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Growth of spherical carbon nitride with crystalline alpha and beta phases

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ABSTRACT

Carbon is a versatile element, and its allotropes play a center role in both science and technology. Further, doping of nitrogen into carbon network has been of great interest as it leads to superior properties such as chemical, mechanical and electronic properties. Though the preparation of ultrahard β-carbon nitride remains challenging one, it owes great attention due to its superior properties. This work reports preparation and characterization of crystalline carbon nitride on silicon (100) substrate. The X-Ray diffraction revealed that the deposited film- have α and β carbon nitride crystalline phases. The calculated lattice parameters are found to be a = 6.26 Å, c = 2.38 Å for β-C_3N_4 and a = 6.8 Å, c = 4.6 Å for α-C_3N_4. The X-Ray photoelectron spectroscopy study confirms that carbon atom is bonded tetrahedrally (sp^3) with nitrogen atoms as expected for the formation of crystalline C_3N_4, and also the presence of $C = N$ trigonal (sp^2) bond. The surface morphology of the film examined by field emission scanning electron microscopy shows the formation of carbon nitride spheres.

1. Introduction

In 1989, Liu and Cohen reported a local density approximation pseudopotential calculation on hypothetical beta carbon nitride (β-C_3N_4) by replacing silicon atom from β-Si_3N_4 structure. The β-C_3N_4 structure consisting of tetragonally bonded sp^3 carbon and trigonal planar sp^2 nitrogen that have short bond length (1.47 Å) and strong bonds with low ionicity (7%), which leads to extreme hardness comparable or greater than that of diamond. The prediction of ultrahard β-C_3N_4 received an immense attention among research community [1]. A considerable research on theoretical and experimental carbon nitride reveals properties such as high hardness, variable bandgap, chemical inertness, high thermal conductivity, and low friction coefficient [2, 3]. All these unique properties make carbon nitride suitable for wide range of applications such as cutting tool, heat dissipative substrates, wear resistant hard coatings [4], photocatalytic agent [5] etc.

Different techniques have been employed to prepare crystalline carbon nitride (C_3N_4) thin films and powders with expected stoichiometric ratio of 1.33. However, due to strong repulsion of nitrogen to the nitrogen in the C−N containing bonds lead to a lower nitrogen content than the expected 57 at.% of Nitrogen [6]. Till now, most of the reports show only a small amount of crystalline carbon nitride embedded in the amorphous matrix [7]. Also, the prepared crystalline carbon nitride samples contain nanostructures such as carbon nitride nanotubes [8], hexagonal crystalline rods [9], fullerene like [10], nano-onion [11], nanoflake [5] and spherical nanospheres [12]. Among, these structures, the fullerene like carbon nitride called as “super hard rubber” shows extreme elasticity and high resistance against plastic deformation. This superior resiliency with low coefficient of friction could be a promising material for the wear resistant coatings when compared to DLC (diamond-like coatings) and amorphous CN_x [13].

In the present work, Triazine (C9H18N6) was used as a precursor since it has the required bonding between carbon and nitrogen for the formation of carbon nitride. For the film preparation, nitrogen gas was used as inert atmosphere and carrier gas. The prepared film was analysed for the nanostructure formation, elemental composition and subsequent bonding occurring between elements.

