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Optimizing hardness of CN_x thin films by dc magnetron sputtering and a statistical approach

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We have investigated the effects of seven sputtering control factors on the hardness of carbon nitride (CN_x) thin films by design of experiments and the analysis of variance (ANOVA) to synthesize hard CN_x thin films. It was determined statistically that the substrate temperature, the sputtering pressure and the target to substrate distance are significant control factors for the hardness of the CN_x thin films within the experimental range of this study. Especially, the distance is the most important control factor of the seven factors; the hardest films are obtained at the distance of 4.5 cm. On the other hand, the effects of the substrate treatment, the dc power, the nitrogen concentration and the sputtering time are not statistically significant. It is suggested that these statistical methods are effective to compare the importance of many sputtering control factors. The CN_x thin films deposited under the optimized sputtering conditions exhibit a relatively high hardness value of 55 ± 11 GPa, Young's modulus of 228 ± 21 GPa and an elastic recovery (%R) of 98%. The compressive stress in the films is a low value of 0.3 GPa.

1. Introduction

Liu and Cohen theoretically predicted in 1989 a new low compressibility covalent solid formed between carbon and nitrogen, β-C_3N_4, which can have a bulk modulus comparable to or greater than diamond [1]. Niu *et al.* discovered the small β-C_3N_4 crystallites (<10 nm) in the CN_x thin films deposited by laser ablation in 1993 [2]. Following these reports, intense theoretical and experimental interest has been directed towards the study of new CN_x materials. A number of techniques have been used to synthesize these CN_x thin films, such as reactive sputtering [3–6], dual ion beam deposition [7–9], ion and vapor deposition (IVD) [10], pulsed laser ablation [2, 11], filtered cathodic arc deposition [12], nitrogen ion implantation [13, 14], ion-assisted carbon condensation method [15] and chemical vapor deposition (CVD) [15–18]. However, CN_x thin films with hardness comparable to or greater than diamond have not been reported so far. The hardness and Young's modulus of diamond films are 80–100 GPa and 500–533 GPa, respectively [19]. The $CN_{0.18}$ thin films deposited by dc reactive magnetron sputtering method indicates the highest hardness of 60 GPa in the CN_x films reported [5].

Experimentation using the Analysis of Variance (ANOVA) method is a statistical approach using the variances of data and error [20–22] to determine optimum conditions. It is widely applied to scientific investigations, such as biometry, agronomy, psychology, analytical chemistry and process engineering [23, 24]. Recently, it was suggested that design of experiments and the ANOVA method were very efficient methods to optimize the sputtering conditions of highly oriented $LiNbO_3$ [25] and AlN [26, 27] thin films by carrying out a small number of experiments.

In the present study, we investigated the effects of seven control factors on the hardness of CN_x thin films deposited using dc reactive magnetron sputtering; namely the substrate treatment, the substrate temperature, the sputtering pressure, the dc power, the nitrogen concentration, the target to substrate distance and the sputtering time. We discuss the mechanical properties of the CN_x thin films deposited under the optimum sputtering conditions determined from the ANOVA method in detail.

2. Experimental

The CN_x thin films were prepared by a dc planar magnetron sputtering system. The sputtering system employed a standard sputtering chamber with a 10 cm-diam high purity graphite target disk (over 99.9% pure). Silicon (111) wafers were used as substrates and their thickness was 356 μm. The substrates were treated in two ways before deposition. One was acetone treatment; the substrates were ultrasonically cleaned in acetone (99.8% pure), iso-propyl alcohol (99.8% pure) and methanol (99.5%). The other was hydrofluoric acid (HF) treatment; the substrates were pretreated in a 5% HF bath for about 5 sec. and rinsed in de-ionized water [28]. The sputtering chamber

TABLE I Sputtering control factors and levels

Factor	Level 1	Level 2	Level 3
A Sub. treat.	Acetone	HF	–
B Sub. temp (°C)	R.T.	200	400
C Pressure (Pa)	0.6	1.0	2.0
D dc power (W)	300	500	700
E N_2 gas flow (%)	50	75	100
F Distance (cm)	3	4.5	6
G Sputt. time (min)	10	20	30
H Error	–	–	–

was evacuated to below 8×10^{-4} Pa, and then high-purity argon (99.999%) and/or nitrogen (99.999%) gases were introduced. The temperature of the substrate holder in the chamber was considered as the substrate temperature.

