

STRUCTURES AND PROPERTIES OF THE CRYSTALLINE Si-C-N USING ADDITIONAL Si-SOURCE AND Co-CATALYST

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Abstract. Si-C-N films were synthesized on Si substrates by microwave plasma chemical vapor deposition (MPCVD) with a mixture of CH₄ and N₂ as gaseous sources, and Co-coated Si columns to act as a catalyst and an additional Si source. Two conditions, conditions 1 and 2, were implemented by varying the time at which the solid sources were introduced. Under condition 1, the solid sources were applied 'before' film deposition. Under condition 2, the solid sources were applied both 'before and during' film depositions. Analytical results indicate, although that both conditions yield crystalline Si-C-N films, the time at which the solid sources are applied is critically affects the films' structures and properties. Synthesizing Si-C-N films under condition 1 yields crystals with more re-nucleation, a structure closer to a pseudo T-Si₃N₄ structure, a higher C content, detectable Si(2p)-C bonding, lower nano-hardness and better field emission properties. Synthesis of film under condition 2 yields, crystals with more facets, a structure closer to pseudo α -Si₃N₄, and an additional thin layer under the crystalline layer. SEM, TEM, XPS, XRD, nanoindentor and field emission were used to characterize the film' structures and properties.

1. INTRODUCTION

Liu and Cohen [1,2] predicted that the covalently bonded β -C₃N₄ could be the superhard material; carbon nitride has attracted extensive interest in academic and technological communities. They theoretically calculated that the hardness of covalent β -C₃N₄ was superior to that of diamond, because of the small ionic radii and low ionicity. Si-C-N crystals were accidentally discovered while synthesizing C-N materials using a Si substrate [3,4]. Also, adding an extra source of Si was reported to enhance crystal growth, and stabilize atomic bonding among Si-containing C-N compounds [5-7]. Many reports on C-N and Si-C-N have been published since the prediction; however, crystalline C-N or Si-C-N structures have still not been convincingly identified. Some investigations [8, 9] state that C-N crystals could match partially theoretically calculated X-ray diffraction results, or that Si-C-N

crystals [10,11] have a structure close to that of α -Si₃N₄ or β -Si₃N₄ as determined by JCPDS.

In the authors' previous work, Si-C-N crystalline films were synthesized on the Si wafer, and the growth was observed to be dominated by two deposition stages, according to the films' structures [12]. In the first stage, a ternary Si-C-N amorphous thin layer with embedded nano-crystals is formed. In contrast, in the second stage, binary Si-N crystals, rather than the ternary Si-C-N crystals, are formed. We posited that Si-N and Si-C-N crystals competitively formed during deposition. The formation of Si-N crystals rather than Si-C-N crystals is much easier, and is energetically favorable at a deposition time beyond 6 hr. Hence, Co is added in this study as a catalyst to increase the carbon content in Si-C-N crystals. As a well-known catalyst, this material assists carbon nanotube growth [13-16] and enhances CH₄ gas decomposition [17]. Additionally, solid sources of both Si precursor and Co catalyst

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Table 1. Effect of timing of application of solid sources on film structures.

Condition	Film deposition time (hr)	Morphology	Crystal structure	Bonding structure types
1	4 ~ 18	Crystals with re-nucleation	pseudo-T-Si ₃ N ₄	Si-C, Si-NC-N, C=N
2	2 ~ 4	Faceted crystals with a under thin layer	pseudo- α -Si ₃ N ₄	Si-N, C-N, C=N