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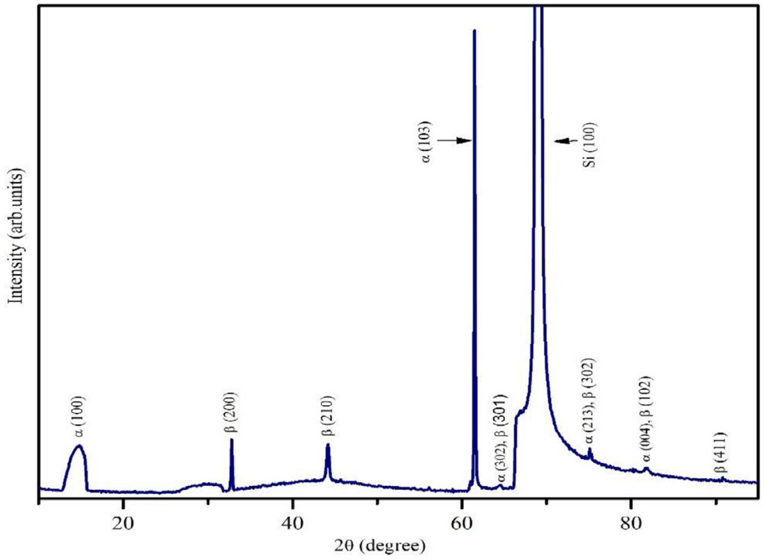

Fig. 1. XRD pattern of the as-deposited carbon nitride film on Si (100) substrate.

2. Experimental details

Carbon nitride film was deposited on silicon (100) substrate by pyrolysis assisted chemical vapor deposition (PVCD) using a two-zone furnace. The experimental setup and the details concerning deposition are reported in our previous work [14]. Triazine ($C_9H_{18}N_6$) powder of 96% purity procured from Sigma Aldrich was used as the precursor. About 0.5 g of the precursor was transferred to closed end of the quartz tube. The oxide layer on the surface of Si was removed by immersing in Hydrofluoric acid for 1 min and washed with deionized water thrice. After that the substrate was cleaned ultrasonically using solvents such as acetone and isopropanol bath. Then the substrate was dried and cleaned with high pure (99.999%) nitrogen gas before loading into the pyrolysis zone. The quartz tube was also purged by the high pure N_2 gas, and evacuated thrice before deposition. After this procedure, the quartz tube was filled with nitrogen gas and then the setup would be ready for the deposition process. Initially temperature of the pyrolysis zone was increased to 800 °C and the temperature was controlled and stablished using a PID temperature controller. Then the temperature of the precursor zone was slowly increased to 400 °C at a rate of 2 °C/min even though the boiling temperature of the precursor is 175 °C. The triazine then would evaporate and dissociates into carbon, nitrogen and hydrogen species entering the pyrolysis zone; and then, deposits on the silicon substrate maintained at 800 °C. After 60 min of deposition, the furnace was allowed to cool down to room temperature. The deposited carbon nitride film was found to well adhered to the crystalline silicon substrate.

The crystal structure of the film was determined by XRD ((Rigaku, Cu K_α radiation ($\lambda = 1.54$ Å)). The optical spectroscopic analysis probed using Raman spectroscopy (LabRAM HR) using visible wavelength of 514 nm and CCD detector at room temperature. The nature of the bonding between the elements were analyzed using XPS (AXIS ULTRA, monochromatic X-ray source (Al Kα, 1486.6 eV, line width 0.5 eV, under a vacuum environment of 2×10^{-9} Torr) and the surface morphology features were investigated by FESEM (Gemini Ultra 55).

2.1. XRD analysis

The XRD pattern of the as-prepared film given in Fig. 1 clearly displays the presence of sharp peaks with considerable background and humps indicating the presence of both the crystalline and amorphous nature. The obtained XRD result is compared with previously reported theoretical and experimental results, as listed in table 1. Peaks observed at d-spacing of 5.92, 2.73, 2.05, 1.50 and 1.08 Å are indexed to carbon nitride of α (100), β (200), β (210), α (103) and β (411) respectively. Other d-spacings at 1.44, 1.26 and 1.17 Å show mixed phase of α and β-C_3N_4 as mentioned in the table 1. A very strong peak observed at $2\theta = 61.56$ corresponds to α-C_3N_4 (103). The secondary phase strong peak observed at $2\theta =$ 44.20 (2.05) corresponds to (210) of β- C_3N_4. Apart from sharp peaks, the presence of broad humps clearly illustrates the presence of amorphous matrix in the deposited film**.** The amorphous carbon nitride is the starting material and the application of temperature induces the formation of more tetrahedral bonded crystalline carbon nitride [1]. The prepared film shows the presence of both α and β phases as the total energy for α-C_3N_4 is lower than for β phase and differs only by 277 meV/ unit cell [15].

