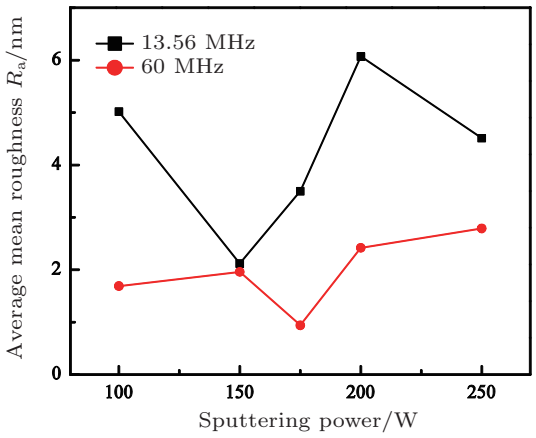


Fig. 3. (color online) Variation of average mean roughness R_a with the sputtering power.

3.3. Bonding properties of a-C films

Figure 4 shows the Raman frequency shifts of the a-C films deposited at the sputtering power of 250 W for the 60 MHz and 13.56 MHz sputtering, respectively. For the 60 MHz sputtering, two weak peaks located at 1340 cm^{-1} (peak 1) and 1472 cm^{-1} (peak 2) can be seen. Usually, the Raman spectra of carbon films have two main peaks, the D peak around 1350 cm^{-1}, corresponding to disorder-allowed phonon modes, and the G peak around 1560 cm^{-1}, corresponding to the E_{2g} symmetry of graphitic sp^2 bonded carbon.[2,7,16] The intensity ratio between the D peak and G peak as well as the position of the G peak are related to the sp^3 content in the carbon films.[2] In this work, peak 1 corresponds to the D peak, but peak 2 diverges from the position of a typical G peak and shifts to a lower wavenumber. This shift of peak position to a lower wavenumber is indicative of the increase of the sp^3 content in the a-C films.[2,7] However, for the 13.56 MHz RF sputtering, a very weak peak centered at about 1590 cm^{-1} (peak 3), corresponding to the G peak, can be found. The weak peaks probed in these Raman spectra may be related to the visible excitation (514 nm) used here because the intensity and the exact peak position of the Raman spectrum depend on the wavelength of excitation.[2] Therefore, more sp^3 content can be obtained in the a-C films deposited by the 60 MHz VHF sputtering.

Figure 5 shows the FTIR spectroscopy of the a-C films deposited at the sputtering power of 250 W. For the a-C films prepared using the 60 MHz VHF sputtering, the main absorption peak is a wide C=C peak at 1650 cm^{-1}. In addition, some small absorption peaks can also be found, including the sp^3 C–C peaks at 1450 cm^{-1} and 1380 cm^{-1}, as well as the C–O peak at 1040 cm^{-1}.[17] However, for the a-C films prepared using the 13.56 MHz RF sputtering, the absorption peaks include a wide C=C peak at 1650 cm^{-1} and a weak C–O peak at 1040 cm^{-1}, and no other absorption is found. The result also shows that the a-C thin films prepared using the 60 MHz VHF sputtering have more sp^3 content.

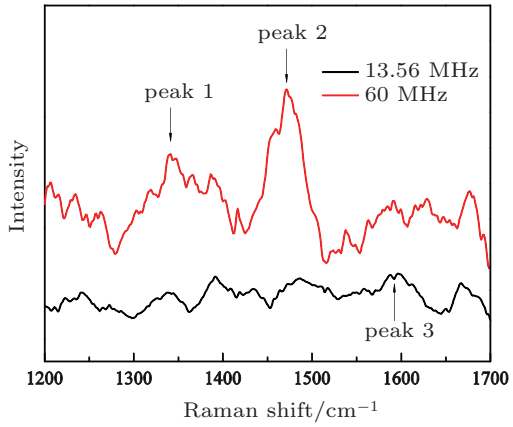


Fig. 4. (color online) Raman frequency shifts of the a-C films.

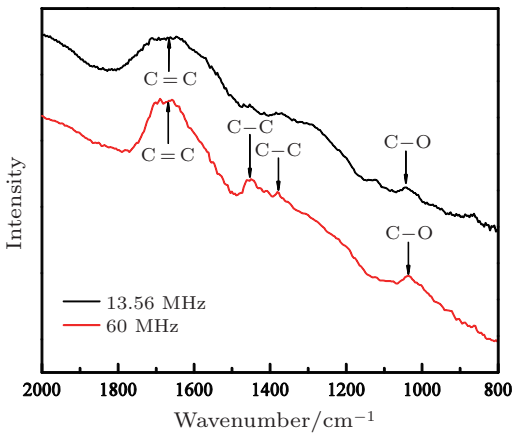


Fig. 5. (color online) FTIR spectroscopy of the a-C thin films.

