Synthesis and characterization of $\text{C}_3\text{N}_4$ hard films

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Abstract  $\text{C}_3\text{N}_4$ films have been synthesized on both Si and Pt substrates by microwave plasma chemical vapor deposition (MPCVD) method. X-ray spectra were calculated for single phase $\alpha$-$\text{C}_3\text{N}_4$ and $\beta$-$\text{C}_3\text{N}_4$ respectively. The experimental X-ray spectra of films deposited on both Si and Pt substrates showed all the strong peaks of $\alpha$-$\text{C}_3\text{N}_4$ and $\beta$-$\text{C}_3\text{N}_4$, so the films are mixtures of $\alpha$-$\text{C}_3\text{N}_4$ and $\beta$-$\text{C}_3\text{N}_4$. The N/C atomic ratio is in the range of 1.0-2.0. X-ray photoelectron spectroscopy (XPS) analysis indicated that the binding energy of C 1s and N 1s are 286.2 eV and 399.5 eV respectively, corresponding to polarized C-N bond. Fourier transform infrared absorption (FT-IR) and Raman spectra support the existence of C-N covalent bond in the films. Nano-indentation hardness tests showed that the bulk modulus of a film deposited on Pt is up to 349 GPa.

Keywords: $\beta$-$\text{C}_3\text{N}_4$, MPCVD, film deposition.

Since Liu and Cohen$^1$ proposed a hypothetical new material $\beta$-$\text{C}_3\text{N}_4$ with a bulk modulus comparable to or greater than that of diamond, lots of researchers have tried to synthesize it in laboratory. However, little progress was achieved before 1996. Most deposited films were not good enough for further analysis, and some of them were even not continuous. A few rings of electron diffraction or a few peaks of XRD are not enough to identify a new phase. The N/C atomic ratio is also much lower than the stoichiometric value of 1.33. Data of hardness of bulk modulus have rarely been published. Someone even threw doubt upon the possibility of synthesizing $\beta$-$\text{C}_3\text{N}_4$.

At the session of hard materials in '94 C-MRS (Materials Research Society of China), we proposed to perform an experiment on a system containing N, C only in order to see the tendency towards C-N phase formation. We implanted high dose of N$^+$ into high purity graphite to obtain C-N films and got a comparatively full X-ray spectrum in accord with the theoretical predicted crystal structure of $\beta$-$\text{C}_3\text{N}_4$$^{2-4}$.

Significant progress has been made all over the world after 1996 and more than a hundred papers on this subject were published every year. A variety of analytical methods have been used to characterize carbon nitride films, but the results were often scattered. It is about time to carefully evaluate those data and establish some reasonable criterion to identify it. Computer simulations can be a useful tool sometimes.

In this paper, we concentrated our attention on the characterization of the films deposited on
Si and Pt substrates by MPCVD. X-ray diffraction (XRD), energy dispersive X-ray spectrometry (EDX), XPS, FT-IR, Raman spectra and nanoindentation were performed, in order to verify whether the films were composed mainly of $\text{C}_3\text{N}_4$ compound.

1 Experimental

Carbon nitride films were deposited on a MPCVD system as shown in fig. 1. Vacuum was provided through a combination of a turbo-molecular pump and a rotary pump. Working gases, $\text{CH}_4$ and $\text{N}_2$, were fed into the deposition chamber through mass flow controllers. Pressure in the chamber was controlled by adjusting a valve between the deposition chamber and the vacuum pumps. The microwave power was adjusted by a four screw adapter and monitored by measuring the back reflection power at the end of water load. Substrate temperature was monitored by an infrared pyrometer.

![Fig. 1. An illustration of the MPCVD deposition device.](image)

The deposition conditions were developed from typical conditions for the growth of diamond films. The substrate temperature ranged from 700 to 950°C, and the working pressure was about 2 500 Pa. The flow rates of $\text{CH}_4$, $\text{N}_2$ were 1 sccm and 100 sccm, respectively. The growth parameters were optimized in the process to get better carbon nitride films.

Most of the samples were deposited for one and half an hours and have a thickness of a few