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Effects of anode layer linear ion source on the microstructure and mechanical properties of amorphous carbon nitride films

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ABSTRACT

In order to study the effects of anode layer linear ion source(ALLIS)on the microstructure and mechanical properties of amorphous carbon nitride (a-CN_x) films, a-CN_x films were deposited by the ALLIS assisted radio frequency magnetron sputtering (RFMS) deposition condition changing the ion source power from 0 to 200 W. The growth rate, structural morphology, surface roughness, nanohardness as well as the bonding states of deposited a-CN_x films were characterized by scanning electron microscope (SEM), atomic force microscope (AFM), nanoindentation, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS), respectively. The H/E and hardness increased relatively with increasing the ion source power up to 100 W. From the Micro Raman analysis, the content of sp^3 carbon in sp^3/sp^2 ratio was increased with increasing the ion source power. The cross-sectional SEM images demonstrated that the ion source enhanced the growth rate of a-CN_x films. Meanwhile, the roughness was increased with the ion source power above 100 W. Therefore, the optimum ion source power is considered to be around 100 W in these experimental conditions.

1. Introduction

Amorphous carbon nitride (a-CN_x) films are structurally analogous diamond-like materials. On account of the high atom density and strong covalent bonds, both of them have prominent physical and chemical properties, such as extreme hardness, outstanding thermal conductivity, high chemical stability, great biocompatibility, good corrosion resistance and excellent wear and friction properties [1,2]. The composition and structure of a-CN_x films are very complex, and the properties of films prepared by different preparation methods and technologies are distinguishing. Recently, significant progress in the synthesis of CN_x films has been made by various physical vapor deposition (PVD) and chemical vapor deposition (CVD) processes, such as the magnetron sputtering [3], pulsed laser deposition [4], ion beam deposition [5], plasma immersion ion implantation [6], filtered cathode arc [7], magnetron sputtering method [8] as well as plasma-enhanced chemical vapor deposition [9]. Nevertheless, it is still lack of in-depth understanding to deposition mechanism, process, microstructure and properties of a-CN_x films. Therefore, it is of practical significance to research the preparation technology and properties of a-CN_x films.

Magnetron sputtering is one of the preferred methods for the synthesis of carbon based amorphous materials such as boron carbides (B_4C), diamond-like carbon (DLC) and CN_x because of its effective dissociation of nitrogen molecule, simple scalability and easy control of deposition conditions [10]. Broitman et al. [11] studied the tribological properties of a-CN_x films prepared at different substrate temperature and nitrogen partial pressure, and found that the film friction coefficients tended to increase for different substrates as the nitrogen content in the film was increased. Wei et al. [12] found that there existed an optimized nitrogen partial pressure where the nanohardness and the wear resistance of the film were the highest. Deposition parameters such as gas flux, substrate bias voltage, ion energy and ion density as well as substrate temperature in magnetron sputtering were also investigated by some researchers [11,12].

The low gas ionization rate has been a major challenge during the preparation of a-CN_x films in magnetron sputtering. In order to improve the ionization rate of gas, auxiliary ion sources such as additional Kaufman ion source [13], end-Hall ion source [14], ion beam [15] as well as anode layer linear ion source (ALLIS) [16,17] were applied to the deposition of films. Kim et al. [17] prepared the DLC films with ALLIS assisted physical vapor deposition, and found that suitable ion source voltage promoted the fraction of sp^3 bonds in the DLC films. Qi Jun et al. [18] studied the effects of argon ion beam on the properties of DLC coatings using dual ion source system, and obtained the highest sp^3-hybridized carbon content of films synthesized with the Ar ion energy of 400 eV. Compared with other auxiliary ion sources, ALLIS is a relatively effective technology for depositing a-CN_x films. The main advantages of this technique are the low cost, simple structure and increase rate of gas

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ionization. ALLIS in the magnetic field makes the electrons bound in the vicinity of the anode surface forming dense plasma region and gas ionize. A low energy, high flow ion beam produced can effectively remove organic pollutants and the oxidation layer on substrate surface, increase adhesion and avoid damage to the substrate during bombardment. To the best of our knowledge, the study on this kind of auxiliary ion source deposition of a-CN_x films has not been reported.

In present study, a variety of a-CN_x films were successfully deposited on the silicon substrate at ion source powers ranging from 0 to 200 W by ALLIS assisted magnetron sputtering method. The influences of ALLIS on the microstructure and bonding configuration of carbon and nitrogen atoms in a-CN_x films were investigated systematically by Raman spectrum and X-ray photoelectron spectroscopy (XPS). Finally, the growth rate, nanomechanical properties of deposited a-CN_x films were characterized by scanning electron microscopy (SEM) and nano-indentation tests, respectively.

