Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Takeo Oku, Günter Schmid, Katsuaki Suganuma, Qiang Sun & Yoshiyuki Kawazoe (2000): Structure of Pd-Intercalated Graphite Onions Formed by Electron Beam Irradiation, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 340:1, 95-100

To link to this article: http://dx.doi.org/10.1080/10587250008025449

Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 95-100
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Structure of Pd-Intercalated Graphite Onions Formed by Electron Beam Irradiation

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Carbon onions were produced in a transmission electron microscope by electron beam irradiation of amorphous carbon with Pd clusters. High-resolution electron microscopy showed Pd atoms were intercalated between the graphite onion sheets, and the structural model for the intercalation was proposed. HREM images and diffraction patterns calculated for the model agrees well with the observed ones. The present work indicates that the electron-beam irradiation to amorphous carbon with Pd clusters is an effective method for the formation of intercalated onions.

Keywords: HREM; carbon onion; Pd; graphite; intercalation

INTRODUCTION

Carbon onions have been formed from carbon soot or diamond by electron-beam irradiation or annealing at elevated temperatures[1-4]. These structures have a potential of studying materials in low dimensions in isolated environment. Nanoclusters encapsulated with these carbon onions are intriguing for both scientific research and future device application such as cluster protection, nano-ball-bearings, nano-optical-magnetic devices, catalysis, and biotechnology[5]. Recently, new carbon onions intercalated with Pd and Al atoms were discovered during electron-beam irradiation in transmission electron microscopes[6,7]. However, it is difficult to determine the atomic structure of intercalated graphite because of nanoscopic scale of the new phase.

The purpose of the present work is to determine the atomic structure

of the Pd-intercalated graphite onion by high-resolution electron microscopy (HREM), image processing, image calculation and diffraction analysis. HREM is a powerful method for investigating the atomic structure in nanoscopic region because each atom can be directly recognized from the HREM images[8-11]. These studies give us a guideline for the formation of intercalated onions.

EXPERIMENTAL

Pd clusters were prepared by the reduction of H_2PdCl_4 with trisodium citrate, and stabilized by p-H_2N-$C_6H_4SO_3Na$[12,13]. These Pd colloidal particles were isolated in the solid state on an amorphous carbon support. The cluster size is 2.5 nm with a size distribution of ± 0.5 nm, and the carbon matrix is found to have an amorphous structure, which were observed by HREM[6].

Samples for HREM observation were prepared by dispersing the materials on holey carbon grids. HREM observation was performed with a 200 kV electron microscope (JEM-2010) having a point-to-point resolution of 0.194 nm. The electron microscope is equipped with the TEM-IP system (PIXsysTEM), and imaging plates (IP) with the benefit of a large detection area of digital data were used to record the observed images. The detection area of the IP is 102×77 mm with a pixel size of 25×25 μm and an image depth of 0~16383 gray scale. The digital data were saved *via* digital data storage (DDS) by Digital Micro-Luminography (Fuji Film Co. Ltd.). For image processing and analysis of the observed HREM images, Image Gauge, L Process (Fuji Film Co. Ltd. Japan), Digital Micrograph (Gatan Inc. CA, USA), CRISP (Calidris Corp. Stockholm, Sweden) and Adobe Photoshop software were used. To compare observed images with calculated ones, HREM images were produced from the multi-slice method using the MacTempas software (Total Resolution. CA, USA). The parameters used in the image calculations were as follows: accelerating voltage = 200 kV, radius of the objective aperture = 5.3 nm^{-1}, spherical aberration C_s = 0.5 mm, focus spread Δ = 7.5 nm, and semi-angle of convergence α = 0.5 mrad.

RESULTS AND DISCUSSION

Pd clusters in amorphous carbon matrix are irradiated with an electron beam for 60 min under a beam current of 150 Acm^{-2} at 200 kV, as shown in Fig. 1(a). This beam current is *ca.* 20 times higher compared to that used for ordinary observation by electron microscopy. Graphitization of amorphous carbon is observed, which is confirmed by the lattice fringes of graphite layers with a spacing of *ca.* 0.34 nm. In addition, Pd clusters combined to form Pd nanoparticles with the size of $\sim$4 nm. Graphite shells with onion structures formed both at the surface and in the carbon matrix. In some onions, dark contrast were observed inside the lattice fringes of the onion layers. Structural change due to the Pd intercalation is observed in the lattice image.

