

Transmission electron microscopy studies of $C_3N_4H_4$ treated at high pressure and high temperature

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 11199

(<http://iopscience.iop.org/0953-8984/14/44/453>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.97

The article was downloaded on 18/05/2010 at 17:17

Please note that [terms and conditions apply](#).

Transmission electron microscopy studies of $C_3N_4H_4$ treated at high pressure and high temperature

R C Yu¹, L C Chen¹, J L Zhu¹, F Y Li¹, Z X Liu¹, Z C Qin¹, T N Yu¹,
C Q Jin¹, X F Duan² and Z Zhang²

¹ Key Laboratory of Extreme Conditions Physics, Institute of Physics and Centre for Condensed Matter Physics, High Pressure Research Centre, Chinese Academy of Sciences, PO Box 603, Beijing 100080, People's Republic of China

² Beijing Laboratory of Electron Microscopy, Institute of Physics, Centre for Condensed Matter Physics, Chinese Academy of Sciences, PO Box 2724, Beijing 100080, People's Republic of China

E-mail: rcyu@aphy.iphy.ac.cn

Received 1 June 2002

Published 25 October 2002

Online at stacks.iop.org/JPhysCM/14/11199

Abstract

$C_3N_4H_4$ was treated at 6.0 GPa and 1500 °C for 2.5 min. Powder x-ray measurement shows that the sample is decomposed and a hexagonal graphite phase forms. Transmission electron microscopy studies show that small amounts of diamond and amorphous carbon phase coexist with the graphite phase. Parallel electron energy-loss spectroscopy analysis was also carried out for these phases.

1. Introduction

Diamond has been widely used due to its superior hardness. It is commonly thought that there is no material that can compete with it. However, in 1985, Cohen predicted, through a theoretical calculation, a new superhard material: a covalently bonded carbon–nitrogen alloy (β - C_3N_4), which has hardness that is the same as or even higher than that of diamond [1]. Later, several *ab initio* calculations which supported Cohen's conjecture were carried out [2–5]. So far, five structures of C_3N_4 have been predicted [6]. Motivated by the prediction, a number of scientists have attempted to synthesize C–N compounds which may not exist in Nature. The goal is not only to obtain a new superhard substance, but also to test the effectiveness of first-principles theories in materials science. Up to now, several hundred papers have been published in this field. Various physical and chemical vapour deposition methods have been reported for synthesizing C–N films, such as ion beam sputtering, rf sputtering, pulsed-laser ablation and arc-plasma jets. A crystalline C_3N_4 film was reported by Chen *et al* [7]. They synthesized carbon nitride crystals on nickel substrates via hot-filament chemical vapour deposition using a bias. Though the lattice parameters are slightly smaller than the predicted ones, the agreement between experiment and theory is very good. The hexagonal morphologies were clearly seen

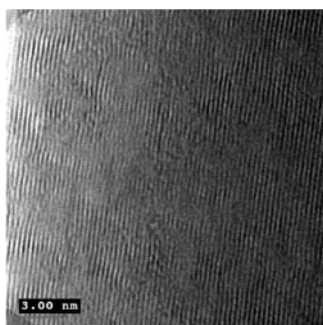


Figure 1. The high-resolution image of the hexagonal graphite phase.

by scanning electron microscopy. In order to synthesize larger carbon nitride crystals, He *et al* [8] attempted to pyrolyse $C_3N_4H_4$ in the presence of a nickel-based alloy or cobalt as a catalyst at a high pressure of 7.0 GPa and temperature of 1400 °C. They obtained carbon nitride crystals that were composed of α - C_3N_4 and β - C_3N_4 . The N content in these crystals was 47–62%. They reported a very good method for synthesizing large C–N crystals, which are necessary for the measurement of physical properties. It is well known that diamond can also be synthesized by using high pressure and high temperature. In this paper, we report on the products of $C_3N_4H_4$ treated by high pressure and high temperature.

