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## LETTER TO THE EDITOR

**Low-temperature synthesis of highly transparent carbon nitride thin films**S Xu<sup>†</sup>, S Kumar<sup>‡</sup>, Y A Li, N Jiang and S LeePlasma Processing Laboratory, School of Science, NIE, Nanyang Technological University,  
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**Abstract.** Highly transparent carbon nitride thin films have been prepared on transparent plastic substrates at low temperatures by radio frequency reactive magnetron sputtering of a graphite target in the plasmas of pure nitrogen and nitrogen-hydrogen gas mixtures. The amorphous films thus obtained have been characterized for their optical transmittance by spectrophotometry, revealing a very high transparency in the visible region of the spectrum. The chemical composition and bonding states of a sample studied by x-ray photoelectron spectroscopy (XPS) showed that nitrogen has been predominately bonded to  $sp^3$ -hybridized carbon, in addition to a small amount of  $sp^2$ -hybridization. The elemental concentration was measured to be C = 51.1 at.%, N = 43.2 at.%, and O = 5.7 at.%. The N/C ratio for the N- $sp^3$ C component is calculated to be 1.29, close to the expected stoichiometric value of 1.33 for  $\beta$ - $C_3N_4$ . Compared to the unhydrogenated C–N thin films, the hydrogenated samples exhibited increased optical transmittance, about 90% in the whole of the visible spectrum. Such transmittance characteristics of the hydrogenated C–N films closely matched those exhibited by the plastic substrate.

Since carbon nitride (C–N) is a relatively new material, synthesis using various growth techniques has been the main focus of almost all the experimental efforts over the last few years. These include laser ablation of graphite in an atomic flux [1,2], Ion beam assisted deposition [3–8], DC or RF reactive sputtering [9–16], high-dose nitrogen implantation of glassy carbon [17], and high-energy shock plasma deposition [18]. Despite the lack of general consensus on the experimental realization of the predicted  $\beta$ - $C_3N_4$  phase of the C–N solid [19], sub-stoichiometric thin films of this material have been reported [20] to exhibit very high values of hardness (up to about 60 GPa). The optical bandgap of the  $\beta$ - $C_3N_4$  phase has also been calculated [21] to be in excess of 6 eV. In view of the above, it is suggested that the C–N thin films may find many applications as hard, transparent optical coatings. Up to now, very little experimental work has been done on the optical properties of the C–N solid. The limited experimental optical data available in the literature [22–26] points to optical bandgap values ranging from very low (close to zero) to 2.8 eV. The maximum bandgap value of this material has been reported to be about 2.8 eV for the reactively sputtered and ion-beam deposited thin films [22, 23]. The low optical bandgap value of the latter C–N thin films and their moderate optical transmittance characteristics need to be considerably improved for realizing the potential of the C–N material as an optical coating, in particular on substrate materials such as plastics that cannot withstand high deposition temperatures. Therefore, the low-temperature

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growth of the C–N thin films with highly smooth surfaces and high transparency in the visible region of the optical spectrum is highly desirable. To the best of authors' knowledge, there has been only one publication [27] that has mentioned, to a very limited extent though, the high optical transmittance characteristics of a 40 nm thick C–N coating that has been grown on a glass substrate by reactive sputtering, with simultaneous bombardment by a nitrogen ion beam of energy 100 eV.

In this Letter, we report on the growth of highly transparent C–N thin films deposited on optically transparent substrates (CR-39; plastic) at low temperatures ( $\sim 70^\circ\text{C}$ ). The films were prepared by rf reactive magnetron sputtering of a graphite target in the plasmas of pure nitrogen and nitrogen-hydrogen gas mixtures, respectively. The films thus obtained were characterized by optical spectrophotometry. It should be stated here that the plastic substrate was chosen for the present studies owing to its ever-increasing use in the modern ophthalmic industry.

A radio frequency reactive magnetron sputtering system described elsewhere [28, 29] was used for depositing the C–N thin films. In summary, a 10 cm diameter high purity ( $> 5\text{ N}$ ) graphite target was located on the rf powered electrode, whereas the stainless steel substrate holder was kept electrically floating. The adjustable target-substrate holder spacing was kept fixed at 6 cm. A base vacuum of  $5 \times 10^{-3}$  Pa was obtained before flushing the stainless steel deposition chamber with oxygen-free, ultra-high-purity nitrogen gas that acted both as a reactive and a sputtering gas in the present case. For obtaining hydrogenated C–N films, varying gas mixtures of nitrogen and hydrogen were used. The rf power at 13.56 MHz was matched into the target and plasma via a matching network. A constant pressure of the reactive gases was maintained during each deposition run using mass flow controllers (D08-4A/ZM). Although no intentional substrate heating was used, the film deposition temperature was recorded to be  $70^\circ\text{C}$ . Typical deposition parameters for the growth of C–N films are given in table 1.

