EFFECTS OF DEPOSITING PARAMETERS ON THE PROPERTIES OF CN_X/TIN_Y MULTILAYERS

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CN_x/TiN_y multilayers were prepared by using ion beam assisted ion beam sputtering method. XPS analysis shows two C-N bonding states of N-sp^2C and N-sp^3C in CNx layer have been defined. With the increasing of substrate temperature, the microhardness and the N contents of the films rise. The assisted ion beam deposition is benefit for increasing the microhardness and the N concentrations of the films. From this experiment, we achieve the films with the microhardness of up to 47.2 GPa, and the total N concentration of 59.00 at. %. It is worth noting that the interfacial bond state between the substrate and film is obviously improved when the substrate temperature increases or the assisted ion beam is used.

1. Introduction

Carbon nitride is a new hypothetical superhard material. It had been predicted by Liu and Cohen in 1989[1,2]. They proposed that the hardness of β-C_3N_4 might be comparable with or greater than that of diamond. The structural and electronic properties of β-C_3N_4 were studied by a first-principle calculation based on β-Si_3N_4 as prototype. The result showed that the cohesive energy of β-C_3N_4 was moderately large, meaning that it could be synthesized. Motivated by these theoretical results, more theoretical calculations had been done to study the structures of C_3N_4, graphitic-C_3N_4, α-C_3N_4, cubic-C_3N_4 and pseudocubic-C_3N_4 also had been proposed [3,4]. At the same time, numerous attempts [5-10] to synthesize β-C_3N_4 had been carried out in the laboratories by using reactive d.c. magnetron sputtering, r.f. sputtering, ion beam sputtering, ion beam assisted deposition, laser ablation, electron cyclotron resonance plasma enhanced chemical vapor deposition, high pressure and electrodeposition etc. Some reports [11-14] declared that crystalline α-,β-, cubic-, graphitic-C_3N_4 had been observed in amorphous CN_x films. Some C-N compounds[15-17] with other structures that were not predicted such as monoclinic-, tetragonal- and fullerenlike-structure had also been found. Up to date, the properties of the CN_x films are studied. Most of the results showed that the hardness of the films was still lower than the theoretical one and the N concentrations of the films were substantially below the stoichiometrical composition for C_3N_4 (57at. %).

C_3N_4 is a metastable phase; therefore, choosing a suitable material as template to promote the formation of crystalline C_3N_4 phase is a valid method. Li et al.[18,19] gave an example that TiN was the better template by their experiments because there were good lattice matches between TiN (111) and β-C_3N_4 (0001).

In this paper, we prepare CN_x/TiN_y multilayers (18 layers) by using ion beam assisted ion beam sputtering method. The structures of the films have been studied by XPS. The effects of substrate temperature and parameters of the assisted ion beam on the microhardness and the N concentrations of the films have also been studied. SEM has been used to observe the film morphology.

2. Experiments

The CN_x/TiN_y multilayers were prepared by using ion beam sputtering apparatus. There were two targets, graphite and titanium. The discharge gas was high pure N_2. During deposition, titanium target was sputtered by N^+ ion beam about 30min at first, then graphite target was sputtered about 90min, thus repeatedly to form CN_x/TiN_y multilayers. The base pressure in the vacuum chamber was $5x10^{-4}$Pa and the total sputtering gas pressure was kept at $7x10^{-2}$Pa. The distance between target and substrate was about 85mm. The substrate temperature ranged from 20°C to 600°C. The energy of the ion beam was about 1000eV, and the assisted ion beam energy was in the range of 100eV~900eV. The ion beam current was 70mA, and the assisted ion beam current was from 10mA to 30mA. The deposition rates of TiN_y and CN_x films were 60nm/h and 20nm/h, respectively, without the assisted ion beam.

The Si (100) slices were be used as substrates for depositing CN_x/TiN_y multilayers. All substrates were cleaned ultrasonically in acetone and ethanol solvents before being introduced into the sputtering system. Before sputtering, we diluted the air remaining in the chamber several times using high pure N_2. The substrates were sputtered by N^+ ion beam about 10min firstly in order to cleaning the adsorptive air on the surfaces of the substrates.

The structures of the films were studied by XPS performed by a VG Scientific ESCALAB 220I-XL spectrometer. Vickers sclerometer model ЛМТ3 was carried out to measure the microhardness of the films. The N concentrations of the films were measured by energy dispersive X-ray (EDX) attached to the scanning electron microscopy model AMMARY-1000B.