3.4. Optical properties of a-C films

Figure 6 shows the variation of refractive index with wavelength for the a-C films prepared using the 60 MHz and 13.56 MHz sputtering at the power of 250 W. It can be seen that the refractive index decreases with the wavelength in the range of 600–1400 nm. The refractive index is about 1.59–1.55 and 1.56–1.52 for the films prepared by the 60 MHz and 13.56 MHz sputtering, respectively. Thus, the a-C film prepared by the 60 MHz sputtering has a bigger refractive index at the same measured wavelength. Because the refractive index of a-C film changes linearly with sp^3 carbon fraction in the film,[16] the bigger refractive index indicates that the a-C film deposited by the 60 MHz sputtering has more sp^3 carbon fraction.

From the above results, compared with that of 13.56 MHz RF sputtering, the a-C films prepared by the 60 MHz VHF sputtering have a lower growth rate, a flat and smooth surface, and more sp^3 carbon fraction. Thus, the 60 MHz VHF sputtering is more suitable for the preparation of ultrathin a-C films.

The deposition of a-C films by magnetron sputtering is related to the following three sequential processes: (i) carbon species (atoms, ions, and radicals) sputtered from the graphite target by impinging energetic Ar^+ ions, (ii) carbon species transport through the plasma space, and (iii) diffusion of carbon species arriving at the substrate surface, resulting in the formation of stable chemical bonds with preexisting carbon atoms.[18] Thus, the film thickness h is thought to depend on the sputtering rate β of the target ($\beta = \gamma J_{Ar+}$, where γ is the sputtering yield, J_{Ar+} is the Ar^+ ion flux) and the deposition time t, while the film roughness and the formation of sp^3 carbon bonding is thought to depend on the ion bombardment, further on the kinetic energy and flux of impinging ions.[4,18,19] In order to understand the possible reason for the growth and structure of a-C films prepared by the 60 MHz VHF sputtering, the energy and flux of ions impinging the substrate were further analyzed.

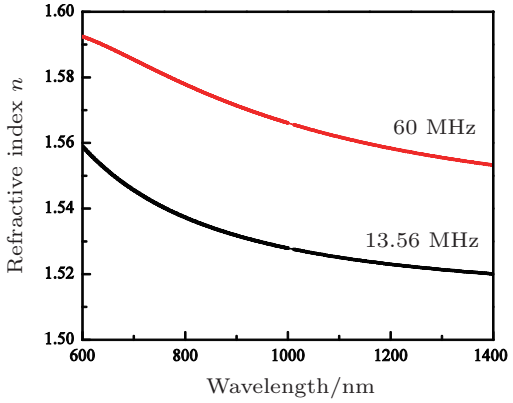


Fig. 6. (color online) Variation of refractive index with wavelength.

Figure 7(a) shows the variation of maximum ion energy E_{max} with sputtering power, which is in the range of 25.8–32.2 eV (60 MHz sputtering) and 16.6–18.3 eV (13.56 MHz sputtering), respectively. It can be seen that the driving frequency causes a difference in ion energy. This energy difference can influence the formation of sp^3 carbon bonding and films roughness.

For the sp^3 carbon bonding, its formation is mainly controlled by the collisions of higher energy impinging ions (usually 20–30 eV[2]) with carbon atoms on the growing film surface.[18,19] For the 60 MHz VHF sputtering, the energy of ions impinging the substrate is equal to that of controlling the formation of sp^3 carbon bonding, thus the collisions can promote the formation of sp^3 carbon bonding.

For the film roughness, its value is also related to the energy of ions impinging the substrate. During depositing films, the collisions of impinging ions can control the plasma-related heating by transferring energy to the surface atom, affecting adatom migration, films growth, and morphology.[20] For the 60 MHz VHF sputtering, because of the higher ion energy, the ions impinging the substrate enhance the carbon atoms surface diffusion and promote the formation of smooth films, thus leading to a lower R_a.

Figure 7(b) shows the variation of ion flux J with sputtering power, which is in the range of 0.021–0.044 A/m^2 (60

MHz sputtering) and 0.049–0.081 A/m^2 (13.56 MHz sputtering), respectively. Because the sputtering rate depends on the sputtering yield and the ion flux J_{Ar+}, the small ion flux J at 60 MHz sputtering leads to a lower sputtering rate. Thus, the film thickness can be easily controlled.