Substrate treatment, substrate temperature, sputtering pressure, dc power, nitrogen concentration, target to substrate distance, and sputtering time were selected as sputtering control factors. We utilized an L18 orthogonal array because this orthogonal array is the most common in process engineering [25, 26]. Table I lists the sputtering control factors and their levels. Table II shows the assignment of the orthogonal array. The mechanical properties of the films were evaluated using a Fisher H100 dynamic indentation system with a Vickers diamond tip. The hardness and Young's modulus were calculated using the plastic displacement obtained from the intercept with the displacement axis of the gradient of the unloading curve at maximum load of 5 mN [29]. The film thickness and the radius of curvature of the silicon substrates were measured by using a Tencor instruments alpha-step 200 surface profilometer. The N concentration in the films was evaluated using Sputtered Neutral Mass Spectrometry (SNMS) with a primary beam of 8 kV O_{2+} ions.

3. Results and discussion

3.1. Importance of control factors

Table II shows the hardness, film thickness and stress of the CN_x thin films deposited under the eighteen sputtering conditions. The hardness shows a large variation from 3.7 to 55 GPa, clearly indicating hardness strongly depends on the sputtering conditions. Table III indicates the results of the hardness analyzed by the ANOVA method. The symbol S is the sums of squares of the deviations around means:

$$S = \sum (x_\mathrm{i} - \bar{x})^2$$

where x_i is a value of the hardness, $\bar{x}$ is the overall mean of the hardness. The S of each factors was calculated according to the L18 orthogonal array shown in Table II [20–22]. The symbol ϕ represents the degrees of freedom. The ϕ of the substrate treatment is one and the ϕ of the other factors is two, because the substrate treatment has two levels and the other factors have three levels as shown in Table I. V is the unbiased estimate of the variance of a control factor:

$$V = \frac{\sum (x_\mathrm{i} - \bar{x})^2}{\phi} = \frac{S}{\phi}$$

The $F = V/\mathrm{Ve}$ is a test statistic, where Ve is the unbiased estimate of the variance of an experimental error and is 36.9 according to Table III. The unbiased estimates of the variances of the dc power and the nitrogen gas flow are much smaller than those of the other control factors, and the effect of these control factors on the hardness

TABLE III Analysis of variance table on hardness of CN_x thin films

Factor	S	ϕ	V	F
A Sub. treat.	214	1	214	5.83
B Sub. temp.	545	2	272	7.39
C Pressure	449	2	224	6.08
D dc power	112	2	55.8	◯
E N_2 gas flow	18.7	2	9.30	◯
F Distance	605	2	303	8.20
G Sputt. time	165	2	82.4	2.23
H Error	91.0	2	45.5	◯
Error (◯ mark pooled)	221	6	36.9	

TABLE II Assignment of L18 orthogonal array and hardness, film thickness and stress of CN_x thin films

	Factor										
No.	A	B	C	D	E	F	G	H	Hardness (GPa)	Film thickness (nm)	Stress (GPa)
1	1	1	1	1	1	1	1	1	20	1150	0.593
2	1	1	2	2	2	2	2	2	.27	320	1.27
3	1	1	3	3	3	3	3	3	4.5	800	0.340
4	1	2	1	1	2	2	3	3	21	100	0.707
5	1	2	2	2	3	3	1	1	3.7	90	1.51
6	1	2	3	3	1	1	2	2	9.2	240	0.076
7	1	3	1	2	1	3	2	3	9.8	240	0.169
8	1	3	2	3	2	1	3	1	4.9	455	0.708
9	1	3	3	1	3	2	1	2	10	115	2.45
10	2	1	1	3	3	2	2	1	55	650	0.325
11	2	1	2	1	1	3	3	2	24	300	0.469
12	2	1	3	2	2	1	1	3	8.2	260	1.24
13	2	2	1	2	3	1	3	2	19	300	0.336
14	2	2	2	3	1	2	1	3	22	220	0.502
15	2	2	3	1	2	3	2	1	9	200	0.680
16	2	3	1	3	2	3	1	2	17	160	0.378
17	2	3	2	1	3	1	2	3	9.8	190	1.01
18	2	3	3	2	1	2	3	1	8.3	290	0.137

are not recognized statistically compared with the other control factors. Hence, the dc power and the nitrogen gas flow are pooled as the experimental error in this study.