2. Experiments

Synthesis experiments were performed with a six-anvil 600 ton high-pressure device. The $C_3N_4H_4$ (2-amino, 1, 3, 5-triazine) powders were wrapped in Pt or Ti thin slices and sealed into a BN sample cell (diameter: 4 mm; height: 3.5 mm). The Ni-based alloy flats were put on both sides of the sample, as the catalyst. In the experiment, we applied a pressure of about 6.0 ± 0.2 GPa, and then heated to a temperature of 1500 ± 50 °C which was then maintained for 2.5 min. After that, the heating power was cut off and the sample was decompressed to ambient pressure after it had been cooled to room temperature. Powder x-ray diffraction (XRD) measurement was carried out on Rigaku rotating-anode powder x-ray diffractometer (RINT2000). High-resolution electron microscopy and parallel electron energy-loss spectroscopy (EELS) measurements were performed on CM 200-FEG electron microscope equipped with a Gatan Imaging Filter system.

3. Results and discussion

Here it should be pointed out that no carbon nitride crystals were obtained in our experiments.

The samples treated at high pressure and high temperature were studied by means of powder XRD. The XRD pattern indicated that $C_3N_4H_4$ was decomposed under high pressure and high temperature, and a graphite phase formed. The samples were also examined by high-resolution transmission electron microscopy (HRTEM). Three morphologies were observed in the HRTEM experiments. The majority phase observed frequently in the sample was the hexagonal graphite phase. Figure 1 is the HRTEM image of the hexagonal graphite phase. The parallel lines corresponding to (002) planes of the graphite phase are clearly seen in the image. The distance between the neighbouring lines is 0.34 nm. This is in good agreement with that of the graphite phase (0.338 nm).

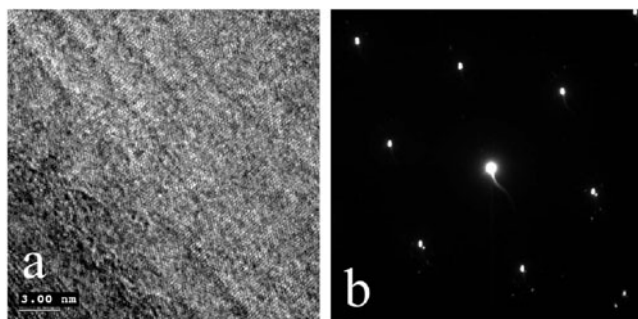


Figure 2. (a) The high-resolution image of the diamond phase along the [111] direction; (b) a selected EDP corresponding to image (a).

Besides the majority graphite phase, a diamond phase was also observed as a minority phase. Figure 2(a) is the HRTEM image along the [111] zone axis of the diamond phase. The lattice lines are clearly observed in the image and the white dots construct regular trigonal arrays. Figure 2(b) is the electron diffraction pattern (EDP) taken for the area shown in figure 2(a). From the HRTEM image and the EDP, the lattice constant was calculated as $a = 0.36$ nm. This is in good agreement with the diamond constant (0.357 nm).

The sample was also examined using Raman spectroscopy. Unfortunately, no 132 nm peak, which corresponds to the diamond phase, was observed. We think that this is due to the fact that the amount of diamond phase in the sample is beyond the detection limit.

Another minority phase, amorphous carbon, was also observed in the sample. The HRTEM image of the amorphous carbon phase is shown in figure 3.

In order to confirm that the phases we observed were different, we performed parallel EELS measurements. Figures 4(a)–(c) show the parallel EELS results corresponding to the areas shown in figures 1, 2(a) and 3, respectively. It is well known that the hybridization in graphite carbon is sp^2 while that in diamond is sp^3 . From figure 4(a), we can see that there are two peaks which correspond to 284 eV (π^*) and 293 eV (σ^*), respectively. The π^* -peak is very sharp and relatively high. This is in very good agreement with the case for graphite carbon. Though the π^* -peak appears in figure 4(b), it is very low. This means that most of the bonds examined in the phase are σ^* -type ones which correspond to the diamond phase. The low π^* -peak might be caused by an imperfect area, such as an amorphous area. Figure 4(c) shows the features of amorphous carbon. Since the π^* -bonds in the amorphous phase are not regular, the π^* -peak is lower than that of the graphite phase, but higher than that of the diamond phase. We should point out that since no nitrogen was detected in the parallel EELS experiments, no carbon nitride crystals formed. However, the experimental conditions that we used were different from those used by He *et al.* The C₃N₄H₄ used in our experiments is an allotrope of the one that He *et al.* used, though the two samples have the same composition. Therefore, it is understandable that different experimental results were obtained. Our experimental results show that the C–H and C=N bonds in C₃N₄H₄ can be destroyed under high pressure and high temperature. Some of the decomposed C elements formed a diamond phase under the action of Ni-based alloy as a catalyst. A similar report was also given by He *et al.* [9]; they synthesized diamond crystals from paraffin [C₂H₆(CH₂)_n] at a high pressure and high temperature. The present results give a new starting material for synthesizing diamond crystals.