2. Experimental

Amorphous carbon nitrogen (a-CN_x) films were deposited by radio frequency magnetron sputtering (RFMS, JSD450-III) at a frequency of 13.56 MHz using anode layer linear ion source (ALLIS). The schematic diagrams of the experimental apparatus and ALLIS are shown in Fig. 1a–b. The target material was a 5 mm thick disk made of pyrolytic graphite with a purity of 99.999%. The direct current component of the substrate potential was referred to the substrate bias voltage. In order to produce denser plasma near the substrate surface and increase the flux density of impinging ions, ALLIS was installed between the target and substrate holder, as shown in Fig. 1a.

Due to the high requirement of the PVD method for the cleanliness of the equipment, the vacuum chamber should be cleaned enough before each experiment, and then the substrate was placed in the vacuum chamber. High-purity single-sided polishing p-type (100) silicon wafer was cut to 1.0 × 1.0 cm^2 substrates. The silicon substrates were immersed into 10% concentration of HF solution for 10 min to wipe off the oxide on its surface and then ultrasonically cleaned, in proper order, in acetone, methanol and deionized water for 10 min to remove the surface contaminants, finally dried in a flow of dry nitrogen. Prior to deposition, the substrates were outgassed at 400 °C in high vacuum for 30 min, and then sputter-cleaned in an Ar discharge with a negative bias of 200 V for 20 min. The magnetron target was pre-sputtered with a closed shutter at 90 W for 10 min. ALLIS is a type of ion generator which can be introduced into various gases. A gas mixture of nitrogen and argon which passed through the slit was ionized and charged particles were accelerated electrostatically. During film deposition, the frequency and duty cycle of ALLIS with defocusing discharge mode (low voltage, high current, high duty cycle) were kept at 38 kHz and 50%. The ion source power was varied from 0 to 200 W (Table 1). The other control factors were fixed.

Table 1
Deposition parameters of a-CN_x films.

Parameters	Values
Total gas flow rate (sccm)	40
Base pressure (Pa)	5×10^{-4}
RF power (W)	250
Anode layer linear ion source power (W)	0–200
Target-to-substrate distance (mm)	90
Substrate temperature (°C)	150
Substrate bias voltage (V)	−50
Working gas pressure (Pa)	0.5
N_2 content in the sputtering gas (%)	50
Deposition time (min)	60

For the characterization, the microstructure of the samples was analyzed using a LABRAM-HR800 Raman spectrometer with excitation wavelength of 514.5 nm. The chemical composition and bonding states of the carbon and nitrogen atoms on the surface of a-CN_x films were characterized using a PERKIN-ELMER CHI 5300 X-ray photoelectron spectroscopy (XPS) with Al-Kα radiation line (1486.6 eV). The samples surface was etched by Ar ion for 10 min conducted to remove contamination prior to XPS analysis. XPSPEAK software was used fitting the C1s and N1s core level spectra in XPS. Shirley function was modeled as the backgrounds. The surface structure and roughness of deposited samples were characterized by Atomic force microscope (AFM) from CSPM 3000, which operated in contact mode with scan area at 1.2 × 1.2 μm^2. The growth rate of a sample was calculated by dividing its thickness by corresponding deposition duration. The cross-sections of the specimens were studied by scanning electron microscopy (SEM, Hitachi-S4800). The hardness (H) and elastic modulus (E) were measured by nano-indentation (Agilent technologies, G-200) tests using continuous stiffness method (CSM).

3. Results and discussion

3.1. Microstructure

The influence of ion source power on the Raman spectra of a-CN_x films and deconvoluted Raman spectrum of the a-CN_x film deposited at an ion source power of 100 W are investigated in Fig. 2a. The curves were displaced vertically for clarity. These spectra of a-CN_x films are