The calculated lattice parameters for β-$C_3N_{4,}$ $a = 6.26$ Å, $c = 2.38$ Å and $c/a = 0.38$; and for α-C_3N_4, $a = 6.8$ Å, $C = 4.6$ Å and $c/a = 0.67$. The calculated parameters are in close agreement with previous reports [19, 20]. There is no peak observed for graphene or diamond phases of carbon allotropes. A high intense sharp peak at $2\theta = 69.5$ is due to silicon (100) substrate and no other evidence for the formation SiC, SiN and SiCN found.

2.2. FESEM

The surface morphology features of the prepared carbon nitride film was obtained by FESEM. The FESEM images show the formation of spherical structures with branches. The size of the spheres ranges from nanometer to micron as shown in Fig. 2. Initially, the dissociated carbon and nitrogen species from the precursor side travel and deposits on silicon substrates maintained at 800 °C in the pyrolysis zone. All the carbon atoms with sp^2 bonding nature form hexagonal rings and grow as basal planes on the substrate. The upcoming nitrogen atoms incorporated into the hexagonal network of carbon basal planes, changes the carbon-sp^2 to reactive carbon sp^3 sites. This reduces the barrier energy for the formation of pentagon structures which leads to the curvature of basal planes of graphene sheets. This process could ultimately evolve as a spherical structure. An illustration of basal plane formation and curvature induced in the basal planes to spherical structure formation are depicted stepwise in Fig. 3. Carbon sites adjacent to

Table 1
d-spacing and hkl values from the present work compared with the values reported in the literature.

S. Matsumoto et al. [16]				J. Wang et al. [8]		Yin et al. [17]		D.J. Johnson et al. [18]		Present work		
β-C_3N_4		α-C_3N_4		β-C_3N_4		β-C_3N_4		α, β-C_3N_4		α, β-C_3N_4		
d (Å)	hkl	d (Å)	hkl	d (Å)	hkl	d (Å)	hkl	d (Å)	hkl	d(Å)	hkl	Phase
5.54	100	5.600	100	–	–	–	–	–	–	5.92	100	α-C_3N_4
2.77	200	2.800	200			2.765	200	2.70	200	2.73	200	β-C_3N_4
2.095	210	–	–	2.069	(210)	2.09	210	2.043	210	2.05	210	β-C_3N_4
1.538	310	1.512	103	–	–	–	–	1.499	310	1.50	103	α-C_3N_4
1.465	301	1.463	302	1.465	(301)	1.46	301	1.423	301	1.44	mixed phase	α (302), β (301)
1.272	302	1.261	213	–	–	1.27	320	1.263	311	1.26	mixed phase	α (213), β (302)
1.175	102	1.177	004	1.197	(002)	1.175	102	–	–	1.17	mixed phase	α (004), β (102)
1.08	411	–	–	–	–	1.10	002	–	–	1.08	411	β (411)

