Names and affiliations of applicants (* indicates experimentalists):

*Dr R J Newport   University of Kent at Canterbury, UK
*Dr J K Walters   University College London, UK
*Dr M Keuhn   Chemnitz-Zwickau Technical University, Germany
*Dr C Spaeth   Chemnitz-Zwickau Technical University, Germany

Report:

Carbon nitride materials have been the subject of considerable attention since theoretical work predicted the ultra-hard structure of β-C_3N_4. Amorphous CN_x materials have interesting and useful properties, and a consequent range of potential applications - e.g. in the field of electronic materials, and wear protective coatings for magnetic storage devices. So far investigation of their physical properties has covered chemical composition, microstructure, electronic, optical and mechanical properties, but there exists only limited knowledge of the atomic scale structure With this in mind, we have carried out X-ray diffraction measurements on four CN, samples, with 0, 5, 20 and 30 at.% N, to investigate the bonding environments of N within the network, and to examine the effects of increasing N incorporation on the overall atomic scale structure.

The samples were prepared by thin film deposition using a filtered cathodic arc, with a high purity graphite cathode A magnetic filter was used to separate macroparticles (of graphite) from the flux of film-forming particles. Nitrogen was incorporated either by introducing N_2 into the deposition chamber, or by bombarding the substrate with nitrogen ions from a Kaufman-type source - which proved necessary to obtain higher N content films. Data was collected over -14 hours for each sample, mostly because of the very small samples used and their weak scattering. Each powder sample was held in a thin aluminium cell with Kapton windows

The data were normalised to allow for variations in the incident flux, corrected for detector deadtime, beam polarization, background scattering effects (including those from the sample container), absorption and the 2θ-variation of the illuminated sample volume. Corrections for inelastic scattering were made by fitting a low order polynomial through the data to remove the underlying residual scattering curve, until the data oscillates about the calculated self-scattering profile.

Figure 1 shows the data for the four samples following a Fourier transformation. Peak positions were obtained by Gaussian fitting and the results are given in Table 1, together with the calculated average bond angles. With increasing N content we see a shift in the average first neighbour distance from 1.55Å to 1 44Å, resulting in a corresponding increase in the average CCC bond angle from $108°$ to $114°$. The results indicate that in addition to N bonding into the network, there is a conversion of sp^3 CC bonds to shorter, graphitic/olefinic sp^2 CC bonds. Significant structural changes to the predominantly tetrahedral network occur with the introduction of only 5 at.% N, and the changes are more dramatic when the N concentration is further increased to 20 at.%.

Sample	N content (at.%)	1st neighbour peak position (±0.01Å)	2nd neighbour peak position (±0.01Å)	Average CCC bond angle ($\pm2°$)
1	0	1.55	2.51	108
2	5	1.50	2.50	113
3	20	1.45	2.43	114
4	30	1.44	2.42	114

Table 1: Results from Gaussian fitting to the Fourier transformed data.