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Attempted preparation of diamond-like carbon nitride by explosive shock compression of poly(methineimine)

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Explosive shock compression of poly(methineimine) produced a large portion of amorphous graphitic carbon nitride of composition $CN_{0.2}$ and small amounts of diamond-like carbon containing a slight amount of nitrogen. Codeposition of the two materials suggests the possibility of cubic phase transformation of heterocyclic C–N compounds under well-designed shock-compression conditions.

Introduction

Diamond and related materials combined or doped with hetero elements such as B, N, Si and P are expected to be promising materials in mechanics and electronics for their potential uses due to their outstanding hardness, thermal conductivity and wide bandgap semiconductivity. The presentations of cubic C–BN by Badzian[1] and β-C_3N_4 by Liu and Cohen[2] have stimulated numerous investigators to search for diamond-like hetero compounds. Cubic C–BN compounds were synthesized in small amounts by Wedlake,[3] Badzian,[1] Nakano,[4] and Knittle[5] under static high pressure and high temperature conditions from 1979 to 1995, and in the next year a considerable amount of purified heterodiamond of composition $BC_{2.5}N$ was synthesized by Komatsu *et al.*[6] using an explosive shock-compression technique. For β-C_3N_4, a great number of papers have been reported, but only a few studies claim the existence of β-C_3N_4 so far. The crystalline carbon nitrides which were synthesized by the groups of Niu,[7] Yu,[8] Li,[9] and Sung[10] using various chemical and physical vapor deposition methods agreed fairly well with the predicted interplanar spacings of β-C_3N_4, however in a strict sense the materials were not completely proved because of unidentified chemical structures and stoichiometry. This essential problem seems to arise from the thermodynamically more unstable β-structure compared to the α-structure.[11,12] There is room for reviewing whether the CVD and PVD methods are suitable for the synthesis of β-C_3N_4 and whether the deposition is quantitatively enough for identification and purification.

An explosive shock-compression technique usually used for diamond synthesis is able to supply an extremely high pressure and high temperature to the sample in microseconds and therefore is desirable to obtain non-equilibrium materials like heterodiamond as a bulk form. Wixom attempted to prepare β-C_3N_4 by shock compression of several pyrolyzed C–H–N compounds under a shock pressure of 30–50 GPa, however he obtained a mixture of amorphous graphitic material and small amounts of diamond.[13] Previously, we studied the phase transformation of poly(aminomethineimine) under an explosive shock pressure of about 40 GPa, but unexpectedly no diamond-like materials were produced except for sp^2-bonded amorphous carbon nitrides having several different morphologies.[14] As one of the causes, a high atomic ratio of hydrogen included as amino groups of the starting material was anticipated, because a large amount of hydrogen seems to terminate a growth of active species into diamond.[15]

In this work, the preparation of diamond-like carbon nitride was attempted by shock compression of poly(methineimine) having no functional groups except for the $-CH{=}N-$ chains.

Experimental

Sample preparation

The starting material was prepared by ring opening polymerization of *s*-triazine with excess $ZnCl_2$ at 250 °C for 5 h in an autoclave, according to ref. 16. The product, which was obtained as a black powder, was heated with conc. HCl in a water bath, filtered with a glass filter, washed with distilled water and vacuum-dried at 200 °C. The starting material thus obtained was mixed with small copper balls in a polymer:copper = 2:98 mass ratio, filled into a steel capsule, and pressed into a disc. The bulk density of the disk was set at 70% of the theoretical value. The disc was shock compressed using a shock compression apparatus shown in Fig. 1. The apparatus was constructed with a detonator, a sheet explosive discharger (the shock wave velocity is 6 km s^{-1}), a high melting point explosive (the shock wave velocity is 9 km s^{-1}), a copper flying plate, a brass-vessel containing the sample disc, and a steel momentum trap surrounding the sample vessel. The net shock pressure and temperature applied to the sample through the sample vessel compacted by the explosively accelerated copper plate was estimated to be 15 GPa and 3500 K, respectively. The recovered sample was machined, immersed in 30% HNO_3 to remove the copper matrix, heated with conc. HCl to remove trace amounts of metallic contaminants, washed with distilled water, and vacuum-dried at 200 °C. A fine black powder was obtained at a yield of 36.5%. The material

