

## Precursor test for the deposition of carbon nitride thin films using microwave plasma enhanced chemical vapor deposition

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Carbon nitride films were grown on Si(100) substrate by microwave plasma enhanced chemical vapor deposition (PECVD). Melamine, 1*H*-1,2,3-triazole, and hexamethylenetetramine (HMTA) were tested as carbon and nitrogen sources where N<sub>2</sub> and H<sub>2</sub> were used as carrier gas. X-ray diffraction (XRD) spectra analysis revealed that the films deposited from HMTA source appear to contain the strong peaks of  $\alpha$ - and  $\beta$ -C<sub>3</sub>N<sub>4</sub>; (210),  $\beta$ -C<sub>3</sub>N<sub>4</sub>(111) and  $\alpha$ -C<sub>3</sub>N<sub>4</sub>(300) as well as some graphitic phases. More graphitic carbon structures might be grown when 1*H*-1,2,3-triazole and melamine were used as precursors. The micro mechanical properties of the deposited films were measured using a nanoindenter. Average micro hardness, calculated for the films deposited from HMTA is 27.7 ± 8.6 GPa. The multiple bonding states between carbon and nitrogen were observed in X-ray photoelectron (XPS) study. From the experimental evidences we propose that HMTA can be used as promising precursors for CVD to deposit carbon nitride films.

**Keywords:** Chemical vapor deposition (CVD); Nitrides; X-ray diffraction; Hardness

### 1. INTRODUCTION

In 1989, Liu and Cohen [1] presented firstly theoretical calculation for C<sub>3</sub>N<sub>4</sub>, a new hypothetical material and suggested that it should be metastable and possesses extreme hardness (comparable to or larger than that of diamond), wide band gap (3.2 eV), high velocity of sound (1.1×10<sup>6</sup> cm/s), large thermal conductivity, low dielectric constant and low friction coefficient. These properties make the material attractive to a wide range of applications such as mechanical cutting tools, protective cutting, optical materials, and insulating layer of ULSI technology [2]. Many researchers have attempted to deposit the carbon nitride films by various CVD processes [3-6]. Only a few techniques, like microwave-PECVD [7-9], have been found to be promising for synthesizing polycrystalline carbon nitride films. However, further study are needed.

So far, CH<sub>3</sub>C≡N, BrC≡N [10], (CH<sub>3</sub>)<sub>3</sub>N + NH<sub>3</sub> etc [11] were used as the precursors for the carbon nitride. However, the synthesized films from the above precursors were hydrogenated amorphous carbon nitrides, in which other C-N bonds (such as C=N and / or C≡N) than sp<sup>3</sup>C-N might exist to compete in their formation. So it is very important to select a precursor which is stereo-chemically favorable for the predicted carbon nitride structure. In this paper we report the deposition of carbon nitride from different precursors; such as melamine+N<sub>2</sub>, 1*H*-1,2,3-triazole+N<sub>2</sub>, and HMTA+H<sub>2</sub>. The structure of HMTA closely resembles that predicted for  $\alpha$ - or  $\beta$ -C<sub>3</sub>N<sub>4</sub>, since all the C atoms are tetrahedrally coordinated with N. Fig. 1 shows the schematic structures of HMTA, Melamine and 1*H*-1,2,3-triazole.

The deposited films were analyzed with respect to

micro microstructure, mechanical properties and states of chemical bonding by XRD, nanoindenter and XPS respectively.

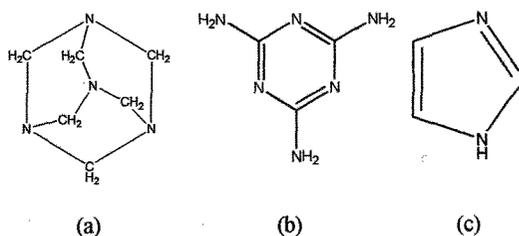


Fig.1 Schematic structures of (a) HMTA, (b) Melamine and (c) 1*H*-1,2,3-triazole.