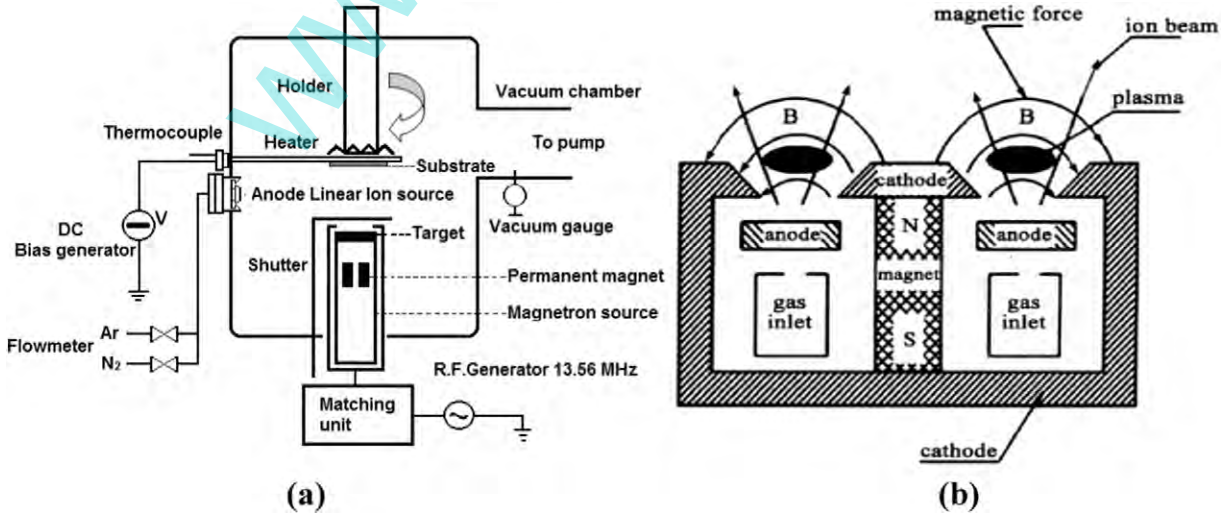

Fig. 1. Schematic diagrams of (a) ALLIS assisted RFMS system and (b) ALLIS.

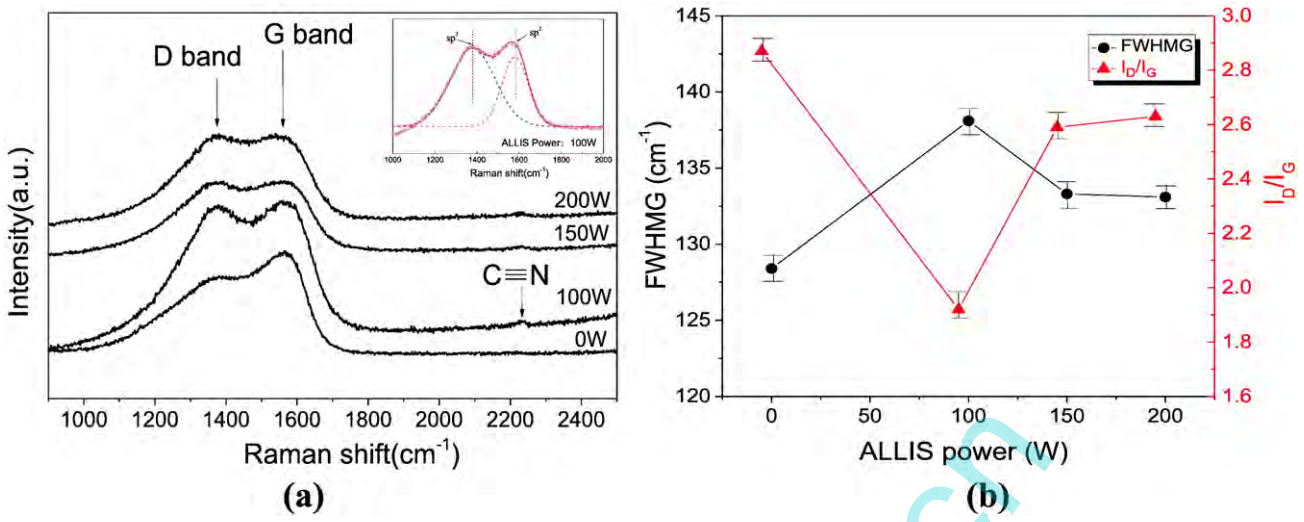

Fig. 2. (a) Raman spectra of a-CN_x films on Si for various ion source powers and the deconvolution of Raman peaks of a-CN_x (100 W) films and (b) the FWHM of G peak (FWHMG), the intensity ratio of D to G peak (I_D/I_G) variations with the ion source power for deposited samples.

practically consistent with the corresponding spectrum of the diamond like carbon film. The intensities and widths of G and D bands of the samples located at approximately 1550 and 1360 cm^{-1} changed obviously at different ion source powers. The weakest D peak observed as a-CN_x films were deposited at 100 W. With further increasing ion source power from 100 to 200 W, the peak position of G mildly shifts toward the high frequencies and the D peak becomes more intense. The width and intensity of D band are related to the lattice disorder induced by N incorporation and the nitrogen ion bombardment in a-CN_x films [19,20]. Beside the typical carbon D and G bands, other additional bands were also observed after the ion source was used. The band observed at approximately 2200 cm^{-1}, can be associated with nitrile radicals (C ≡N bond) [20]. The Raman spectra of samples were deconvoluted into two Gaussian bands, which were D band and G band. The D band arises from the breathing modes of sp^2 carbon atoms in clusters of six-fold rings. The G band originates from the bond-stretching modes of sp^2 carbon atoms in both six-fold rings and chains [21]. Fig. 2b shows the full width at half maximum of G band (FWHMG), and the intensity ratio of D to G peaks (I_D/I_G) as a function of ion source power.