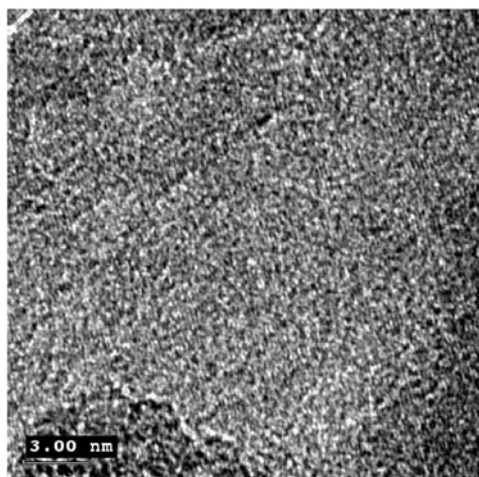


Figure 3. The high-resolution image of amorphous carbon.

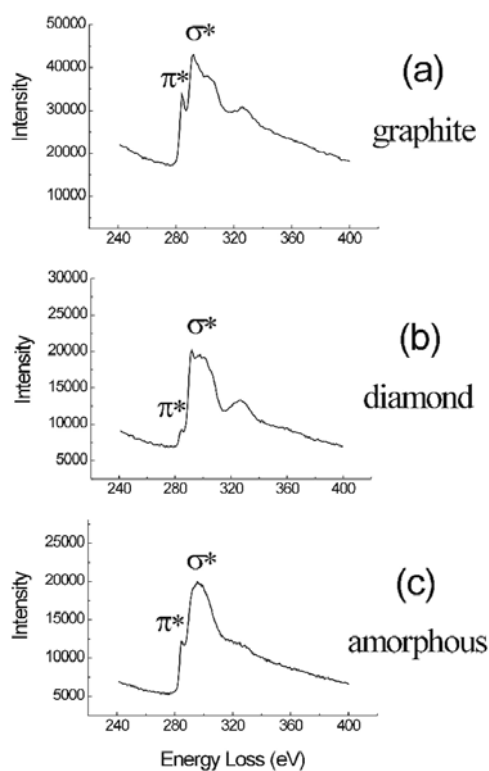


Figure 4. (a)–(c) Parallel EELS spectra corresponding to the areas shown in figures 1, 2(a) and 3, respectively.

4. Conclusions

The C–H and C=N bonds in $C_3N_4H_4$ were destroyed under high pressure and high temperature. Hexagonal graphite, diamond and amorphous carbon phases formed from the treatment. Organic materials could be a new starting material for synthesizing diamond crystals.

Acknowledgments

This work was supported by the ‘Hundreds of Talents’ Programme of the Chinese Academy of Sciences and the ‘Outstanding Youth Fund’ of the Natural Science Foundation of China (grant No 59725105).

References

- [1] Cohen M L 1985 *Phys. Rev. B* **32** 7988
- [2] Liu A Y and Cohen M L 1989 *Science* **245** 841
- [3] Liu A Y and Wentzcovitch R M 1994 *Phys. Rev. B* **50** 10 362
- [4] Ortega J and Sankey O F 1995 *Phys. Rev. B* **51** 2624
- [5] Teter D M and Hemley R J 1996 *Science* **271** 53
- [6] Cote M and Cohen M L 1997 *Phys. Rev. B* **55** 5684
- [7] Chen Y, Guo L P and Wang E G 1997 *Phil. Mag. Lett.* **75** 155
- [8] He D W, Zhang F X, Zhang X Y, Qin Z C, Zhang M, Liu R P, Xu Y F and Wang W K 1998 *J. Mater. Res.* **13** 3458
- [9] He D W, Luo X J and Din L Y 1995 *Chin. J. Atom. Mol. Phys.* **12** 49