In general, a probability of 5% is considered quite low in the field of mathematical statistics. Therefore, if the value of F for a control factor is larger than $F_{(\phi 1,\phi 2:5\%)}$, the effect of a control factor is accepted at the 5% level, and the control factor is recognized as a significant control factor. $F_{(\phi 1,\phi 2:5\%)}$ denotes the F statistic at the 5% level with ϕ_1 and ϕ_2 obtained from the F distribution table given in reference 22, with ϕ_1 and ϕ_2 being the degree of freedom of a control factor and the experimental error, respectively. $F_{(1,6:5\%)} = 5.99$ and $F_{(2,6:5\%)} = 5.14$ according to the F distribution table [22]. The F statistics of the substrate temperature, the sputtering pressure and the distance are 7.39, 6.08 and 8.20, respectively. These F values are larger than 5.14; therefore, their effects are statistically accepted, and these control factors are significant for the hardness of the CN_x thin films. Especially, the F statistic of the distance indicates the largest value, so that the distance is the most important control factor in the examined range. On the other hand, the F statistics of the substrate treatment and the sputtering time are smaller than 5.99 and 5.14, respectively. Thus the effect of the control factors are not statistically accepted in this study. It is an interesting result that the distance is the most important factor for controlling the hardness of the CN_x thin films, which has not been reported so far. In addition, the effect of the sputtering control factors on the hardness was expressed numerically using the Design of Experiments and the ANOVA method, and the importance of the control factors is clarified through our study. Hence, these statistical methods are effective for comparing the importance of many sputtering control factors.

The result of the dc power is the same as that reported by Li *et al.* [30], so that it is considered that the hardness of CN_x films does not strongly depend on the dc power. Considering the nitrogen concentration, we suppose that this seldom influences the hardness because the atomic fraction of N in the CN_x films hardly changes in the region from 40 to 100% [31]. The nitrogen concentration measured by SNMS confirmed this. The nitrogen concentration of the films deposited under the three different gas Ar/N_2 mixtures varied from 9×10^{22} atoms cm^{-3} to 8×10^{22} atoms cm^{-3}. The actual concentrations are nominal values. What is important is the insignificant variation between them. The values of 9×10^{22} atoms cm^{-3} measured from the optimum sample would represent a nitrogen fraction of 51% if a structure factor (approximately proportional to density) of diamond was assumed. The impurity in the film was only Si, and the impurity level was less than 0.5%. If a lower structure factor is used, then the nitrogen concentration would be lower. In the absence of a well calibrated structure factor for CN, it is difficult to determine the absolute nitrogen fraction accurately using SNMS. The thickness of a thin film strongly depends on sputtering time, and the hardness value measured of a thin film is influenced by the thickness due to the mechanical properties of the substrate. Consequently, the sputtering time is thought to influence the measured hardness [32]. In the present study, the thickness of the CN_x films drastically changes from 90 to 1150 nm; however, the effect of the sputtering time is not statistically accepted.

3.2. Optimizing sputtering conditions

Fig. 1a–c shows the variation of the mean hardness as a function of the substrate temperature, the sputtering pressure and the distance. The mean hardness decreases with increasing the substrate temperature. This tendency is the same as that reported by Li *et al.* [31]. The drop in hardness with increasing the substrate temperature is likely to be due to the transformation of the film structure to graphite like structure at higher temperature [31]. The mean hardness increases with decreasing the sputtering pressure, in accordance with the report by Li *et al.* [30]. Finally, the mean hardness reaches a maximum at the distance of 4.5 cm. This is an interesting result because the relationship between

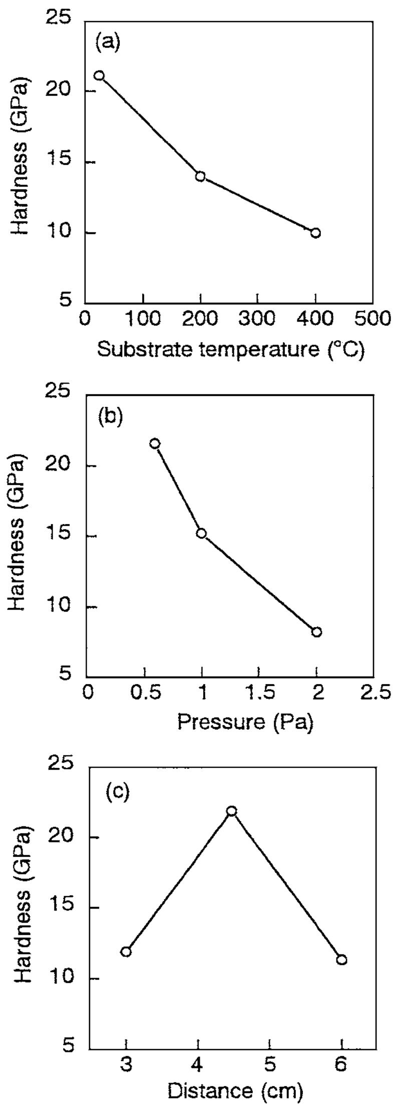

Figure 1 Dependence of mean hardness of CN_x thin films on substrate temperature (a), sputtering pressure (b) and distance between target and substrates (c).