According to Raman analysis, the synthesized films in this work were a-CN_x, which contained a mixture of π and σ bonding [20]. Since Raman scattering from π bonds is 50–230 times stronger than that from σ bonds [22], the D and G modes caused by π bonding dominated the Raman spectra of deposited films. The positions of the G peaks were in the range of 1552–1571 cm^{-1}, lower than graphite (1580 cm^{-1}), which was due to bond angle distortions and other disorders [22]. The FWHMG is related to the bond angle distortions in the excited configurations, and low value of FWHMG corresponds to high ordered sp^2 configurations [16]. The variation of I_D/I_G ratio with increasing ion source power showed a different trend with the FWHMG. Usually, high content of sp^2 carbon clusters corresponds to high I_D/I_G ratio [22,23]. Accordingly, the content of sp^2 carbon clusters decreased with ion source power up to 100 W, however, further increasing ion source power resulted in the sp^3 structure transforming to graphite structure. The ionization rate of gas and gas reaction activity increased with the increasing of ion source power. In the surface layer of materials, incident ions caused 'thermal spike' which instantaneously induced high temperature and high pressure in a rather limited area, promoting the formation of sp^3 configuration [24]. Meanwhile, over high ion bombarding energy causes the sp^3 transforming into sp^2 configuration, which is possibly due to the thermally activated diffusion [24–26]. In addition, since Raman spectra is sensitive to sp^2 hybridization and insensitive to sp^3 hybridization, the real sp^2 fraction in a-CN_x films is lower than that suggested by experimental I_D/I_G ratio [27].

For deeply investigating the bonding states of a-CN_x films, the C1s and N1s high resolution XPS spectra were decomposed, as presented in Fig. 3. The C1s spectra of deposited films contained four well-resolved peaks (denoted by C1s-1, C1s-2, C1s-3 and C1s-4) with a FWHM about 1.6 eV in the range of 284–289 eV (Fig. 3a). The peak C1s-1 corresponds to sp^2 carbon bonding, and the peak C1s-2 is assigned to sp^3 carbon bonding [28,29]. The peak C1s-3 and C1s-4 correspond to carbon multiple bonding with nitrogen [28,30] and carbon bonding with oxygen caused by foreign impurity in the films [31], respectively. The N1s spectra contained four main components with a FWHM about 1.5 eV, as

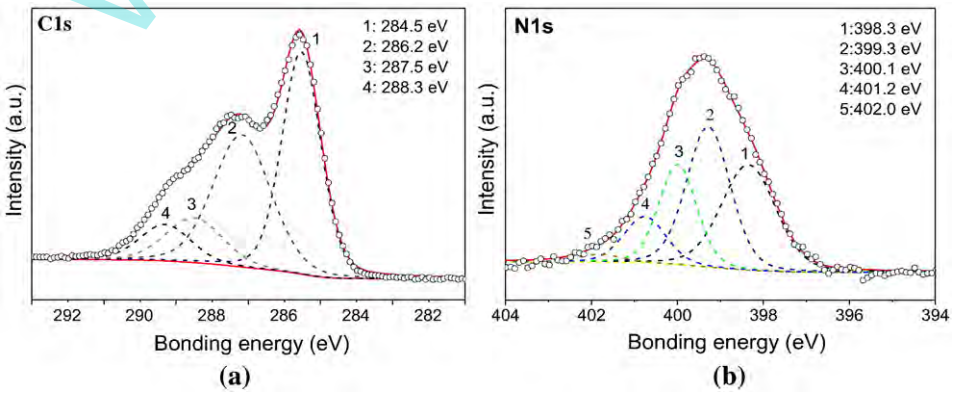

Fig. 3. XPS high resolution spectra of the a-CN_x (100 W) film (a) C1s and (b) N1s.

shown in Fig. 3b. The five peaks (denoted by N1s-1, N1s-2, N1s-3, N1s-4 and N1s-5) were at the binding energy of 398.3, 399.3, 400.1, 401.2 and 402.0 eV, respectively. Peaks N1s-1, N1s-2, N1s-3 and N1s-4 correspond to N—C, N≡C, N═C and N═N (N_2) bonds, respectively [23]. Peak N1s-5 is likely to be non-polar nitrogen molecule bond [31].

XPS spectra can be not only used for the qualitative determination of the elements of the a-CN_x film, but also be used for quantitative determination of the elements. The N/C ratio of the deposited a-CN_x films can be determined from the ratio of integrated net intensities of the N1s (A_N) to C1s lines (A_C) in the XPS spectra of deposited films by using

$$\frac{n_N}{n_C} = [(A_N/0.5)/(A_C/0.31)]$$

where the constants of 0.51 and 0.31 are the atomic sensitivity factors of nitrogen and carbon, respectively [32].