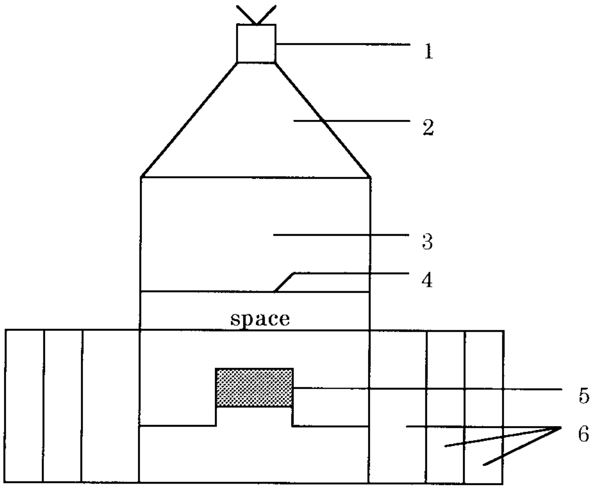


Fig. 1 Section of a plain shock-compression apparatus: 1, detonator; 2, sheet explosive discharge; 3, HMX explosive; 4, copper flying plate; 5, brass vessel containing the sample disk; 6, steel momentum trap.

Table 1 Elemental analysis of the starting material and shock-compression product

Starting material						Shock-compression product					
Elemental analysis (%)			Atomic ratio			Elemental analysis (%)			Atomic ratio		
C	H	N	C	H	N	C	H	N	C	H	N
49.2	3.9	41.2	1.0	0.9	0.7	41.9	0.1	11.5	1.0	0.0	0.2

obtained was checked in terms of the presence or absence of a diamond-like material with an analytical transmission electron microscope.

Measurements

The chemical compositions of the samples were determined using a Holiba CHN analyzer. The crystalline structures were determined using a Rigaku RINT-2500 X-ray powder diffractometer (XRD) equipped with a position-sensitive proportional counter and graphite monochromater on the detector. Ni-filtered Cu-Kα radiation generated at 50 kV and 200 mA was used. The crystalline structure, elemental composition, and chemical bonding nature in the microscopic regions of the samples were investigated using a Hitachi HF-2000 field-emission transmission electron microscope (FETEM) equipped with an electron diffractometer (ED), a parallel recording electron energy-loss spectroscope (PEELS), and an energy-dispersive X-ray analyzer (EDX). These measurements were made at 200 kV accelerating voltage. The infrared (IR) spectra of the samples were measured in KBr disk form using a Perkin-Elmer FTIR-1640 spectrometer.

Results and discussion

Chemical analysis

Table 1 gives the elemental analysis of the starting material and the shock-compression product. The chemical composition of the starting material was approximately $CH_{0.9}N_{0.7}$ and that of the shock-compression product was close to carbon nitride of composition $CN_{0.2}$ in which a large portion of hydrogen atoms and significant amounts of nitrogen atoms of the starting material were lost. Such a remarkable change in composition after shock compression indicates that some molecular reconstruction has been induced by shock compression. The following IR and XRD results suggest that this change is possibly due to complicated cyclization of the starting material accompanying elimination of π-bonding nitrogen atoms.

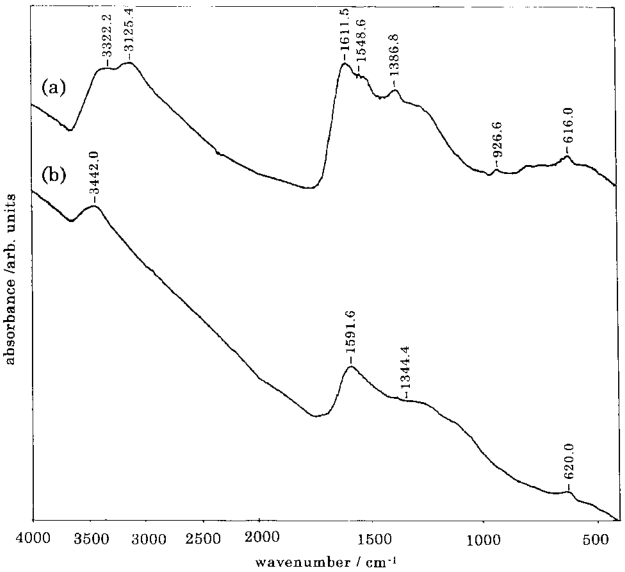


Fig. 2 IR spectra showing the chemical structure change before and after shock compression: (a) the starting material, (b) the shock-compression product.