### 2. EXPERIMENTAL

A microwave PECVD reactor, shown in Fig.2 was used for the deposition process. The reaction chamber is a quartz tube, sealed to a stainless steel flanges at each end, of 420 mm in length and 46 mm in inner diameter. Si(100) single crystals (~1×1 cm<sup>2</sup>) with the thickness 625 ± 18 μm (Osaka Titanium co. ltd) were used as the substrate. Prior to loading into the reaction tube, it was scratched with diamond powder, and then cleaned with ethanol by an ultrasonic cleaner and dried using a stream of nitrogen gas. An optical pyrometer (Model IR-U, CHINO, Japan) was used to measure the substrate temperature. Melamine (Wako Pure Chemical), HMTA (99%, Wako Pure Chemical) and 1*H*-1,2,3-Triazole (97% Aldrich Chemical Co.) were put in a quartz crucible hung from the ceiling of the reactor,

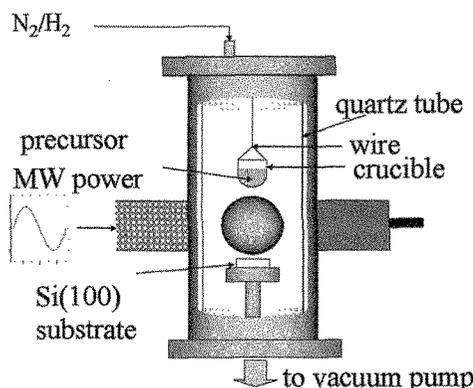


Fig. 2. Schematic diagram of reaction chamber for microwave PECVD.

which were vaporized by plasma heating. The vaporization rate was controlled by varying the distance of crucible from the plasma. The flow rate of gases ( $N_2$ , 99.999%,  $H_2$ , 99.9%) was controlled by using mass flow controller. Table I shows the typical experimental conditions for the  $CN_x$  deposition.

Table I. The experimental conditions used for the carbon nitride film deposition.

Precursor / Parameters	Melamine (M) $N_2$	1H-1,2,3-triazole (T) $N_2$	HMTA (H) $H_2$
MW Power (2.45 GHz)	400 W	300 W	400 W
Flow rate (sccm)	M: $7.42 \times 10^{-3}$ $N_2$ : 50	T: 0.015 $N_2$ : 80	H: 0.26 $H_2$ : 95
Substrate temperature	850 °C	950 °C	850 °C
Deposition time min	90	60	180
Reaction pressure	40 Torr	40 Torr	40 Torr

Crystallinity of the deposited films were investigated by XRD (Rigaku Rint 700) using  $Cu-K\alpha$  radiation. The micro mechanical properties of the deposited films and substrates were measured with a nanoindenter (ENT-1100 Micro Hardness Tester, Elionix). Indentations were made with maximum 5mN load, at 10 indents sequences for each load. Micro hardness, Young modulus and elastic recovery,  $E_r$  of the films were determined from the load versus displacement curves obtained in nanoindentation tests, where  $E_r$  was defined as:

$$E_r = (D_{max} - D_{min}) / D_{max}$$

Where,

$D_{max}$ : displacement at maximum load after loading

$D_{min}$ : residual displacement after unloading

Chemical bonding and composition of the deposited films were determined by XPS (Physical Electronics PHI 5800 ESCA)

### 3. RESULTS AND DISCUSSION

#### 3.1 Crystal structure

The XRD spectra of the deposited films are shown in Fig. 3. The films deposited from HMTA source shows the peaks centered at  $2\theta$  values of 26.4°(c.1), 29.08°(c.2), 33.0°(c.3), 39.16°(c.4), 42.9°(c.5), 47.26°(c.6) and 48.28°(d.7) which correspond to graphitic- $C_3N_4$ (002) or graphitic-C(005), graphitic-C(300), Silicon, graphitic-C(205),  $\alpha$ - and  $\beta$ - $C_3N_4$ (210),  $\beta$ - $C_3N_4$ (111) and  $\alpha$ - $C_3N_4$ (300) [JCPDS 48-1206, 22-1069; 8,12], respectively. The XRD patterns from the films deposited from 1H-1,2,3-Triazole and melamine show peaks a.1 and b.1, and peaks a.3 and b.2 with the same  $2\theta$  values of peaks c.1 and c.3, respectively. Peak b.3 is composed of two peaks at  $2\theta$  values of 43.64 and 44.40° which are ascribed to graphitic-C(002) and (101), respectively [JCPDS 19-0268,75-1621]. XRD of the films deposited from melamine shows peak a.2 with the same  $2\theta$  value of peak c.2.