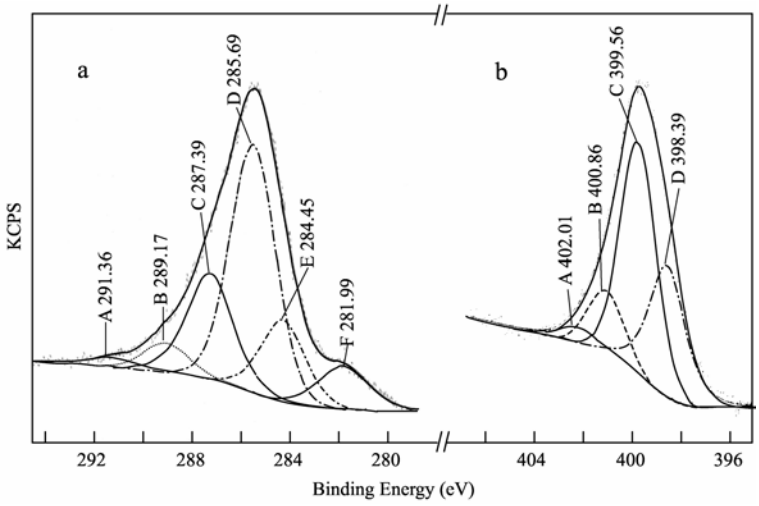


Fig. 1. XPS spectra of the CN_x layer in CN_x/TiN_y multilayers

3. Results and discussion

The typical XPS C1s and N1s spectra for CN_x layers in CN_x/TiN_y multilayers are shown in Fig. 1(a) and (b). Table 1 shows the date of the bond energies and the ratio of every peak. Based on published XPS data [14,20], the chemical states corresponding to every peak in Fig. 1. The C1s spectrum can be deconvoluted inFto six peaks marked A, B, C, D, E and F at binding energies of 291.36eV, 289.17eV, 287.39eV, 285.69eV, 284.45eV and 281.99eV. The weakest peak (A) is corresponding to π-π^* bond in carbon. Peak B reflects the CO type bonds. Peak C and D are associated with N-sp^3C (C-N) and N-sp^2C (C=N), respectively. Peak E originates from pure carbon. Peak F is due to the contribution of metal carbides on the surface of the film. For N1s spectrum, the peaks marked A, B, C and D at 402.01eV, 400.86eV, 399.56 eV and 398.39eV are attributed to NO, N-N, C=N and C-N bonds, respectively. These results show that there are C-N and C=N in the CN_x/TiN_y multilayers. The concentration of carbon nitride bond in the CN_x layer, including C-N and C=N, are 69 at. % and 82 at. %, the intensity ratio C-N/C=N reach to 0.447 and 0.585 calculated from the C1s and N1s spectra, respectively. The film is mainly composed of carbon nitride bond. It is the basis of

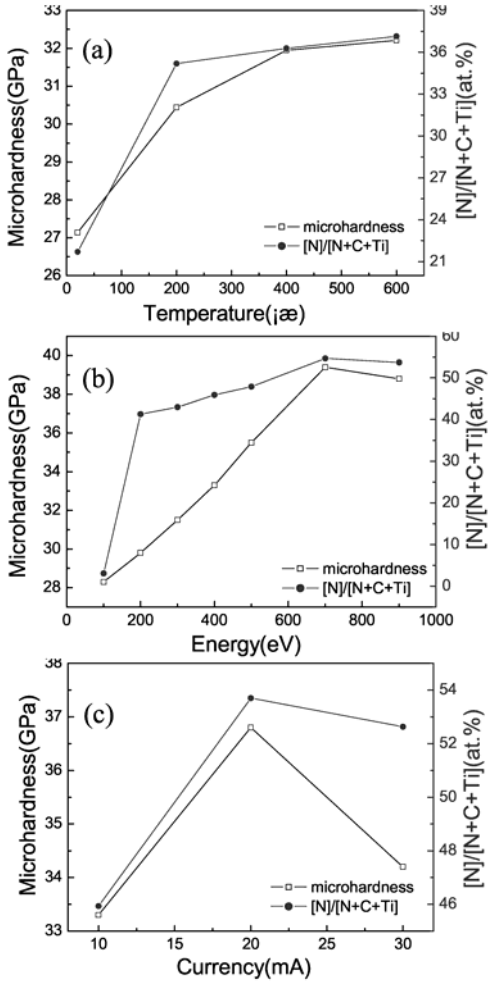


Fig.2. The microhardness and the N concentrations of CNx/TiNy multilayers

forming carbon nitride crystal in the CN_x/TiN_y multilayers.

Table 1

Quantitative data calculated from C1s and N1s spectra

C1s C–N / C=N = 0.447				N1s C–N / C=N = 0.585			
Peak	Binding Energy (eV)	[AT]%	Bonding Type	Peak	Binding Energy (eV)	[AT]%	Bonding Type
A	291.36	1.791	π-π^* (C)	A	402.01	3.285	NO
B	289.17	5.564	CO	B	400.86	13.947	NO
C	287.39	21.701	C–N	C	399.56	52.211	C=N
D	285.69	48.585	C=N	D	398.39	30.557	C–N
E	284.45	15.774	Pure C				
F	281.99	6.585	Metal carbides				

Fig. 2 is the variation of the microhardness and N concentrations ([N]/[N+C+Ti]) of the CN_x/TiN_y multilayers prepared under different depositing parameters. Table 2 shows the data of the mircohardness and N concentrations of the films by using the assisted ion beam. In the left of the table, the mark of "—" means the experiment is limited by apparatus. The mark of "***" in the right of table means no film is deposited in the substrates.