The [N]/[C] and sp^3/sp^2 carbon ratio of a-CN_x films with different ion source powers are seen in Fig. 4, respectively. [N]/[C] ratio is an important factor influencing the microstructure of a-CN_x films. It can be seen that the use of the ALLIS greatly increased nitrogen fraction and sp^3/sp^2 in the films. The ratio of N/C in the film increased to a maximum of 0.55 at an ion source power of 100 W. However, a further increase in the ion source power would slightly decrease the N/C ratio in the films. When a-CN_x films were deposited without the ion source, the carbon species interacted solely with the N_2 molecules in the ambient gas, and a lower incorporation of N atoms in the film occurs. When ALLIS was used during the film deposition, the carbon species would interact with reactive nitrogen atoms and N^+ ion supplied by the RF discharge. This would improve the incorporation of N atoms in the films. The amount of nitrogen in the films depends on their sticking probabilities and sputtering yield at the growing film surface [33]. However, with ion source power further increasing, the sputtering effect of N ions became stronger, the carbon atoms on the film surface might lose their nitrogen neighbors due to preferential sputtering of nitrogen [34]. The kinetic energy of N ions partially translated into thermal energy when N ions impacted on film surfaces [35]. Sufficient thermal energy made film atoms to achieve more thermally activated mobility. Therefore the chemical reactions happened between incident N ions and the N atoms in CN species to form N≡N bonding. N escaped from the film in the style of nitrogen molecule, caused chemical re-sputtering. The chemical re-sputtering was thermally activated and was enhanced by increasing ion source power. That was the main reason for the decrease of nitrogen content in the films. The sp^3/sp^2 ratio was calculated according to the ratio of C1s-1 to C1s-2 peak area. It was found that the variation of the sp^3/sp^2 ratio had the similar trend with the [N]/[C] ratio. XPS analysis indicated that increasing N content would increase sp^2 carbon and reduce sp^3 carbon in the films.

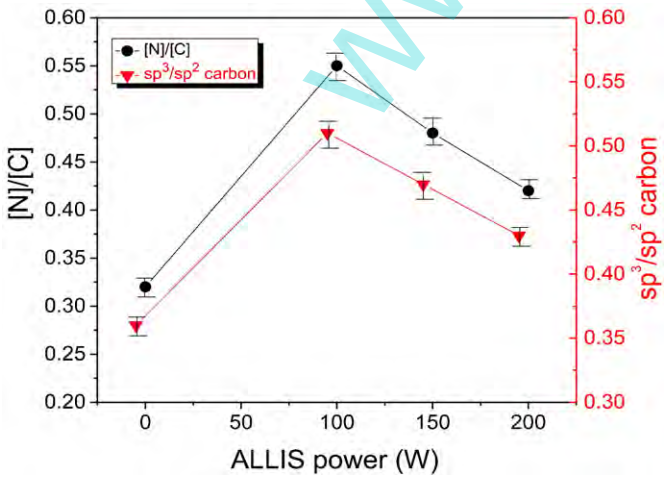

Fig. 4. [N]/[C] and sp^3/sp^2 carbon ratio of a-CN_x films as a function of ion source power.

The three-dimensional AFM images of the samples are demonstrated in Fig. 5a–d. It can be seen that the surface micrograph of a-CN_x films was obviously dependent on the ion source power. The surface of a-CN_x (100 W) is relatively smooth without visible protuberance compared to other samples. With further increasing the ion source power, the film surface changed from smooth to a peak-and-valley structure, and the film surface became rougher. The rms values of the samples increased from 1.6 to 2.71 nm, and the rms value of a-CN_x (100 W) was minimum (Fig. 5e). For compared, a-CN_x (0 W) has the bigger roughness, this indicates that ALLIS has obvious influence on the film surface microtopography. ALLIS can effectively improve the nitrogen ionization rate, and increase ions bombarding energy. The ballistic effects of incident N^+ ions increased the mobility of film atoms, which resulted in downhill diffusion along the inclined surface, leading to the smoothness of the film surface [36]. On the contrary, sputtering effect was enhanced by increasing bombarding energy, induced film surface roughing.

In addition, cross-sectional SEM images were taken in order to study the effect of the ion source power on the growth rate of the a-CN_x film. As shown in Fig. 6a–d, the thickness of samples increased from around 200 to around 300 nm with increasing the ion source power. This is because the number of high-energy ions increases with increasing ion source power, and therefore, the number of particles deposited on the substrate increases. The growth rate gradually increased from 3.3 to 5 nm/min (Fig. 6e), which indicated that ALLIS had obvious promoting effect on the deposition rate of a-CN_x films.

3.2. Nanomechanical properties

Fig. 7a showed the H and E behavior as function of the indentation depth of representative a-CN_x (100 W) sample. With the increased indentation depth, the hardness of deposited films also enhanced from nearly 0 to the maximum, and then followed by a slow downward trend (Fig. 7a). The nanohardness and [N—C]/[N≡C] of samples as function of ion source power are presented in Fig. 7b. The highest hardness observed as a-CN_x films were deposited at an ion source power of 100 W. Compared with the case without ion source, nanohardness of deposited films had greatly promoted, this suggested that the ALLIS had an obvious effect to improve the nanohardness of the a-CN_x film.