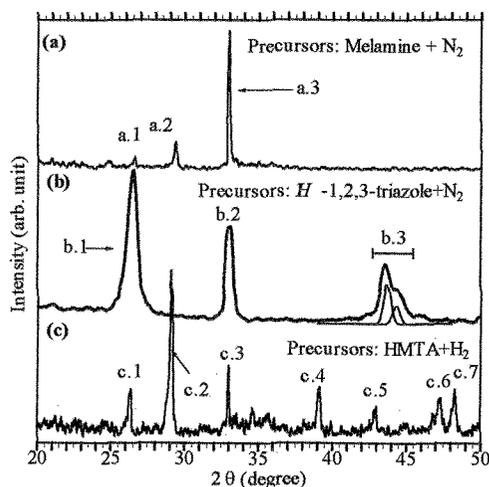


Fig. 3 XRD spectra of carbon nitride films deposited on Si(100) substrate using (a) Melamine, (b) 1H-1,2,3-triazole and (c) HMTA sources under the process conditions stated in Table I.

The XRD studies reveal that the films deposited from HMTA source have some reflections of  $\alpha$ - and  $\beta$ - $C_3N_4$  with some graphitic structure of carbon and  $C_3N_4$  where as the films deposited from 1H-1,2,3-Triazole and melamine sources composed of mainly graphitic structure of carbon and may be that of C and N. We also report that some of the peaks observed in Fig 3.c are also matched with graphitic  $Si_3N_4$  structure

[JCPDS 41-0360]. Overlapping of the X-ray diffraction peaks made the structure analysis more complicated.

### 3.2 Mechanical properties

Typical load-displacement curves from carbon nitride films deposited on Si(100) from different precursors and that of substrate for a maximum load of 5 mN are compared in Fig.4. Fig.4 for CN<sub>x</sub> films deposited from HMTA sources (solid line) shows hardness, Young Modulus and  $E_r$  as  $27.7 \pm 8.6$ ,  $541.9 \pm 162.9$  GPa and 84.8 %, respectively. Hardness, Young Modulus and  $E_r$  of Si(100) substrate are also observed as reference shown in Fig.4 (gray line) which are  $28.5 \pm 3.8$ ,  $569.7 \pm 84.3$  GPa, and 99.4 %, respectively. Fig.4 for CN<sub>x</sub> films deposited from 1H-1,2,3-triazole source (inset curve) shows hardness, Young Modulus and  $E_r$  as  $0.46 \pm 0.3$ ,  $40.61 \pm 13.68$  GPa and 40 %, respectively. The high mechanical properties are indicative of the formation of C<sub>3</sub>N<sub>4</sub> phase when HMTA was used as a precursor. Mechanical properties which are observed for the films deposited from HMTA source on Si(100) with the optimum experimental conditions stated in Table I are comparable to the reported values elsewhere [13].

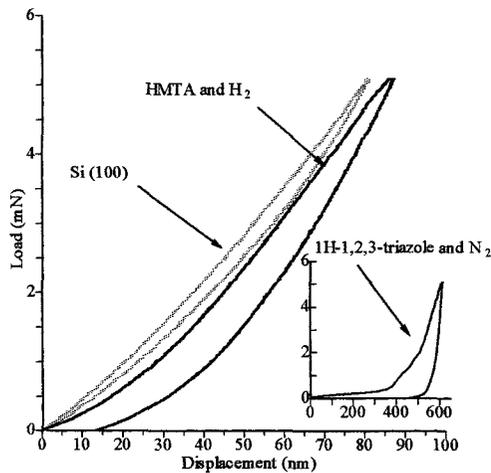


Fig.4. Typical Load-displacement curves for Si(100) substrate (gray line), CN<sub>x</sub> films deposited from HMTA (solid line) and CN<sub>x</sub> films deposited from 1H-1,2,3-triazole (inset curve) with maximum load of 5mN.