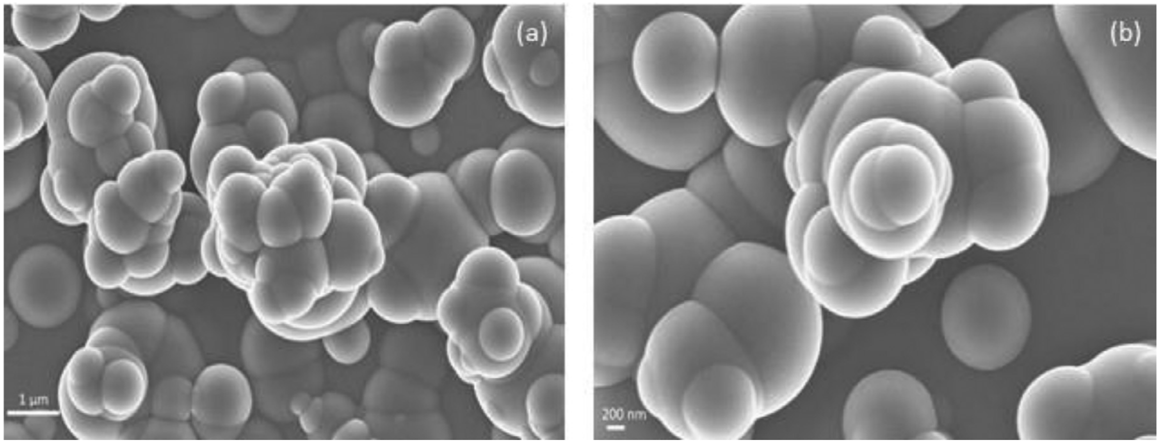

Fig. 2. FESEM images of the carbon nitride spheres prepared at 800 °C with different magnifications are (a) 1 μm and (b) 200 nm.

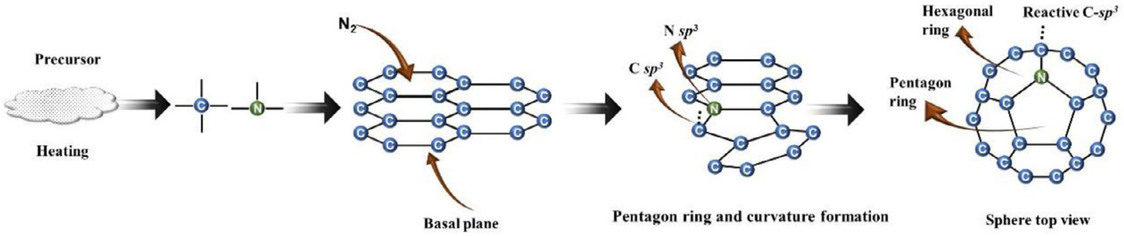

Fig. 3. Possible representation of the formation of basal planes, nitrogen substitution and pentagon formation, induction of curvature and formation of spherical structure respectively.

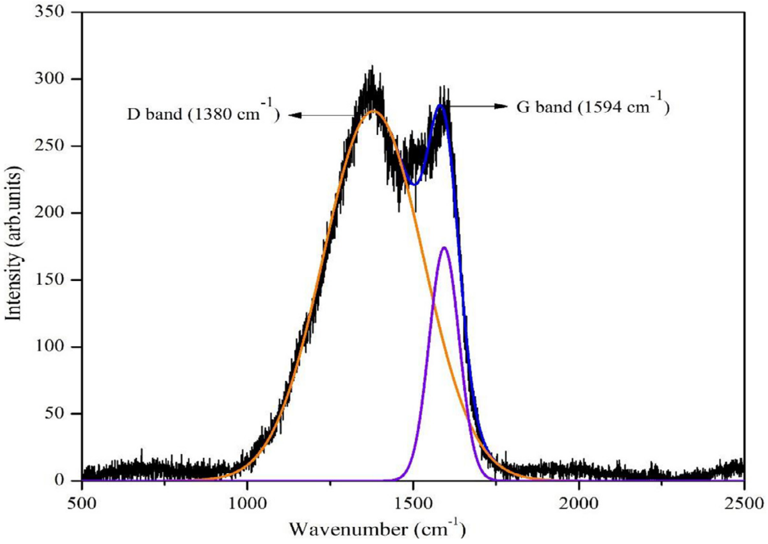

Fig. 4. Raman spectrum of the carbon nitride thin film on silicon substrate.

nitrogen are highly reactive. These reactive sites can directly bond with the already formed adjacent domes of a spherical structure. These spherical structures which are already present can also act as nuclei for the growth of new spheres. The spheres grow vertically up and their size and growth decreases as they grow vertically up from the substrate. This implies that the nucleation started from the substate covers a greater number of carbon and nitrogen molecules, and consequently, grow wider compared to that of the top. These domes grow vertically from the substrate and perpendicular from the initial dome, thus form microscopic tree like structures [11, 13]. The cross-sectional measurement gives a thickness value of about 2 micrometer for the film matrix above which nanostructures are grown.