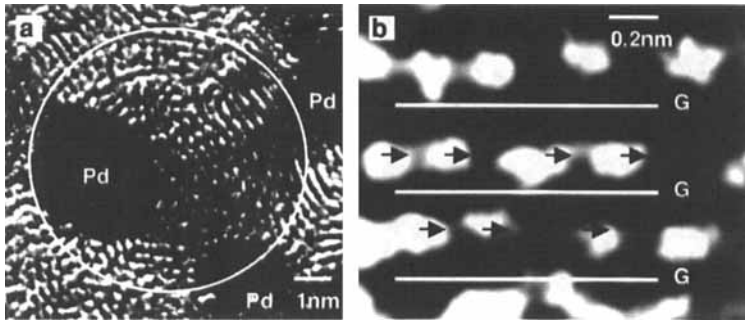

FIGURE 1 (a) HREM image of graphite onion-structure with Pd. (b) Enlarged HREM image of graphite {002} planes in (a). The graphite {002} planes are indicated by white lines with G.

The Pd clusters show black contrast which is due to the higher atomic number compared to carbon, and {111} lattice fringes with a separation of 0.23 nm are observed around the onion. Inside the onion, the graphite sheets show larger lattice distances (0.38~0.44 nm) compared to that of ordinary graphite carbon (0.336 nm = $c_G/2$)[14]. An enlarged HREM image of graphite {002} planes in Fig. 1(a) is shown in Fig. 1(b). Dark lines corresponding to graphite {002} planes are indicated by the white bars marked G. Dark contrast is observed at several ordered positions between the graphite sheets as indicated by arrows. The distances between these dark dots are in the range of 0.27~0.52 nm.

The HREM image of Fig. 1(b) was averaged and processed in real and reciprocal spaces, as shown in Fig. 2(a). As a first step, the digital images were masked and fast Fourier transformed. The reciprocal lattice was indexed, and the lattice parameters were determined using the positions of the strongest peaks in the transform. The local background was subtracted, and the amplitudes and phases of the peaks were refined by using symmetrization[15]. Before correcting the phases, the phase origin was determined by investigating the origin shift which gave the best accordance with the phase conditions for the two-dimensional space group. In the present work, two dimensional space group of *cmm* was applied for the image processing. Averaged symmetrized image of Fig. 2(a) was reconstructed from the corrected Fourier transform. The graphite {002} planes are indicated by G, and show lattice distances of 0.40 nm. Dark contrast with a distance of 0.40 nm is observed between the graphite sheets, which is believed to be Pd atoms. The distances between these dark dots are in the range of 0.27~0.52 nm, and the averaged value is 0.40 nm, which roughly corresponds to 0.426 nm (= $a_G \sqrt{3}$, a_G = 0.246 nm, graphite system[14]). This indicates that the direction of the incident beam is aligned to the [100] direction of the graphite when the Pd atoms are assumed to be just above the center of hexagonal carbon bonding.

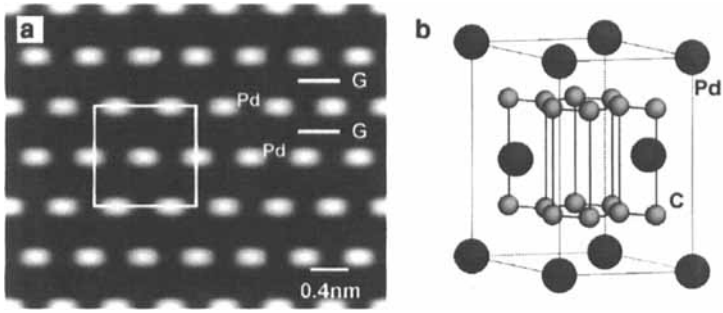

FIGURE 2 (a) Averaged, processed HREM image of Fig. 1(b). (b) Perspective structural models for (a) Pd-intercalated graphite.

Based on these experimental results, a structural model for Pd intercalation in graphite is constructed as shown in Fig. 2(b). The new lattice parameters are a_{Pd} = 0.492 nm and c_{Pd} = 0.80 nm, and the atomic ratio of Pd to C is 1:8. The space group is $P6_3/mmc$, a_G = 0.246 nm, and c_G = 0.671 nm[14]. By the Pd intercalation, a lattice parameter along *c*-axis increases to 0.8 nm. However, *a*-axis is stable, which is believed to be due to the strong σ bonding in the graphite sheets and weak π bonding perpendicular to the *c*-planes. Total energy calculated by *ab initio* ultrasoft pseudopotential[16] show the minima at 0.492 nm and 0.83 nm for *a*-axis and *c*-.axis, respectively. These values agree well with the experimental data, which indicates the Pd-intercalated graphite is stable for these lattice parameters. Although normal graphite shows the stacking sequence ABAB$\cdots$, the first stage intercalation shows the stacking sequence AAAA$\cdots$[17], as shown in Fig. 2(b). Several types of structural models can be considered, which depend on the atomic ratio of Pd and C.