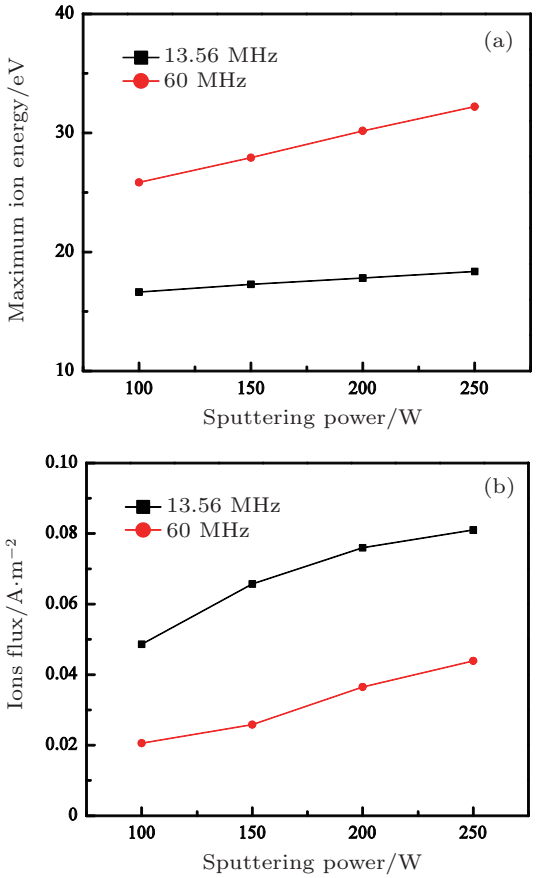


Fig. 7. (color online) Variation of (a) maximum ion energy and (b) ion flux with sputtering power.

To sum up, the 60 MHz VHF sputtering is a kind of sputtering with higher ion energy and lower ion flux. The higher ion energy can promote the formation of sp^3 bonded films and enhance the adatom surface diffusion to form smooth films, while the lower ion flux can reduce the growth rate and make it easy to control film thickness. Therefore, the 60 MHz VHF sputtering is more suitable for the preparation of ultrathin a-C films.

4. Conclusions

We investigated the growth and structural properties of a-C films prepared by the 60 MHz VHF magnetron sputtering. The ion energy and ion flux onto the substrate were also analyzed. The surface morphology analysis by AFM shows that the a-C films have a very flat and smooth surface with a lower average mean roughness. The bonding properties analysis by Raman and FTIR and the optical property analysis by SE show that the a-C films have more sp^3 content. The thickness measurement shows that the a-C films have a lower growth rate. By measuring the ion energy and ion flux, it is found that these features are related to the higher ion energy and the lower ion flux of the 60 MHz VHF sputtering. Therefore, the 60 MHz VHF sputtering is more suitable for the preparation of ultrathin a-C films with more sp^3 content.

References

[1] Wan D and Komvopoulos K 2007 *J. Phys. Chem. C* **111** 9891
[2] Dwivedi N, Yeo R J, Goohpattader P S, Satyanarayana N, Tripathy S and Bhatia C S 2015 *Diamond Relat. Mater.* **51** 14
[3] Lu W, Komvopoulos K and Yeh S W 2001 *J. Appl. Phys.* **89** 2422
[4] Xie J and Komvopoulos K 2015 *Surf. Coat. Technol.* **262** 15
[5] Matlak J and Komvopoulos K 2015 *Thin Solid Films* **579** 167
[6] Coskun Ö D and Zerrin T 2015 *Diamond Relat. Mater.* **56** 29
[7] Sun P, Hu M, Zhang F, Ji Y Q, Liu H S, Liu D D and Leng J 2015 *Chin. Phys. B* **24** 067803
[8] Catena A, McJunkin T, Agnello S, Gelardi F M, Wehner S and Fischer C B 2015 *Appl. Surf. Sci.* **347** 657
[9] Wang Y J, Li H X, Ji L, Liu X H, Wu Y X, Zhou H D and Chen J M 2012 *Chin. Phys. B* **21** 016101
[10] Jiang J L, Wang Y B, Wang Q, Huang H, Wei Z Q and Hao J Y 2016 *Chin. Phys. B* **25** 048101
[11] Wang J, Liu G C, Wang L D, Deng X L and Xu J 2008 *Chin. Phys. B* **17** 3108
[12] Huang F P, Ye C, He H J, Liu Y, Wang X Y and Ning Z Y 2014 *Plasma Sources Sci. Technol.* **23** 015003
[13] Ye C, He H J, Huang F P, Liu Y and Wang X Y 2014 *Phys. Plasma* **21** 043509
[14] He H J, Ye C, Wang X Y, Huang F P and Liu Y 2014 *ECS J. Solid State Sci. Technol.* **3** Q74
[15] He Y S, Ye C, Wang X Y, Gao M W, Guo J M and Yang P F 2016 *Appl. Surf. Sci.* **363** 477
[16] Dai H Y, Cheng X R, Wang C F, Xue Y C and Chen Z P 2015 *Optik* **126** 861
[17] Tolstoy V P, Chernyshova I V and Skryshevsky V A 2003 *Handbook of Infrared Spectroscopy of Ultrathin Films* (Hoboken: John Wiley & Sons, Inc.)
[18] Wan D and Komvopoulos K 2006 *J. Appl. Phys.* **100** 063307
[19] Wan D and Komvopoulos K 2006 *Appl. Phys. Lett.* **88** 221908
[20] Ostrikova K, Neytsb E C and Meyyappanc M 2013 *Adv. Phys.* **62** 113