2.3. Raman spectroscopic analysis

Fig. 4 shows the Raman spectrum measured between 500 cm^{-1} and 2500 cm^{-1} for the carbon nitride thin film deposited on silicon substrate. The appearance of D and G band are the fingerprints of any carbon material. The spectrum shows the presence of D (1380 cm^{-1}) and G (1594 cm^{-1}) band as observed in previous reports [14, 15].

The observed peaks are analogous to amorphous carbon (D band (1360 cm^{-1}) and G (1575 cm^{-1})) signal of Raman spectrum [21]. The incorporation of nitrogen into the carbon matrix makes shift in the peak positions and broadening of the peaks. The shift of the G band above 1580 cm^{-1} indicates an increase in the crys-

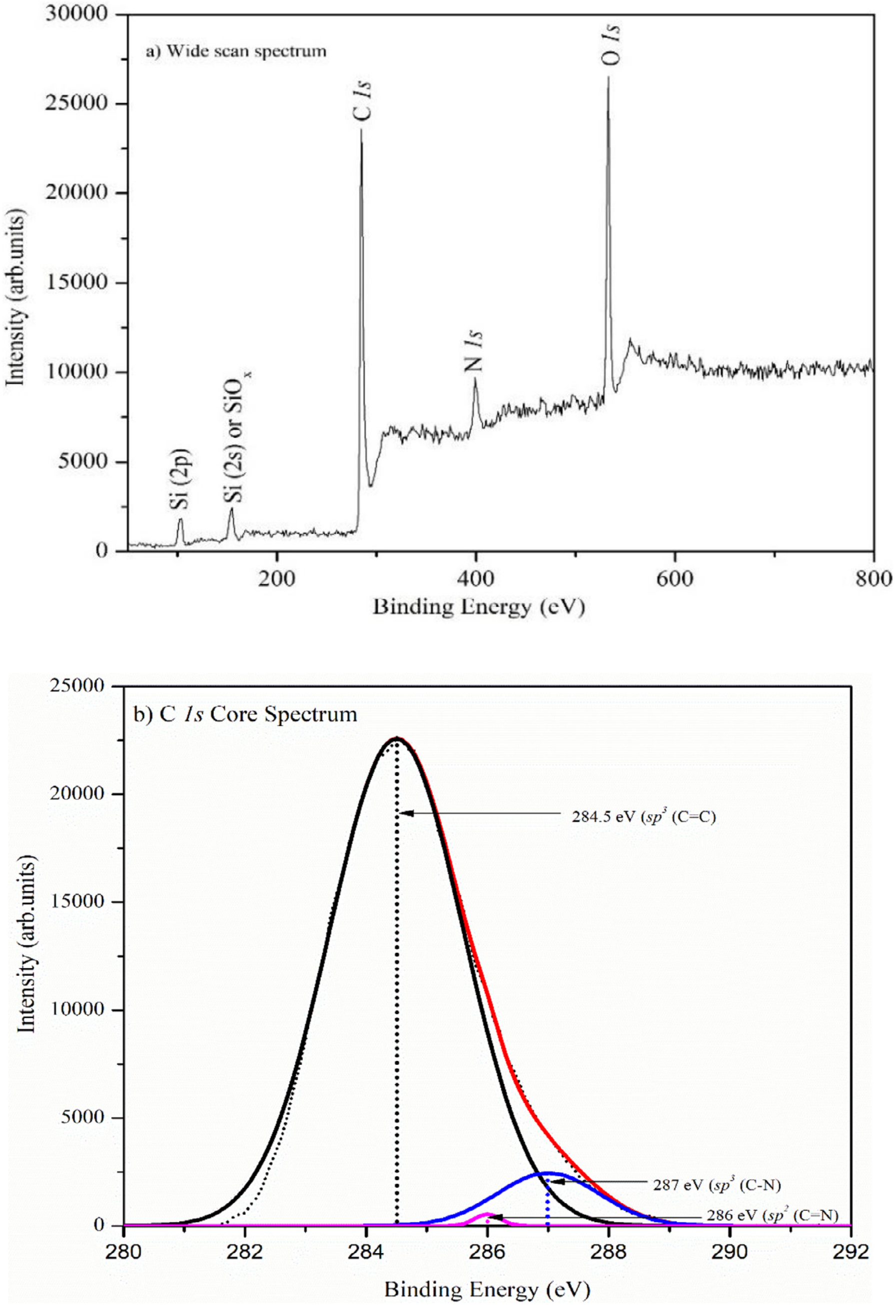

Fig. 5. X-Ray photoelectron spectra of the carbon nitride thin film on Si substrate, a) Wide scan spectrum, b) Carbon 1 s core spectrum and c) Nitrogen 1 s core spectrum.

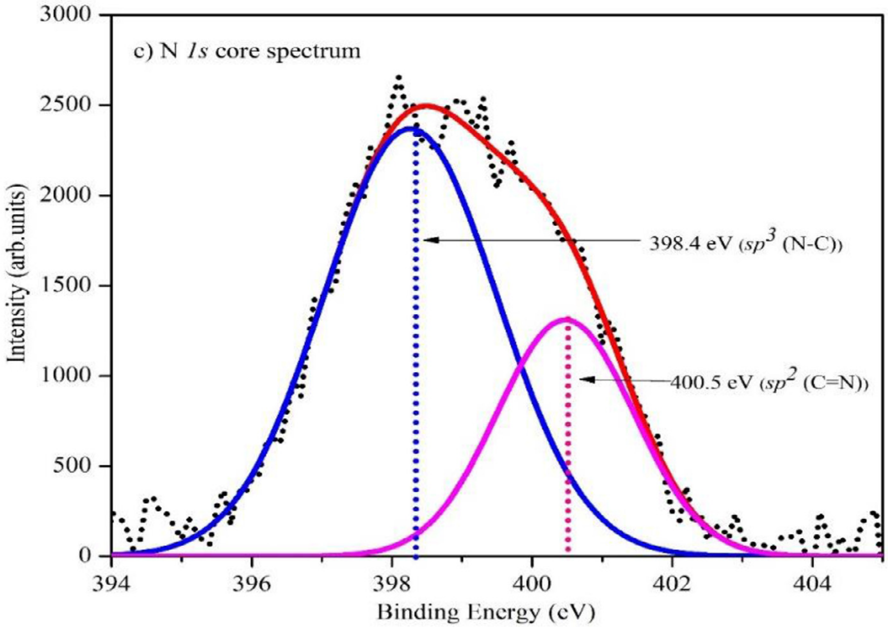

Fig. 5. Continued

tallinity of the film. The shift of the D band indicates an increase in the number of sp^3 bonds between carbon and nitrogen [22]. The increased FWHM of D band is 355 cm^{-1} clearly indicates that the sp^3 bonded C–N crystallites are embedded in the amorphous sp^2 bonded $C = N$ [23]. All these observations favor the formation of crystalline C_3N_4. The calculated intensity ratio of I_D/I_G value is 1.5 indicates the possibility of growth of the large number of microdomains of sp^2 bonded carbon nitride [24].

Theoretically, the Raman vibration frequencies for beta and alpha carbon nitride are calculated using Hooke's law since tetrahedrally bonded C–N is similar to Si-N [25]. However, very rarely Raman peaks have been observed for crystalline carbon nitride phases prepared experimentally [9, 26-28]. Most of the prepared crystalline samples showed pattern similar to amorphous carbon in Raman spectra [29, 30]. From these reports, it is understood that still there are no tentative or universally accepted Raman peaks available even though there are a few reports with Raman peaks apart from D and G peaks for carbon nitride.