**Table 1.** Deposition conditions for the growth of C–N films.

Target	High-purity graphite
Reactive/sputtering gases	Ultra-high-purity nitrogen and hydrogen
Substrates	Plastic (CR-39)
Base pressure	$5 \times 10^{-3}$ Pa
Deposition pressure	20 Pa
Substrate temperature	$70^\circ\text{C}$
Deposition power	45 W
Deposition time	12–20 min

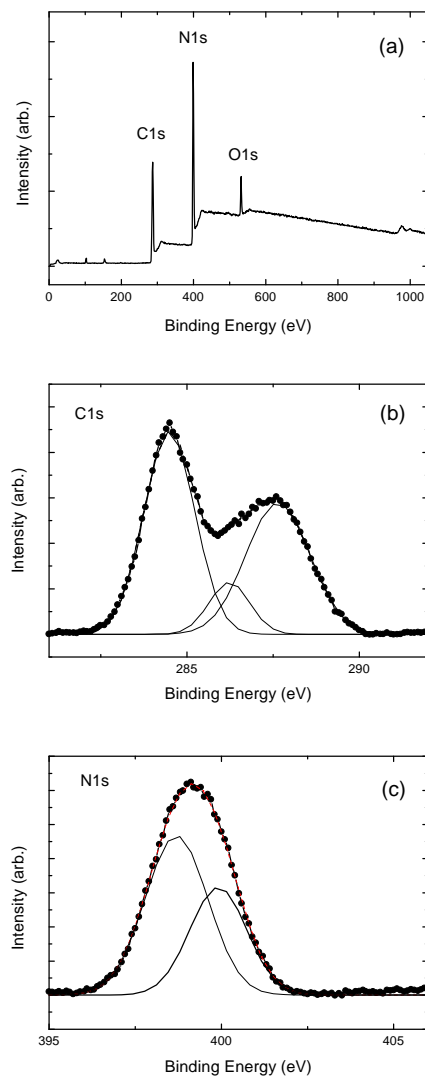
Film thickness was measured using a surface profiler (Dektak II). The chemical composition of both the as-deposited and sputter-cleaned films was determined *ex situ* by VG ESCALAB 220i-XL x-ray photoelectron spectroscopy (XPS) using an Al  $K_\alpha$  (1486.6 eV) x-ray source. The surface microroughness of the films was measured by using a Digital Instruments Nanoscope IIIa atomic force microscope (AFM). The optical transmittance of the films was recorded in the wavelength range 200–800 nm using a Hitachi single-beam spectrophotometer.

The films obtained were quite adherent to the substrates, and were found to be amorphous in nature by x-ray diffraction and transmission electron microscopy. For all the samples used for the present study, the film thickness was measured to be about 140 nm.

The surface roughness of C–N films deposited on a plastic substrate was characterized by AFM. The measured average surface roughness  $R_a$  is about 1.1 nm, which is of the same order as that of the plastic substrate. This result suggests that the film surface is remarkably smooth. It is important to note here that surface smoothness is a highly desired parameter for

the coatings that are used for optical applications in order to reduce the reflection loss due to roughness-induced surface scattering.

The amount of nitrogen incorporated into our C–N films was determined by *ex-situ* XPS. Figure 1 (a) shows the XPS survey scan of an unhydrogenated sample. This spectrum clearly shows the presence of C, N and a small amount of O in the film. The existence of oxygen in the sample could come from two sources: the environmental O<sub>2</sub> in the air and the residual O in the growth chamber. The percentage atomic concentrations of the total elements present in the film, calculated using the transmission function and the sensitivity factors for each of the constituent atoms, provided with the VG analytical software, were C = 51.1 at.%, N = 43.2

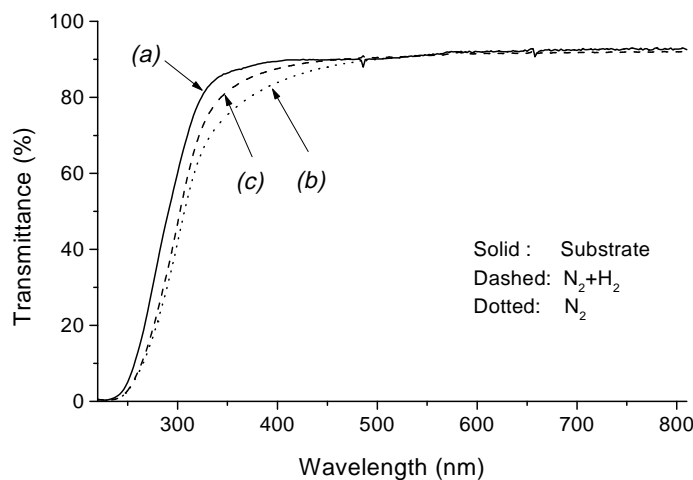


**Figure 1.** XPS photoelectron spectra of (a) survey scan (b) C 1s and (c) N 1s of an unhydrogenated C–N sample prepared using pure nitrogen, indicating high concentration of nitrogen in the film.

at.%, and O = 5.7 at.%. The amount of nitrogen observed in the films is quite close to the highest values reported for reactively sputtered C–N thin films [27–29] measured by XPS.