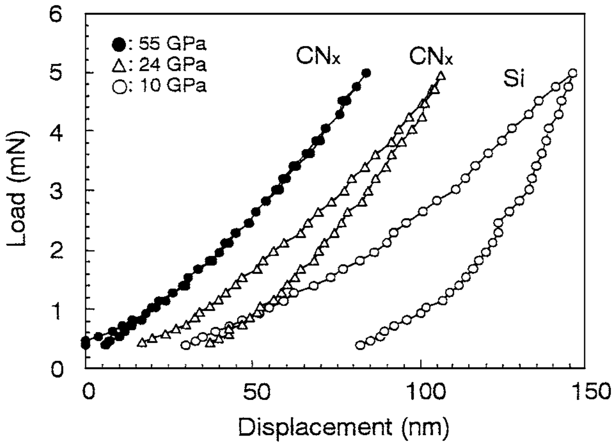

Figure 2 Load-displacement curves of Si substrate (○), CN_x film deposited under the sputtering conditions of No. 11 in Table II (△) and CN_x film deposited under the optimized sputtering conditions (●). The hardnesses are 10, 24 and 55 GPa, respectively.

the hardness and the distance has not been investigated before. From these results, the optimum sputtering conditions are the substrate temperature of room temperature (no heating), the sputtering pressure of 0.6 Pa and the distance of 4.5 cm.

Fig. 2 compares the load-displacement curves for the Si substrate, the CN_x film deposited under the sputtering conditions of No. 11 in Table II and the CN_x film deposited under the optimized sputtering conditions: HF substrate treatment, substrate temperature of room temperature, sputtering pressure of 0.6 Pa, dc power of 700 W, N_2 concentration of 100%, distance of 4.5 cm and sputtering time of 20 min. The CN_x film thicknesses are 300 and 650 nm, respectively. The indentation depth at maximum load decreases from 146 to 84 nm. The residual indentation was reduced from 64 to 4 nm giving an increase recovery ($\%R$) of 56 to 98%. This result suggests that a large proportion of the deformation of the film deposited under the optimized conditions is elastic. According to the unload-displacement curves of the CN_x films, the harnesses are 55 ± 11 and 24 ± 5 GPa, the Young's moduli are 228 ± 21 and 167 ± 6 Gpa. The hardness and the $\%R$ of the film deposited under the optimized conditions are comparatively high values for the CN_x films reported elsewhere [4, 5].

We measured the stress in the CN_x thin films, because it is generally known that the hardness of a thin film is increased by the stress in the film [33, 34]. The stress in the films was determined by measuring the radius of curvature of the Si substrates and following equation [33]:

$$\sigma = \frac{4E_s d_s^2 \delta}{3(1 - V_s) l^2 d_f}$$

where E_s, V_s are the Young's modulus and Poisson's ratio of the Si substrate; δ, l, d_s, d_f are the maximum deflection, the scanning length, the thickness of Si substrate and CN_x thin film, respectively. The measured average of the maximum deflection δ of the CN_x film deposited under the optimized conditions is 35 nm. Thus the calculated corresponding stress exhibits a low compressive stress value of 0.3 GPa. The stress in all the 18 samples are shown in Table II, suggesting that the high hardness of the film is not related to the compressive stress in the film.

4. Conclusions

We applied design of experiments and the ANOVA methods to optimize the sputtering conditions for preparing hard and elastic CN_x thin films. It is found that the effects of the substrate temperature, the sputtering pressure and the target to substrate distance are statistically significant control factors within the experimental range of this study. Especially, the distance is the most significant factor. On the other hand, the effects of the substrate treatment, the dc power, the nitrogen gas flow and the sputtering time are not statistically significant. The optimum sputtering condition is achieved at low substrate temperature (no heating), a low pressure of 0.6 Pa and the distance of 4.5 cm.

The CN_x thin film deposited under the optimized sputtering conditions indicates a hardness of 55 ± 11 GPa, a Young's modulus of 259 ± 21 GPa and an elastic recovery of 98%. The hardness and the $\%R$ values are comparatively high compared to other published results. According to the measurement of the stress in the film, the hardness of the film is not due to the compressive stress. These CN_x films require further experimental and theoretical study, their relative ease of deposition makes them particularly suitable as protective coatings.

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