Additionally, Jing Ni et al. [37] suggested that [N—C]/[N≡C] ratio had a close relationship with the hardness of CN_x films. Because the N≡C bond as terminating group breaks the continuity of the network in the structure of CN_x films, high concentration of the N≡C bond makes the film structure less compact [21]. The decrease of [N-C]/[N≡C] ratio with increased ion source power above 100 W also contributes to the softened a-CN_x films. The sp^3 content has great influences on the mechanical properties of a-CN_x films, and high sp^3 content is accompanied by large hardness and elastic modulus. Raman spectra showed the sp^3 content of samples increased with increasing the ion source power, and then decreased with further increase in ion source power, the sp^2 content had opposite tend with that. The films transformed between the graphitization and cubic phase, thus hardness and elastic modulus were changing. Contrarily, sp^2 configuration not only contains weak π bonding, but also damages the connectivity of the covalent network, which leads the film softening. Therefore, increasing sp^3/sp^2 carbon ratio improves the hardness of the film [38]. In this work, the high fraction of sp^2 bonding and low fraction of sp^3 bonding coexisted in a-CN_x films as indicated in XPS results shown in Fig. 4. It was found that with increasing ion source power above 100 W, the sp^3/sp^2 carbon ratio decreased from 0.51 to 0.43, so the hardness gradually decreased.

The variations of the H/E and H^3/E^2 ratio of a-CN_x films as a function of ion source power are investigated in Fig. 8. The ratio of the hardness to elastic modulus (H/E) of the film is the plastic index, which is an effective mean to explain the deformation mechanism of films, and it is also one of the indexes to predict the wear resistance of the material [39].