### 3.3 XPS study

Narrow scan of N(1s) and C(1s) regions for 30 second sputtered films are shown in Fig.5(a) and (b). The intensities of the photoelectron peaks for the films deposited from melamine+N<sub>2</sub> sources are not good enough to get any spectral feature (not shown here). N(1s) photo-electron peak can be decomposed into five peaks at  $\sim 398$  (a<sub>1</sub>),  $\sim 398.9$  (a<sub>2</sub>),  $\sim 399.72$  (a<sub>3</sub>),  $\sim 401.1$  (a<sub>4</sub>) and  $\sim 403$

(a<sub>5</sub>) eV, which are attributed to N-Si, N-sp<sup>3</sup>C, N-sp<sup>2</sup>C, N-N and NC<sub>x</sub> (x=2 to 5), and N-O bonding structures, respectively [14,15,16,17]. C(1s) photo-electron peak can be decomposed into four peaks at  $\sim 284.8$  (b<sub>1</sub>),  $\sim 286$  (b<sub>2</sub>),  $\sim 287.7$  (b<sub>3</sub>) and  $\sim 289.2$  eV (b<sub>4</sub>), which are attributed to adventitious carbon including C-C, sp<sup>2</sup>-CN, sp<sup>3</sup>-CN, and C-O bonding structures [16], respectively. The C(1s) peak due to C-Si bonding is not detected in the vicinity of 282.8 eV [14]. It is clear that carbon does not have a bond to Si. The films grown from HMTA source consist of sp<sup>2</sup>- and sp<sup>3</sup>-CN bonding states as well as N-Si, N-N and NC<sub>x</sub> (x=2 to 5) and adventitious carbon including C-C bonding structures. No NO and CO bonding states observed in the spectra. Fig.5 also reveals that the films grown from 1H-1,2,3-triazole and N<sub>2</sub> sources are mainly consist of N-N, NC<sub>x</sub> (x=2~5), adventitious carbon including C-C as well as small sp<sup>2</sup>-CN, NO and C-O bonding structures. These XPS observations support the XRD analyses that have been discussed in the section 3.1.

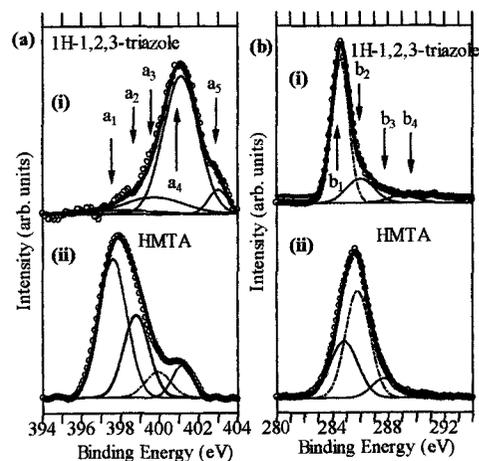


Fig.5. XPS scans of (a) N(1s) and (b) C(1s) for the 30 second sputtered films deposited from (i) 1H-1,2,3-triazole and (ii) HMTA under the process condition stated in Table I.

## 4. CONCLUSION

Carbon nitride films were grown on Si(100) substrates from melamine, 1H-1,2,3-triazole and HMTA precursors using microwave PECVD. The X-ray diffraction pattern analysis indicates that the deposited films from HMTA source are mixture of both  $\alpha$ - and  $\beta$ -C<sub>3</sub>N<sub>4</sub> structure as well as other graphitic phases which are not easily distinguished. The films grown from other sources are mainly composed of graphitic carbon structures. Hardness, Young Modulus and elastic recovery values for the films deposited from HMTA are  $27.7 \pm 8.6$ ,  $541.9 \pm 162.9$  GPa and 84.8 %, respectively. XPS spectra deconvolution

analysis shows the presence of  $sp^2$ - and  $sp^3$ -CN bonding states as well as N-Si, N-N and  $NC_x$  ( $x=2$  to 5) and adventitious carbon including C-C bonding structures for the films deposited from HMTA. From these experimental evidences it is suggested that HMTA can be used as an important reacting materials for the CVD to deposit carbon nitride films.

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