IR spectra

Carbon nitrides are IR active owing to an increased polarity and breaking of symmetric vibrations by incorporation of nitrogen with carbon. The materials show generally two vibrational modes in the range 1600–1300 cm^{-1} which are related to the Raman G and D bands of amorphous carbon. Fig. 2(a) shows the IR spectrum of the starting material. The spectrum was simple and broad and resembled the IR spectrum of paracyanogen[17] and those of several amorphous CN_x thin films.[18–20] The middle absorption band at 3322 cm^{-1} was assigned to N—H stretching of imine, the middle band at 3125 cm^{-1} to =C—H stretching, the strong bands at 1612 cm^{-1} and 1549 cm^{-1} to C=N and C=C stretching (related to the G band), the middle plateau band ranging from 1260 cm^{-1} to 1450 cm^{-1} (showing a peak at 1387 cm^{-1}) to ring stretching and C—N stretching (related to the D band), and the small band at 927 cm^{-1} to =C—H bending. The small peak at 616 cm^{-1} was unassigned. The chemical structure of the starting material is an incomplete poly(methineimine) structure including sp^3 carbon and nitrogen possibly

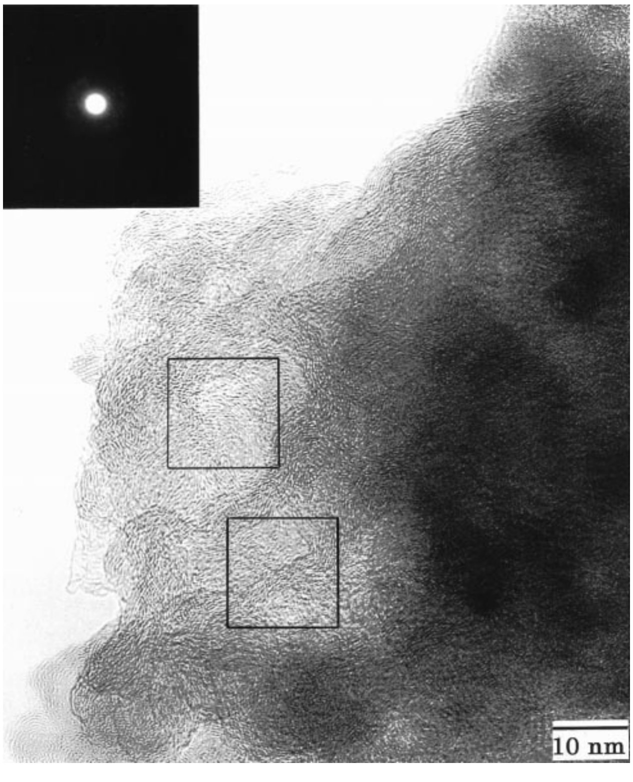
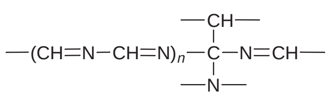


Fig. 3 FETEM image and ED pattern of a large portion of particles included in the shock compression product.

cross-linked with adjacent polymer chains, as depicted on the next page.



$$\text{—(CH=N—CH=N)}_n\text{—}\overset{\displaystyle\text{—CH—}}{\underset{\displaystyle\text{—N—}}{\text{C}}}\text{—N=CH—}$$

On the other hand, the shock-compression product showed a more simple broad spectrum as several peaks of the starting material disappeared, as shown in Fig. 2(b). The broad band centered at 1592 cm^{-1} was assigned to a superposition of C=N stretching and C=C stretching and the plateau band around 1344 cm^{-1} was assigned to ring stretching. The band at 3442 cm^{-1} is due to moisture contained in the IR specimen. The simple IR bands and decreased IR activity of the shock-compression product must be related to the graphitic ring formation and the remarkable decrease in nitrogen content compared to the starting material.