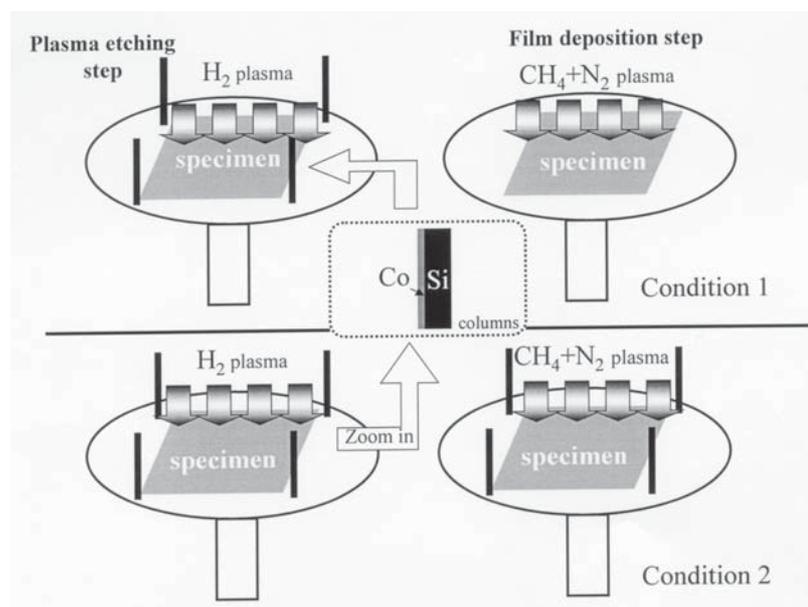
are applied at different times, to investigate the competitive mechanisms of various crystal phases.

2. EXPERIMENTAL DETAILS

Si-C-N films were deposited on the Si wafer by MPCVD. Table 1 lists the detailed parameters and results of each sample. Physical vapor deposition (PVD) Co films (1000 E), coated on one side of Si columns with a diameter of about ~ 2 mm, were used as a catalyst and additional source of Si (solid sources or solid columns). These solid columns were symmetrically inserted into a specimen holder around the specimen. Fig. 1 schematically depicts the two conditions. Condition 1 involves applying the solid sources to the substrate by H₂ etching for 10 min., 'before' film deposition; these solid sources are removed before process gases are introduced. Condition 1 can be restated as substrate pretreatment. In contrast, condition 2 applies the solid

sources 'before + during' film deposition. The conditions for film deposition were as follows: microwave power, 800 W; deposition pressure, 12 Torr; deposition temperature, 1000 °C and flow ratio, CH₄/N₂ = 10/100 sccm/sccm, 2~18 hr.

The film compositions were determined by X-ray photoemission spectroscopy (VG Microteck MT-500), using a monochromatic X-ray source of an Mg K _{α} line at 1253.6 eV with a line width of 0.7 eV. The pass energy of the spectra scan was 23.5 eV and the diameter of the analyzed area was ~ 800 mm. Scanning electron microscopy (SEM) was used to examine the films' morphologies. Transmission electron microscopy (TEM) characterized microstructures of the Si-C-N crystals, and X-ray energy dispersive spectroscopy (EDS) was used to determine their composition. X-ray diffraction was used to identify the films' structure. The field emission properties of the films were obtained from I-V measurements taken at pressure of 10⁻⁶ Torr, at an electrode