Fourier transform of Fig. 2(a) is shown in Fig. 3(a). Electron diffraction patterns were also calculated for the Pd-intercalation model and normal graphite along the [100] direction, as shown in Figs. 3(b) and 3(c), respectively. The calculated diffraction of Pd-intercalation agrees well with the experimental diffractogram of Fig. 3(a), and the graphite shows completely different patterns. The results indicate that Pd atoms are intercalated in the graphite sheets.

Atomic intercalation in the graphite sheets has been studied for various elements such as Cs, Rb and K[17]. For the ordinary intercalation, the d-value between graphite {002} planes is in the range of 0.4~0.6 nm, which is fairly larger compared to the present Pd intercalation (0.38~0.44 nm). In addition, the image contrast of Pd positions in the experimental image is not so dark compared to the simulated image. This indicates that the Pd intercalation in the graphite layer in the present work is incomplete, *i.e.* the

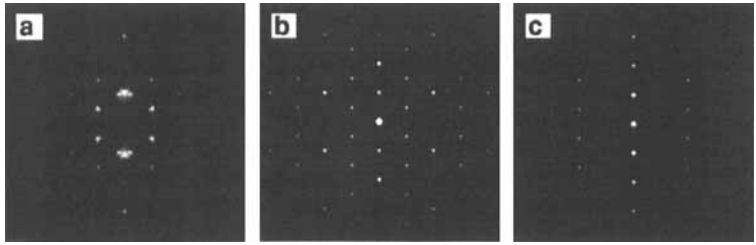

FIGURE 3 (a) Fourier transform of Fig. 2(a). Electron diffraction patterns calculated for the (b) Pd-intercalation model and (c) graphite along the [100] direction

occupancy of Pd in the graphite sheets is less than unity.

Pd intercalation in the graphite layers was observed in the present work. Atomic intercalation of Al in the carbon onions has been reported[7], which leads to spherical structures whereas Pd intercalation results in the disordering of the onion structure as shown in the present work, which would be due to the larger atomic number (size) of Pd *cf.* Al. For both metals, onions formed in the graphite matrix, although onions generally form on the surface of carbon matrix. This also suggests that distortions in the atomic-intercalated onions are relaxed in the carbon matrix. The formation of atomic-intercalated onions with low strain is interesting in terms of scientific research and applications, and can be readily synthesized by the electron-beam irradiation.

The graphitization of amorphous carbon and the crystal growth of Pd clusters were observed by electron-beam irradiation, as observed in Fig. 1. Various types of transition metals accelerate the graphitization of carbon[18] by the solution-precipitation mechanism, which results in disconnection of carbon-carbon bonds by the catalytic particles. The carbon atoms dissolve in the metal particles, and diffuse and precipitate as graphite at the particle surfaces. The encapsulation of small Pd particles in the graphite structure was reported, and the Pd-catalyzed graphitization of amorphous carbon occurred after annealing at temperatures above 600℃[18]. In the present work, the temperature of the samples was estimated to be below 100℃[7], which is fairly low compared to the ordinary graphitization mechanism. The graphitization of amorphous carbon in the present work is attributed to both the energy transfer from electron beam and the catalytic effect by Pd clusters, which results in the disconnection of carbon-carbon bonding and graphitization. The Pd clusters with the size of 2.5 nm have high percentage of surface area compared to the bulk structure, which results in the effective catalysis for transformation of amorphous carbon into graphite at the surface of Pd clusters. The driving force of this graphitization would be the free energy difference between the initial and final form of carbon.

CONCLUSION

Pd-intercalated graphite onions were produced by electron-beam irradiation of amorphous carbon with Pd clusters. HREM observation showed the increase of the lattice distance (~0.4 nm) of graphite {002} planes and appearance of ordered black contrast between the graphite {002} planes with a periodicity of ~0.4 nm, which indicates that the Pd atoms are intercalated in the graphite {002}. The structural model for Pd intercalation was proposed, and diffraction calculation based on this model agree well with the experimental results. The present work indicates that the electron-beam irradiation to amorphous carbon with Pd clusters is an effective method for the formation of intercalated onions.

Acknowledgements

This work was partly supported by The Iketani Science and Technology Foundation, and Grant-in-Aid for Scientific Research Ministry of Education, Science, Sports and Culture, Japan.

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