2.4. XPS analysis

X-ray photoelectron spectroscopy is employed to identify elements present, composition, and the chemical bonding states of the elements in the thin film developed. Fig. 5(a) shows the wide spectrum of the film. The wide spectrum shows that the thin film contains carbon, nitrogen, oxygen and traceable amount of Si (2p) and Si (2 s) or SiO_x due to the substrate effect. The intense peak of oxygen is due to air exposure of the film [31]. The inclusion of nitrogen into carbon matrix induces charge transfer from less electronegative carbon atoms to high electronegative nitrogen atoms. Consequently, the electron density in the carbon atom reduces and moves towards higher binding energy and replace the homopolar bonds (C–C) with heteropolar bonds (C–N) [7]. It is very essential to identify the types of bonding state of nitrogen to carbon and also to estimate the N/C ratio of the film and phases. The XPS of the core spectra of carbon and nitrogen are most effectively deconvoluted as a sum of two Gaussian components. The deconvoluted C 1 s spectrum is comprised of two peaks (Fig. 5(b)). The major peak at 284.5 eV [32] is originating from sp^2 bonding of $C = C$. The peak centered at 287 eV [5] with low intensity is due to the presence of sp^3 bonded of C–N bonds which is reported to be the source for the formation of β-C_3N_4. The low intensity peak at 286 eV is identified as originating from sp^2 bonding ($C = N$) [32-34]. Another core spectra N1s is shown in Fig. 5(c), is deconvoluted into two peaks centered at 398.4 eV [14, 35] and 400.5 eV [35] which are identified to be originating from sp^3(N–C) and sp^2 ($C = N$) bonding respectively. Those binding energies obtained from those two species at 287 eV and 398.4 eV are favorable for the formation of crystalline α/β-C_3N_4. Apart from sp^2 and sp^3, the binding energy corresponds to sp^1 bonding between C and N is not observed and none of the Si-C and Si-N bonding formation is observed.

The atomic fraction of nitrogen ($f = N/[N + C]$) in the sp^3 bonded carbon and nitrogen is calculated by dividing the area under corresponding peaks by appropriate relative sensitivity factors of carbon (1) and nitrogen (1.8). The calculated at.% of nitrogen and carbon are 59 and 41 respectively, and the corresponding stoichiometric value of 1.4 for carbon nitride, are higher than the theoretical value of 1.33. Though the overall N/C is little away from stoichiometric value, the film area where α/β-C_3N_4 exists, nitrogen is in well agreement with the stoichiometric ratio.

3. Conclusions

In summary, crystalline C_3N_4 thin film was successfully prepared by CVD technique on silicon substrate using Triazine ($C_9H_{18}N_6$) as a precursor. The film contains both α and β-C_3N_4 crystalline phases. Silicon substrate found to be favorable for the growth of both α and β-C_3N_4 crystalline phases. The Raman peak shifts confirm the presence of nitrogen in the carbon matrix. The XPS analysis confirms the presence of tetrahedral bonding between carbon and nitrogen favoring the formation of crystalline C_3N_4 and also the sp^2 bonding between them. The surface morphology analyses show the formation of tree like spherical structures due to nitrogen incorporation into carbon network. This causes sp^3 bonding between carbon and nitrogen to form curvature in the basal planes and cross linkage to form tree like spherical structures. A further research to obtain purely single-phase carbon nitride is worth expecting. Also, this nitrogen incorporated carbon nitride spheres are a promising coating material for mechanical and tribological application.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Venkatesh Ramasamy: Conceptualization, Methodology, Data curation, Investigation, Writing – original draft. **Prashantha Murahari:** Investigation, Data curation. **N.R. Banapurmath:** Investigation. **K. Ramesh:** Conceptualization, Methodology, Investigation, Writing – review & editing, Supervision, Project administration.

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