**Fig. 1.** Positions of four Co-coated Si columns under conditions 1 and 2.

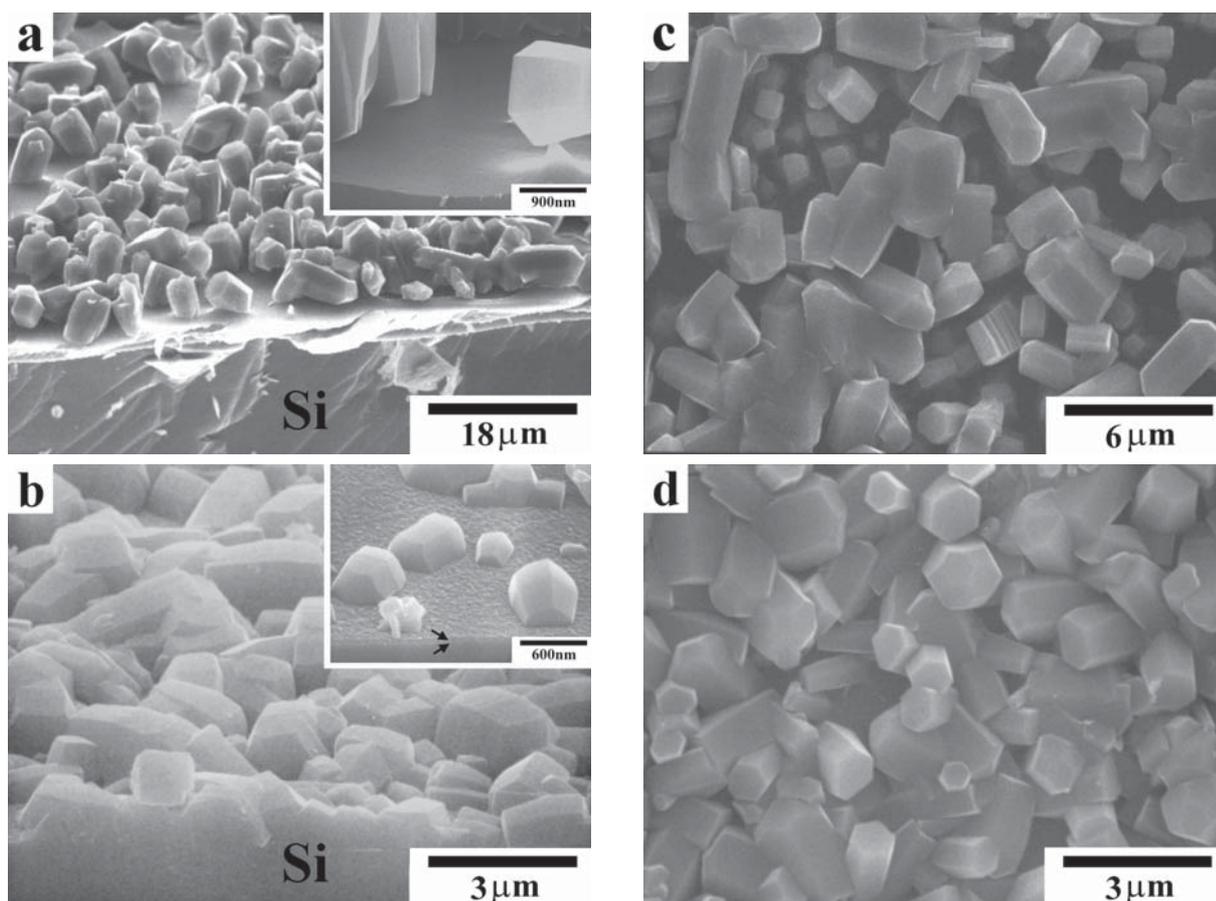


Fig. 2. SEM morphologies of the films deposited under (a) condition 1 (cross section view at two different magnifications) for 12 hr deposition, (b) condition 2 (cross section view at two different magnifications) for 2 hr deposition, (c) condition 1 (top view) for 18 hr deposition and (d) condition 2 (top view) for 4 hr deposition.

separation of 50 μm . Nano-hardness and the reduced modulus of the films were derived from a load-depth sensing technique by a nano-indentation probe (Hysitron Triboscope).

3. RESULTS AND DISCUSSION

3.1. SEM morphology

Figs. 2a-2d depict the SEM morphologies of the films deposited under conditions 1 and 2, as described under “Experimental details” and as shown in Fig. 1. Comparing Figs. 2a and 2b clearly reveals that an additional interlayer layer (approximately 180 nm thick) below the deposited crystals was observed under condition 2, but no interlayer was observed under condition 1. This result is consistent with the authors’ previous studies of an additional Si-C-N amorphous layer under the crystalline layer, formed by continuously supplying an Si source during film deposition [12]. The formation of an additional thin

layer under condition 2 is suggested to follow from the incorporation of the additional Si source during film deposition. The involvement of Si essentially increases the crystal formation rate [18]. Consequently, the residual H_2 in the chamber formed by the change of gas sources from H_2 to CH_4/N_2 , may influence initial phase formation under condition 2. Condition 2 supports a higher deposition rate ($\sim 1.5 \mu\text{m/hr}$) of the film than condition 1 ($\sim 0.5 \mu\text{m/hr}$). Comparing Figs. 2c and 2d reveals that, condition 1 promotes re-nucleation and less faceted crystals. Notably, no crystal growth was observed when no solid source of Co or Si was present. Introducing an additional Si or Co source causes crystal growth, which result is consistent with the difficulties of growing large binary C-N crystals. Consequently, properly treating the substrate enhances crystals growth, and introducing additional solid source during film growth also affects crystal growth rate.