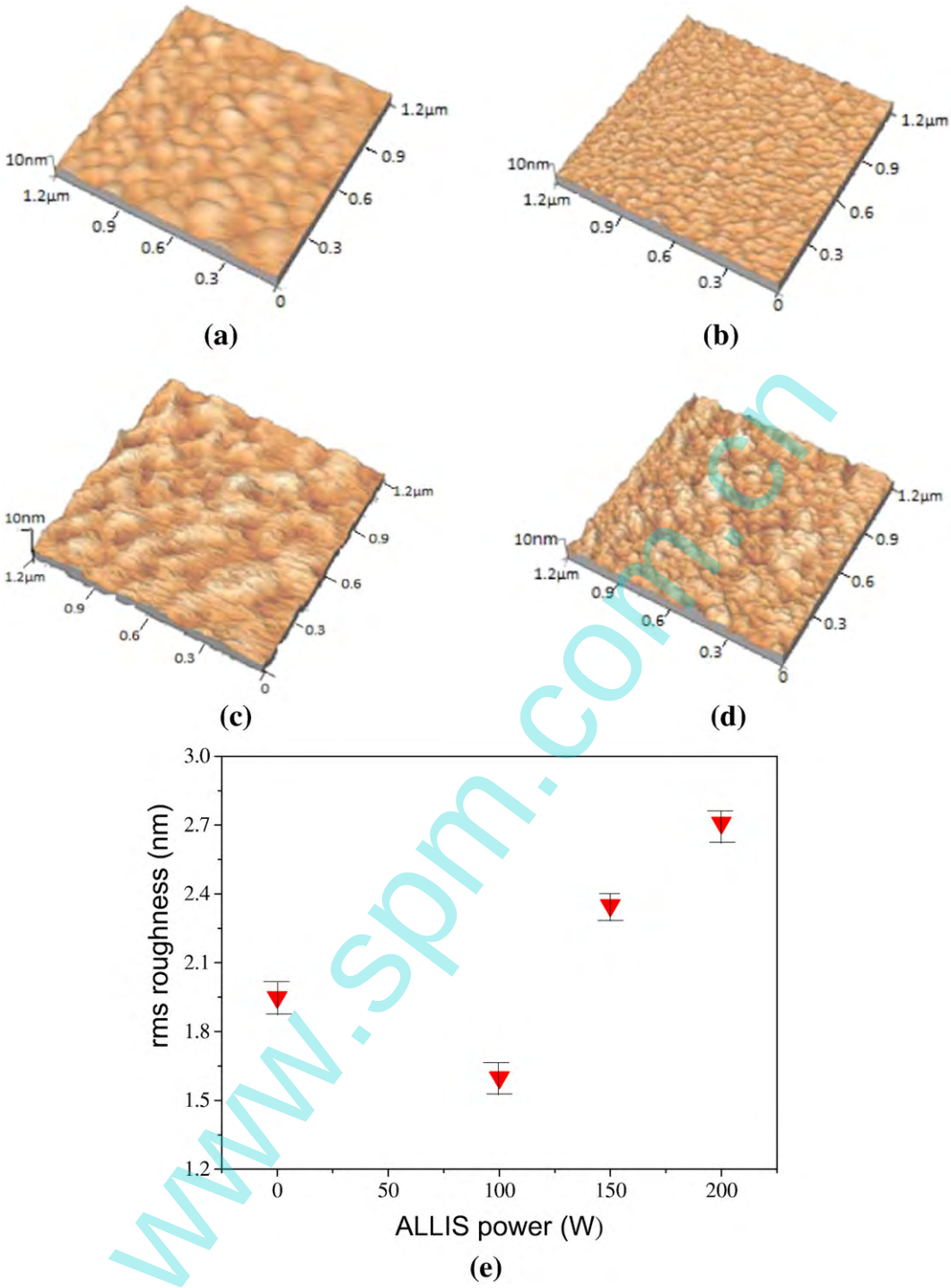

Fig. 5. Three-dimensional AFM images of a-CN_x films with different ion source powers (a) 0 W, (b) 100 W, (c) 150 W, (d) 200 W, and (e) the root mean square (rms) roughness of a-CN_x films as function of ion source power.

The value of H/E varies between 0 (plastic behavior) and 0.1 (elastic behavior) for carbon coatings [40], and high value of H/E means that these films are highly resistant to plastic deformation [41]. The term H^3/E^2 combines the H and E values of a material and sets the amount of the elasticity exhibited by the film. Particularly, high (low) values of H^3/E^2 are correlated to the high elasticity (plasticity) deformation, and the greater values of H^3/E^2 represent the better fracture toughness of the film [39]. The value of H/E without ALIS was 0.098, while the value of the a-CN_x (100 W) film was promoted to 0.123, then dropped to 0.109 with the power increasing to 200 W. These results indicated appropriate ion source power was beneficial to the improvement of elasticity but exorbitant ion source power made elasticity of the film decline. Values of H^3/E^2 displayed the same trend with the ratio of H/E which illustrated the fracture toughness of films increased firstly and then decreased.

4. Conclusions

By using anode layer linear ion source (ALLIS) assisted RFMS technology, amorphous carbon nitride (a-CN_x) films were successfully prepared on the Si (100) substrate. The effects of ALLIS on the surface chemical bonding configuration and mechanical properties of a-CN_x