The efforts of substrate temperature on the mircohardness and N concentrations of the films are shown in Fig. 2 (a). The microhardness of the films increase from 27.14GPa to 32.21GPa upon increasing the substrate temperature from 20°C to 600°C, and the N concentrations also increase from 21.7 at. % to 37.15 at. %. The result shows that the high temperature is favorable for increasing the microhardness and N concentrations of the films.

Fig. 2 (b) and (c) show the variations in microhardness and N concentrations of the films determined using different sputtering parameters of the assisted ion beam. The microhardness of the films rise when the current of the assisted ion beam is 10mA. But when the current of the assisted ion beam is higher than 20mA, the microhardness decrease with the increasing of the energy and the films disappear at the energy of 500eV (see table 2). The assisted ion beam has an effect on not only the N^+ implanted but also anti-sputtering the films. The films are deposited by sputtering and anti-sputtering at the same time. The films become thin or even disappearance when the anti-sputtering take the main effect. That is to say, the energy and current of the assisted ion beam should be limited in a certain range. The N concentrations have the same tendency as the microhardness. It suggests that the N concentrations of the films should be connected with the microhardness. It considers the increasing of N concentrations lead to the increasing of microhardness of the films. The highest microhardness of 47.2 GPa with the highest N concentration of 59.00 at. % of the films is achieved when the energy is 200eV and the ion beam current is 20mA.

Fig. 3. The micrographs of the films: (a) at ambient temperature, (b) at 600°C, (c) using the assisted ion beam

Table 2

The microhardness and N concentrations of the films by using the assisted ion beam

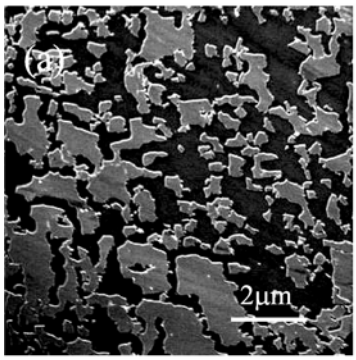
Current (mA)		Energy (eV)						
		100	200	300	400	500	700	900
10	Hv (GPa)	28.30	29.80	31.50	33.30	35.50	39.40	38.80
	[N] at.%	30.76	41.30	43.00	45.93	47.88	54.67	53.71
20	Hv (GPa)	—	47.20	40.50	36.80	***	***	***
	[N] at.%		59.00	56.00	53.70			
30	Hv (GPa)	—	—	36.50	34.20	***	***	***
	[N] at.%			54.37	52.63			

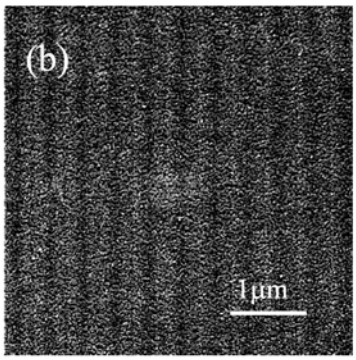
— represents limited by apparatus *** represents no films

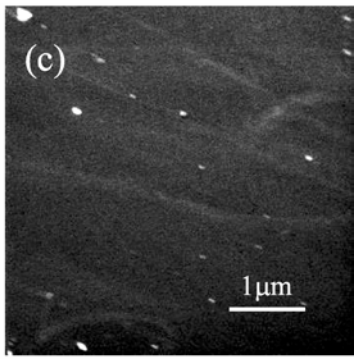
Fig. 3 is the micrographs of the films. (a), (b) and (c) are the films morphology at ambient temperature, 600°C and using the assisted ion beam. The films are not continuous, and often fall from the substrates (see Fig. 3 (a)). The interfacial bond state between the substrate and film is poor. When the substrate temperature increases or the assisted ion beam is used, the films are smooth and the interfacial bond states between the substrate and film are excellent (see Fig. 3(b) and (c)). The results show that increasing the substrate temperature or using the assisted ion beam will be benefit for the interfacial bond state between the substrate and film and the growth of the film.

4. Conclusion

CN_x/TiN_y multilayers were prepared by using ion beam assisted ion beam sputtering method. Two C-N bonding states of N-sp^2C and N-sp^3C in CN_x layer have been defined by XPS analysis, and they are the main compositions of chemical bond in CN_x layer. With the increasing of substrate temperature, the microhardness and the N contents of the films rise. The assisted ion beam deposition is benefit for increasing the hardness and the N concentrations of the films, but the energy and the current of the assisted ion beam should be limited in a certain range. From this experiment, we achieved the film of the highest hardness of up to 47.2 GPa with the total N concentration of 59.00 at. % when the energy of the assisted ion beam is 200V and the current of it is 20mA. The interfacial bond state between the substrate and film is improved when the substrate temperature increases or the assisted ion beam is used.







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Article is delivered in editing 9.07.2002