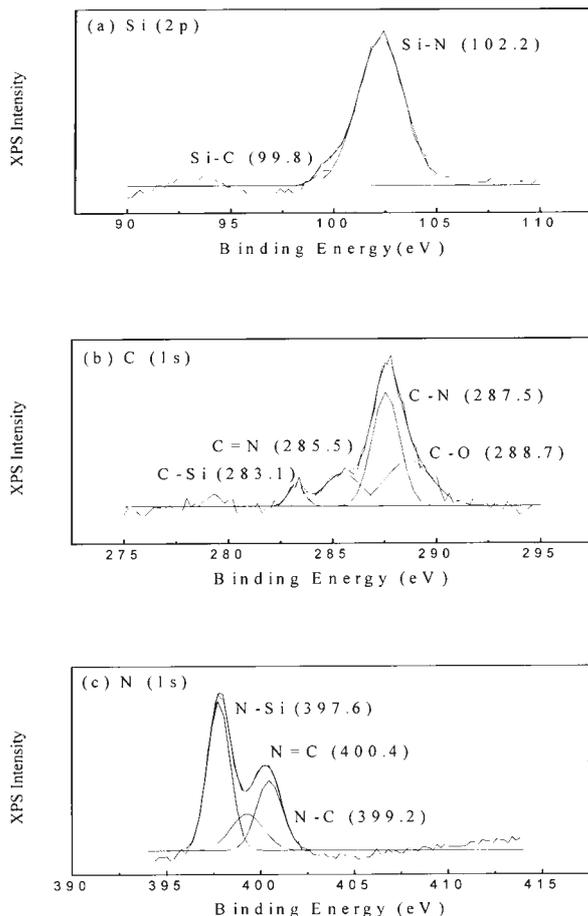


Fig. 3. XPS spectra of the films deposited under condition 1: (a) Si(2p) core level, (b) C(1s) core level and (c) N(1s) core level.

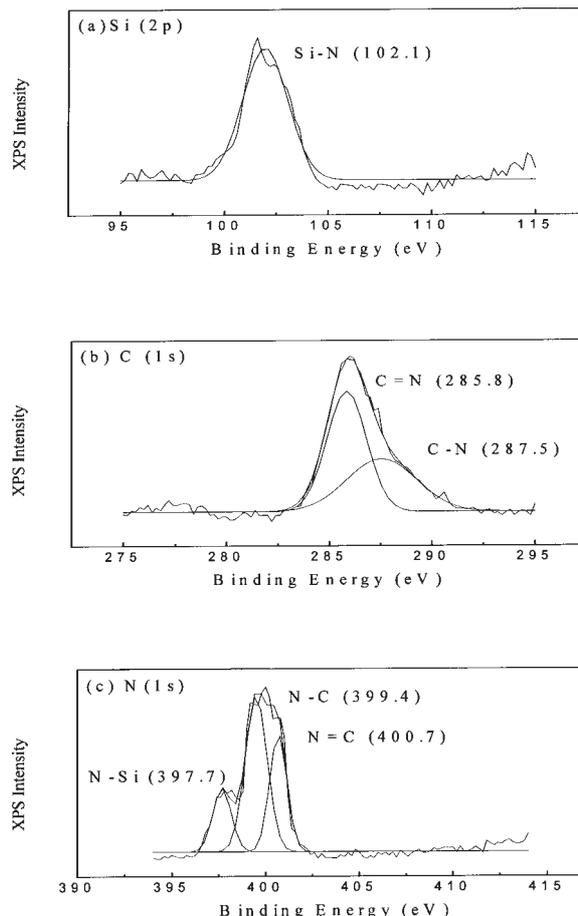


Fig. 4. XPS spectra of films deposited under condition 2: (a) Si(2p) core level, (b) C(1s) core level and (c) N(1s) core level.

3.2. XPS bonding structures

Figs. 3 and 4 present the XPS core level spectra of Si(2p), C(1s) and N(1s) for films synthesized under conditions 1 and 2. The spectra can be deconvoluted by Gaussian fitting into sub-peaks, revealing the multiple bonding structures of Si-C-N crystals. Under condition 1, Si(2p)-N, C(1s)-N, C(1s)=N, N(1s)-Si, N(1s)-C and N(1s)=C bonds are at 102.2 eV, 287.5 eV, 285.5 eV, 397.6 eV, 399.2 eV and 400.4 eV, respectively. Si(2p)-C and C(1s)-Si bonds are at 99.8 eV and 283.1 eV, respectively. In contrast, under condition 2, Si(2p)-N, C(1s)-N, C(1s)=N, N(1s)-Si, N(1s)-C and N(1s)=C bonds are at 102.1 eV, 287.5 eV, 285.8 eV, 397.7 eV, 399.4 eV and 400.7 eV, respectively. Interestingly, no separate peak matches Si(2p)-C bond, which result is also consistent with no C(1s)-Si bond. In most literature on the Si-C-N bonding structure [3-4, 19-20], Si(2p)-C or C(1s)-Si bonding is barely detected. One report