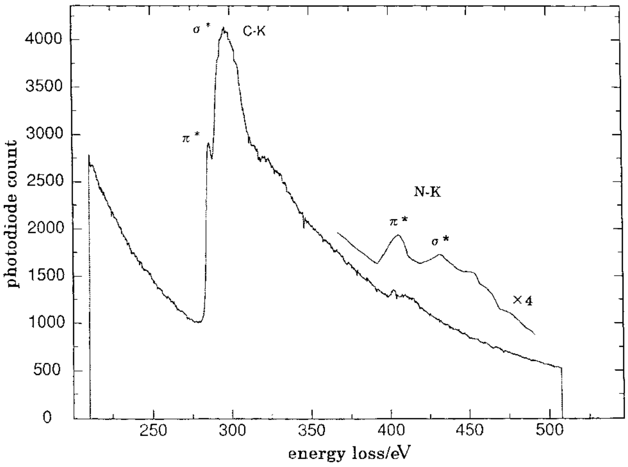


Fig. 4 PEEL spectrum of the particle observed in Fig. 3. Note the presence of carbon and nitrogen both having π features.

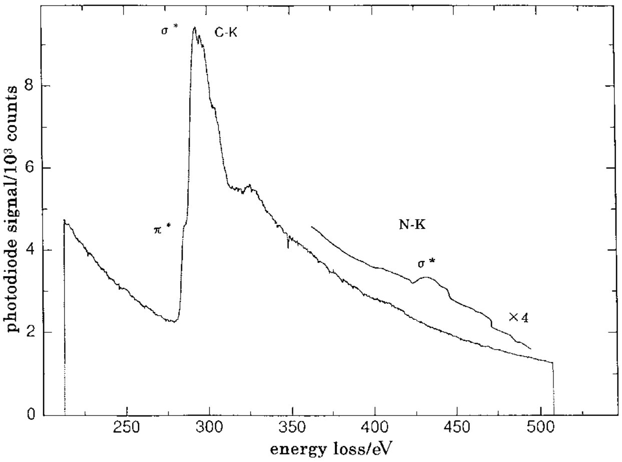


Fig. 6 PEEL spectrum of the particle observed in Fig. 5. Note the presence of a large amount of carbon and a small amount of nitrogen and the carbons having a large σ-bonding feature relative to the π feature. An expanded N-K edge shows only a σ* peak.

X-Ray diffraction

The XRD patterns of the samples before and after shock compression were almost identical: the pattern of the starting material consists of two broad peaks centered at $2\theta = 26.08°$ (strong peak, $d = 0.350$ nm) and 42.63° (weak, 0.227 nm), and that of the shock-compression product consists of two broad peaks at $2\theta = 26.21°$ (strong, 0.349 nm) and 42.75° (weak, 0.227 nm) but no patterns of diamond-like materials. These patterns, which are similar to the pattern of amorphous carbon, indicate amorphous structures.

TEM analysis

Fig. 3 and 4 show a representative TEM image and ED pattern and a PEEL spectrum of the shock-compression product, respectively. The TEM image and ED pattern show a dis-