Subsequent binding state investigation was performed using both the C 1s and N 1s photoelectron spectra. Figures 1(b) and (c) show a narrow scan of C 1s and N 1s spectra, respectively. The broadness and asymmetry of the curves indicate the presence of multi-component peaks. The spectra were therefore fitted with Gaussian peak components mixed with Lorentzian shapes using a least squares routine, after Shirley background subtraction. The result of peak fitting performed on C 1s spectrum yields three peaks, located at binding energy (BE) = 284.5 eV (FWHM 1.5 eV), 286.2 eV (FWHM 1.2 eV) and 287.6 eV (FWHM 1.8 eV), respectively. The lowest peak is due to CH species and the adventitious carbon species on the surface, and two higher BE peaks located at 286.2 eV and 287.6 eV are attributed to  $sp^2$ CN and  $sp^3$ CN bondings as suggested by Marton [30], based on the XPS data in pyridine ( $C_5H_5N$ ) and urotropine (hexamethylene-tetramine;  $C_6H_{12}N_4$ ). Three similar peaks have also been observed by others (for example, [30]). For the N 1s, however, the broadness (FWHM of 2.7 eV) and asymmetry of the spectrum implies that the N curve consists several overlapping peaks. Fitting routine yields two decomposed peaks located at BE = 398.7 eV (FWHM 1.8 eV) and 399.9 eV (FWHM 1.7 eV), respectively. These peaks are attributed to N- $sp^3$ C and N- $sp^2$ C bondings. Peaks corresponding to physisorbed  $N_2$  (BE = 404 eV) [31] and atomic N (BE = 409.9 eV) were not observed in the N 1s spectrum, which implies that all N atoms in the film were indeed bonded to C atoms. From the peak areas of the C 1s and N 1s spectra, the N/C ratio calculated from the N- $sp^3$ C component yields a value of 1.29, close to the expected stoichiometric value of 1.33 for  $\beta$ - $C_3N_4$ . The fractional concentration of the N- $sp^3$ C bonding is calculated to be 68.7%, indicating that the present film contains predominately an amorphous tetrahedral component of carbon nitride.

The optical transmittance spectrum of a C–N film prepared using only pure nitrogen as a reactive gas is shown in figure 2 (curve *b*). Similar characteristics for the plastic substrates are also shown in the figure 2 (curve *a*). A comparison of the two spectral characteristics (curves *a* and *b*) indicates that the C–N is as transparent as the plastic substrate ( $\sim 90\%$  T) in the wavelength region 550 to 800 nm. Note that the main component of the rest of the incident light is lost due to surface reflection whereas a very small amount is absorbed.



**Figure 2.** The optical transmittance spectra of C–N films prepared using pure nitrogen (curve *b*), nitrogen and hydrogen gas mixtures (curve *c*), and a bare plastic substrate (curve *a*).

The onset of band edge and interband absorption results in the fall of transmittance of the C–N sample. This feature is undesirable from the optical applications point of view because optical coatings are required to be transparent in the whole of the visible spectrum, that is, in the wavelength region 400 to 780 nm (3.1–1.6 eV). In order to improve the optical transmittance of the above-mentioned C–N film, C–N samples were further prepared by using a series of nitrogen and hydrogen gas mixtures as reactive gases for sputtering the graphite target. The addition of hydrogen to otherwise pure nitrogen gas used for reactive sputtering results in the C–N:H (hydrogenated C–N) films which, unlike the C–N films, are as transparent as the plastic substrate in very nearly the whole of the visible spectrum (curve *c*). In particular, there is a significant amount of reduction in the band edge absorption [32]. This kind of behaviour can be explained in terms of the reduced density of states at the band edges of the amorphous C–N material as a consequence of the passivation of the dangling bonds due to the incorporation of hydrogen in the films. This behaviour is analogous to the one observed for hydrogenated amorphous silicon [33]. Note that both the C–N and C–N:H films in question were found to be amorphous, as revealed by the XRD and TEM studies. The transmittance curves *b* and *c* in figure 2 were obtained from the C–N and C–N:H films of almost equal thicknesses. It is pointed out that a series of C–N:H samples were prepared by varying the nitrogen/hydrogen gas ratio. The result presented in figure 2 corresponds to the sample which exhibited the highest transmittance. The sample was prepared by using a gas mixture containing hydrogen to nitrogen partial pressures on the ratio of 1.5. The results obtained at other partial pressure ratios will be presented in detail in a separate communication.

The optical bandgap values (corresponding to an optical absorption coefficient,  $\alpha$ , of  $10^5 \text{ cm}^{-1}$ ) for both the C–N and C–N:H coatings were estimated to be in excess of 4 eV from the spectra in figure 2. These values are close to those calculated by Cohen *et al* [21].

In conclusion, thin films of C–N and C–N:H deposited at low temperatures onto plastic substrates using the radio frequency reactive magnetron sputtering technique exhibit high transparency (about 90%) in very nearly the whole of the visible spectrum.

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