[21] on Si-C-N films, prepared by hot-filament chemical vapor deposition (HFCVD), states that most of Si-C bonds are formed at a temperature above 1100 °C, since the C-N bond dissociates at this temperature, indicating that C-N bonds are stable at a lower temperature than in Si-C bonds.

Condition 1 is similar to condition for the synthesis of carbon nitride on the CoSi_x substrate, and gives C atoms good chance to react with Si substrate. Hence, condition 1 better supports the formation of Si-C or C-Si bonds. The reported states that Si-C bonds may be formed at temperatures above 1100 °C higher than the deposition temperature used in this study, implying that a Co catalyst can effectively lower the formation energy barrier to Si-C bond. Condition 2 supplies more Si sources and greatly reduces the catalytic effect of Co. Si atoms may quickly combine with N_2 due to a lower energy of formation yielding no Si-C or C-Si bonds.

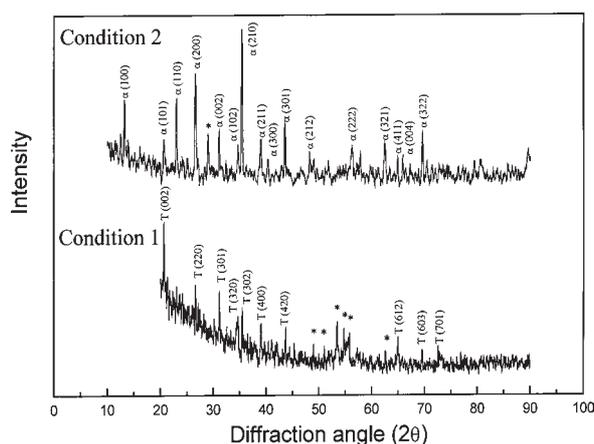


Fig. 5. XRD patterns of the films deposited under conditions 1 and 2, both with deposition times of 4 hr.

3.3. Chemical compositions and crystal structures

XPS analyses of film composition show the presence of Si, C, N and O in both conditions 1 and 2, whereas most O content is greatly reduced after Ar sputtering. No Co signal is observed. Notably, the carbon content of the film under condition 1 increases with deposition time, the compositions corresponding to deposition times of 8 hr and 18 hr are $\text{Si}_{7.5}\text{C}_{7.6}\text{N}_{4.0}\text{O}_{0.7}$ and $\text{Si}_{4.3}\text{C}_{12.9}\text{N}_{4.0}\text{O}_{0.3}$, respectively. Moreover, the film thickness at deposition times of 8 hrs and 18 hrs is 4.5 μm and 8.8 μm , respectively. In the absence of an additional Si source, much carbon is incorporated into the films, revealing that the growth mechanism of crystal varies with deposition time. When the crystals cover the substrate, the effect of pretreating the substrate with Co and Si is lost. Consequently, carbon rich Si-C-N is favored over a long deposition time. The lack of Co and Si incorporation in films synthesized under condition 1 over a long deposition time, suggests a condition resembling that of binary CN growth. Zhang *et al.* reported that the dominant phase in carbon nitride prepared by pulsed laser ablation was C_2N [22]. The carbon-rich C-N phase may be more stable than the C_3N_4 phase. In contrast, the film compositions are almost independent of deposition time under condition 2: 2 to 4 hr yield similar compositions close to $\text{Si}_{2.7}\text{C}_{4.6}\text{N}_{4.0}\text{O}_{1.7}$. In the presence of Co and Si sources for films synthesized under condition 2, the incorporation of Si may serve as a stabilizer in the network dominated by CN [18]. The different amounts of Si and Co supplied at films syn-