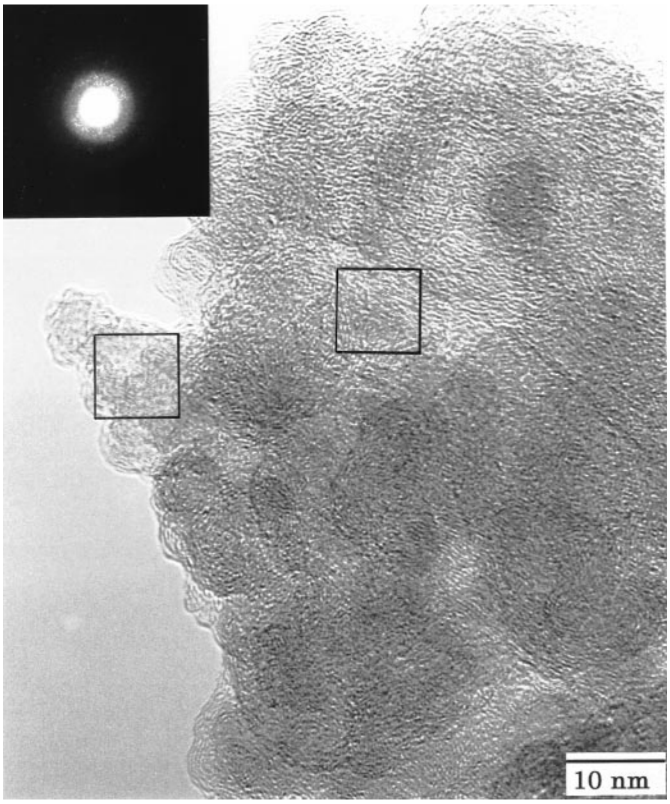


Fig. 5 FETEM image and ED pattern of small amounts of nanoparticles microdiffused in the matrix of the shock-compression product.

ordered structure peculiar to amorphous carbon, and the PEEL spectrum indicates the material is composed of a large amount of carbon and a small amount of nitrogen both having clear $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transitions at the carbon and nitrogen K-edges. This means that the grain is combined with sp^2-bonding carbon and nitrogen. Mixed with this grain, small amounts of microdiffused nanoparticles showing a different bonding nature were observed. The particle was amorphous or slightly crystalline, from the TEM image and ED pattern shown in Fig. 5. Considering the influence from the graphitic material underneath, the measurements of the TEM and PEEL spectrum of this particle were made as nearly as possible on such thin fringes. From the PEEL spectrum shown in Fig. 6, it was found that the material is composed of a large portion of carbon and trace amounts of nitrogen and that the carbon K-edge shows a large σ^* feature relative to the π^* feature. This indicates a mixture of sp^3- and sp^2-bonding carbons. The ratio of sp^3-carbon to total carbons, $sp^3/(sp^2+sp^3)$, was estimated from the following equation according to ref. 21:

$$sp^3/(sp^2+sp^3) = 3(\gamma_{std} - \gamma_{exp})/(3\gamma_{std} + \gamma_{exp})$$

$$\gamma_{std} = (I_{\pi*}/I_{\sigma*})_{std}, \; \gamma_{exp} = (I_{\pi*}/I_{\sigma*})_{exp}$$

where $(I_{\pi*}/I_{\sigma}{}^*)$ is the intensity ratio of the π^* and σ^* peaks at the carbon K-edge, and the subscripts std and exp, respectively, refer to the standard and experimental, and graphite was used as the standard. The result ranged from 40% to 60% for many particles. In order to clarify the difference in the bonding nature of nitrogen in this material and the earlier graphitic material, the nitrogen K-edges in Fig. 6 and 4 were expanded and compared with each other. The π^* and σ^* peak positions in the N–K edge of the graphitic material appeared at 401.7 and 408.4 eV. On the other hand the noted material showed an appreciable σ^* peak but an insignificant π^* peak in these positions. The nitrogen content was too small to estimate the C/N ratio of the material by PEELS analysis. The PEEL spectrum resembled those of amorphous CN_x thin films[22,23] and diamond-like carbon.[21] Therefore, the material was assigned as amorphous diamond-like CN_x.

Although the content of the diamond-like CN_x was slight in comparison with the formation of graphitic carbon nitride $CN_{0.2}$, codeposition of the two materials suggests the synthesis of diamond-structured carbon nitrides to be possible by shock compression of heterocyclic C–N compounds. The large nitrogen loss after shock compression is possibly due to phase separation of an unidentified intermediate material because the high nitrogen ratio of heterocyclic C–N compounds means they tend to lose nitrogen at mild temperatures.[17,24] Balance of the applied shock pressure and temperature to the sample, preferably high pressure and low temperature conditions, must be important for creation of a C–N heterodiamond which is supposed to be kinetically much more unstable than diamond.

Conclusions

Explosive shock compression of poly(methineimine) was carried out under 15 GPa, 3500 K conditions in order to prepare diamond-like carbon nitride. A large portion of amorphous graphitic $CN_{0.2}$ and small amounts of diamond-like carbon combined with a slight amount of nitrogen were confirmed by analytical TEM. The low nitrogen concentration of the shock-compression product compared to the starting material may be due to phase separation of an unidentified intermediate material. The finding of diamond-like and graphitic carbon nitrides in the shock-compression product suggests the possibility of producing diamond-structured carbon nitrides by shock compression of heterocyclic C–N compounds.

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