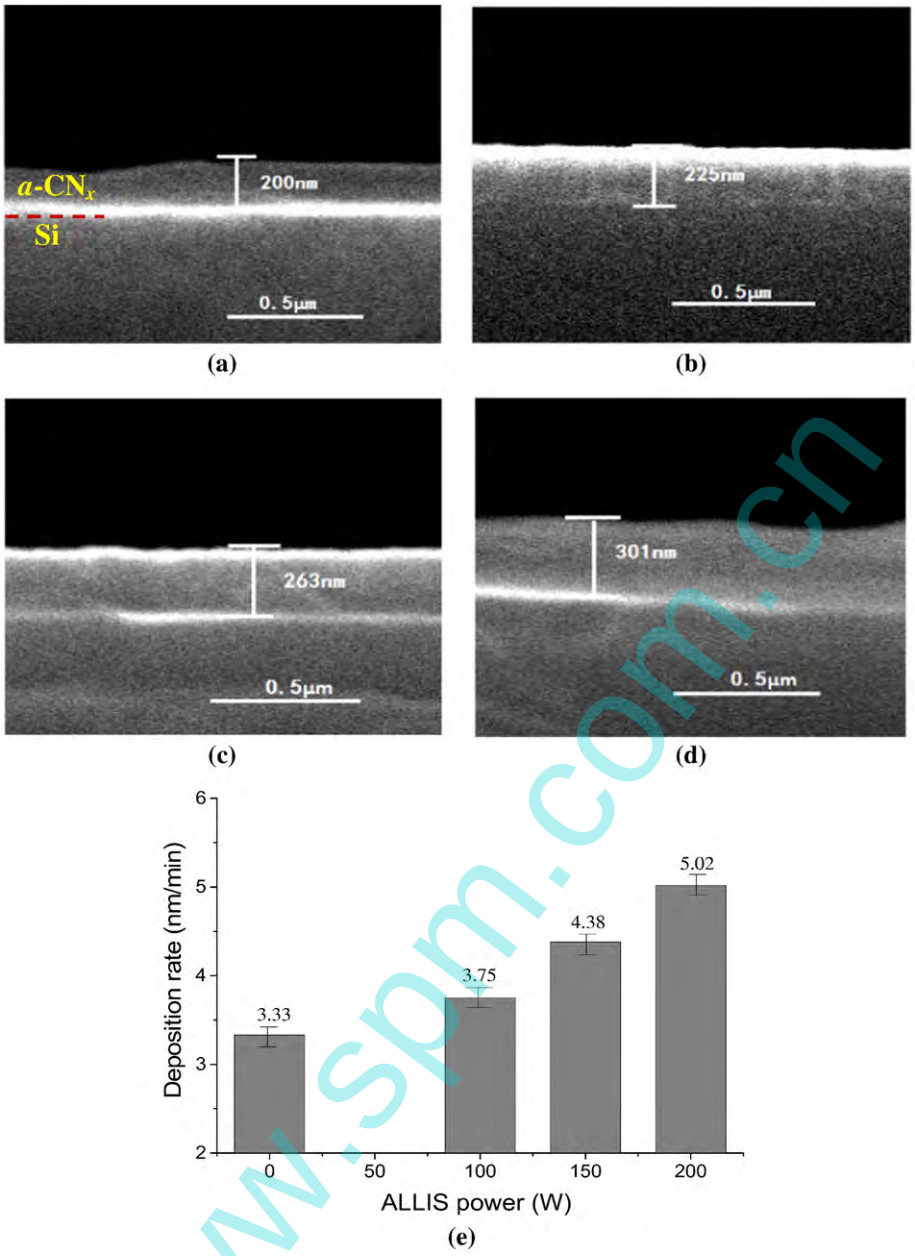

Fig. 6. The cross-sectional images of SEM in deposited a-CN_x films with different ion source powers (a) 0 W, (b) 100 W, (c) 150 W, (d) 200 W, and (e) the growth rate variations with the ion source power for deposited samples.

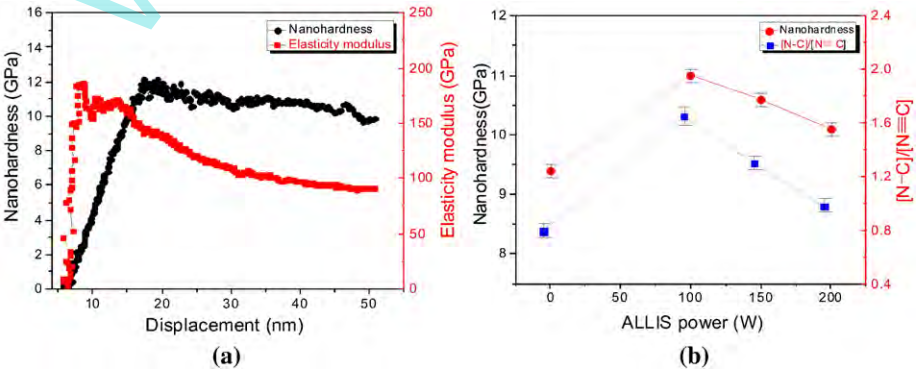

Fig. 7. (a) Nanohardness and elasticity modulus variations with the displacement for the a-CN_x (100 W) film and (b) nanohardness and [N—C]/[N≡C] ratio of a-CN_x films as function of ion source power.

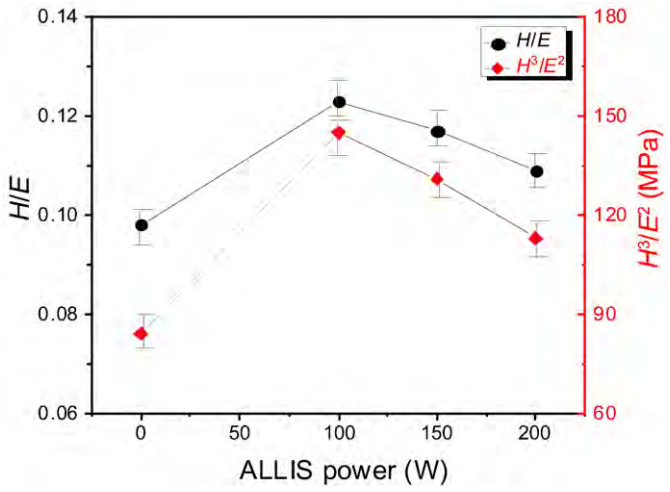

Fig. 8. H/E and H^3/E^2 ratio variations with the ion source power for a-CN_x films.

films have been investigated systematically. The conclusions could be summarized as:

(1) With an increase in ALLIS power, the deposition rate of films increased from 3.3 to 5 nm/min and surface quality had been significantly improved while the minimum surface roughness of a-CN_x films was obtained at an ion source power of 100 W in the range of experiment condition.

(2) The existence of ALLIS effectively enhanced the sp^3 carbon bond content and hardness of the film. Moreover, films prepared at an ion source power of 100 W presented maximum hardness, highest content of cubic phase and better fracture toughness. Thus ALLIS has played an enormous role in the improvement of mechanical properties of a-CN_x films.

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