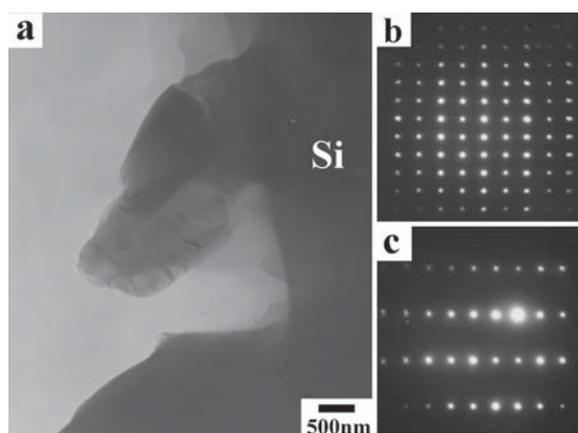


Fig. 6. (a) TEM micrograph and (b) ED pattern of zoom axis [001] and (c) zoom axis [110] for the films deposited under condition 1 for 12 hr.

thesized under conditions 1 and 2 explain the different film composition.

X-ray diffraction was used to analyze the crystal structure under both conditions, with Cu radiation (1.5406 Å) as the source for diffraction, with a grazing angle of 2 degrees. Fig. 5 displays the XRD spectra of films formed under conditions 1 and 2. The XRD spectra of Si-C-N crystals show several sharp lines. A signal ($2\theta \sim 56$ degrees) corresponding to the Si(100) substrate is absent for two reasons. The measured film is several microns in thick, and the deposited film almost covers the Si substrate. X-ray diffraction peaks could be roughly indexed as pseudo T- Si_3N_4 and pseudo α - Si_3N_4 for condition 1 and condition 2 films, respectively. The reason for saying 'pseudo'- Si_3N_4 is that some of the positions of the peaks with correct intensities differ between the experimental and the standard structure. The composition of the condition 1 film that much deviate stoichiometry C_3N_4 or Si_3N_4 exhibit multiple peaks marked by asterisks, which cannot be indexed as α - Si_3N_4 , β - Si_3N_4 or T- Si_3N_4 . The condition 1 film is considered to preserve the main structure framework of pseudo T- Si_3N_4 . In contrast, a different structure was obtained for the film deposited under condition 2. As in the report of [4], the most likely structure of all the possible C_3N_4 structures is that of α - Si_3N_4 . Here, a continuous supply by solid sources favors the formation of a pseudo α - Si_3N_4 like structure, revealing that applying an additional Si source is crucial to obtaining stabilized films.

Transmission electron microscopy was further utilized to investigate the film structure. Fig. 6 displays the TEM image and the corresponding elec-

Table 2. Effect of timing of application of solid sources on mechanical and field emission properties of films.

Solid source application condition	Deposition time (hr)	Film thickness (μm)	Mechanical properties		Field emission	
			Reduced modulus (GPa)	Nano-hardness (GPa)	$E_{\text{turn on}}$ at $I=1 \mu\text{A}$ ($\text{V}/\mu\text{m}$)	J at $20\text{V}/\mu\text{m}$ ($\mu\text{A}/\text{cm}^2$)
1	4		—	—	17.8	940
1	5		—	—	17.7	730
1	6		—	—	16.6	1530
1	8	~ 4.5	16.24	293.5	15.7	720
1	12		—	—	14.4	4040
1	18	~ 8.8	14.52	186.1	3.9	9360
2	2	~ 1.2	30.70	322.0	13.7	1710
2	3		—	—	10.4	990
2	4	~ 4.0	37.92	322.4	18.7	160

tron diffraction (ED) pattern. Some single-crystal diffraction patterns identified a structure of tetragonal Si-C-N. However, many phases could have been present in the condition 1 film, as well as variation in the chemical compositions of individual crystals within the polycrystalline film, yielding a complex structural analysis. X-ray energy dispersive spectroscopy (EDS), equipped with TEM, revealed the presence of Si, C and N in Si-C-N crystals. This technique detects the structure of an individual crystal, unlike XPS, which analyzes bulk film. These studies indeed revealed the presence of multiple phases. The atomic ratios of silicon-carbon-nitrogen in the crystals in Fig. 6a is 10: 9: 4. The TEM results for films synthesized under various conditions will be detailed in further work.

3.4. Field emission property

Table 2 lists the field emission properties of samples formed under conditions 1 and 2, for various deposition times. The turn-on electric field is defined as the electric field required for the emission current to reach $2 \mu\text{A}/\text{cm}^2$, that is for which the emission current = $1 \mu\text{A}$ with anode area = 0.5 cm^2 . The field emission properties of films obtained under condition 1 are better than under those films obtained under condition 2. The Si-C-N film with the best field emission properties was formed under condition 1 with a deposition time of 18 hr, the turn on electric field was $3.88 \text{ V}/\mu\text{m}$ and the emission current density was $9360 \mu\text{A}/\text{cm}^2$ at $20\text{V}/\mu\text{m}$. Fig. 7 presents its J-E plot, and the corresponding F-N plot. According to the Fowler-Nordheim equation [23], the work function Φ , effective emission current area A , and field enhanced factor β are the three main parameters that govern the field emission. The emission area and field enhanced factor are similar for films synthesized under the different conditions, since both films synthesized under different conditions have crystal surfaces. The promising field emission characteristics of the condition 1 film are thought to be related to its high carbon content and the presence of multiple phases. Excess carbon atoms may cluster in the Si-C-N matrix. Although the fact that field emission from C-film is not completely understood, some authors have demonstrated that the applied field can be greatly increased at the conductive sp^2 carbon, and, carbon with mixed sp^2/sp^3 bonding emits at a lower field and a higher emission site density than carbon in single phase films [24-26]. Consequently, the field

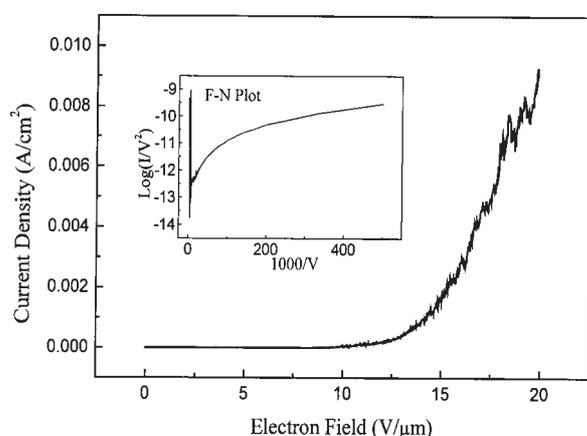


Fig. 7. Field emission I-V curve and corresponding F-N plot for the films deposited under condition 1 for 18 hr.

can be enhanced at the interface between multiple phases, and at carbon clusters which attribute the field emission of condition 1 film.

3.5. Mechanical properties

Nano-indentation tests were used to elucidate the mechanical properties of the films. Table 1 lists the results for both condition 1 and 2 films. The nano-hardnesses of condition 1 films ranged from 14.58 GPa to 16.24 GPa, lower than those of condition 2 films, which ranged from 30.70 GPa to 37.92 GPa. The nanohardness of condition 2 films are similar to the values reported in the literature [27]. Here, the substrate effect can be ignored because the films for test are several μm in thick as shown in Table 2, and the considered regions of Si-C-N films cover all substrate surfaces. The lower hardness of condition 1 films may be due to the greater re-nucleation and multiphase structures, with more weak grain boundaries and defects. The reported C_2N phase may be one of the possible multiphases of the condition 1 crystal, whose graphite-like structure reduces its hardness [22].

4. CONCLUSIONS

This work explores how the timing of applying solid source affects the compositions, bonding, crystal structures and properties of Si-C-N films. The timing of applying solid sources importantly determines the formation of the film. This phenomenon, has not before been extensively addressed. This work thus increases understanding of film deposition mechanisms for C-N, Si-C-N, Si-N and Si-C, and similar film. The results also explain why no bulk C_3N_4 crystals have yet been successfully deposited.

Solid sources were applied under two conditions. The condition 1 film, has a higher C content, which increases with deposition time, re-nucleation, detectable Si-C bond, similar to a pseudo T- Si_3N_4 crystal structure, decreasing deposition rate ($0.5 \mu\text{m}/\text{hr}$), better field emission properties, and decreasing nano-hardness. In contrast, the composition of the condition 2 film, negligibly varies with deposition time, has increasing crystal size with less re-nucleation, no Si-C bonds, similarity to pseudo α - Si_3N_4 crystal structure, or deposition rate ($1.5 \mu\text{m}/\text{hr}$). The structures and properties of Si-C-N films were adjusted by varying time at which solid sources were applied. The introduction of catalytic material has opened an interesting area in the study of the synthesis of Si-C-N crystals.

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