

SELF-ASSEMBLED CLOSED CURVED GRAPHITE-LIKE STRUCTURES (CCGS) FORMATION ON DIAMOND SURFACE

V. L. Kuznetsov, Y. V. Butenko, A. L. Chuvilin, A.I. Boronin, R. Kvon, S.V. Kosheev
Boriskov Institute of Catalysis SB RAS, Novosibirsk 630090, Russia
S.V. Stankus, R.A. Khairulin
Institute of Thermophysics SB RAS, Novosibirsk 630090, Russia

Introduction

We have found that diamond annealing leads to the formation of CCGS (onion-like carbon (OLC) [1-3], nanotubes [3] etc.). At the same time graphite-like structures are important for understanding the CVD diamond growth and for developing diamond vacuum microelectronics. In the present study we investigate the thermal treatment (from room temperature up to 2000 °C) of ultra disperse (d~2-5 nm) and micron size diamonds with TEM, XPS, FTIR, TPD, and the bulk density measurements to get new data on the CCGS formation.

Experimental

Ultra disperse diamond (UDD, d=2.0-5.0 nm) has been isolated from the detonation soot [1]. Synthetic diamond ASM 1/0 (d~1µm) and natural diamond (type IIa, d~1-20 µm) were also used.

Diamond annealing was performed in a vacuum furnace equipped with a narrow beam of gamma quanta of ¹³⁷Cs source, and with a scintillation detector for the **bulk density change registration**. Data on the bulk density measurements were used to estimate the kinetic parameters of the diamond to graphite-like carbon transformation.

The micrographs of diamond and annealing products were obtained with transmission electron microscope (TEM) JEM-4000EX. Distance between dark lines corresponding to the (111) lattice planes of diamond was used to scale the magnification of the TEM images.

XPS experiments were carried out with photoelectron spectrometer VG ESCALAB HP (Al K_α radiation). XPS spectra were calibrated against Au 4f7/2 (BE=84.0 eV) and Cu 2p3/2 (BE=932.7 eV) lines. The FTIR spectra were obtained with Bruker IFS 115. The TPD spectra of CO, CO₂ and H₂ were obtained with mass-spectrometer MX 7304.

Results and Discussion

We have combined TPD, XPS and FTIR spectroscopy to study the surface composition of UDD in order to characterize the processes proceeding before graphitization. We have found that surface oxygen-containing species presented by COOH, -OC=O, >C=O and C-O-C decompose at 200 - 400, 450 - 600, 750 and 800 °C respectively. UDD has a high concentration of bulk oxygen-containing defects. Hydrogen desorption is observed at 800 - 1150 °C (T_{max}~1100 °C). Hydrogen evolution from the diamond surface coincides with the closed curved graphite-like species formation (TEM data). Further UDD annealing up to 1630 °C produces the onion-like carbon.

The XPS C1s spectra of UDD and ASM treated at different temperature, have been fitted with four components. Three of them were attributed to sp² bonded carbon and one to the sp³ bonded carbon. The C1s shape of the graphite components is used to extract the graphite fraction from the integral C1s line of the OLC samples. The C1s line consists of the diamond component solely when diamond annealing up to 850 °C is performed. The following annealing at 950 °C results in the appearance of the peaks corresponding to the graphite-like structures. At T=1630 °C the diamond peak almost disappears from the C1s spectra and mainly graphite components are present in the spectra. The XPS spectra analysis of ultra disperse diamond annealing products (heated up to 1630 °C) allows to propose the existence of the sp³ carbon stabilized inside OLC shells as a small cluster. However, annealing at a temperature higher than 1750 °C causes the transformation of OLC to hollow closed particle (TEM data), where sp³ carbon disappears.

Figure 1 shows the change of bulk density for UDD (d~ 2nm and 5 nm) and ASM. One can see that the UDD annealing proceeds easier than that of the micron size diamond due to the larger surface of small particles. Activation energy for the UDD annealing (average particle diameter, 4.7 nm) is estimated as 43±3 kcal/mol (at temperatures 1150 - 1550 °C). The migration rate of the interface "diamond - graphite" varies from 0.04 to 1.5 nm/hr. Those values correlate with the formation of a thin

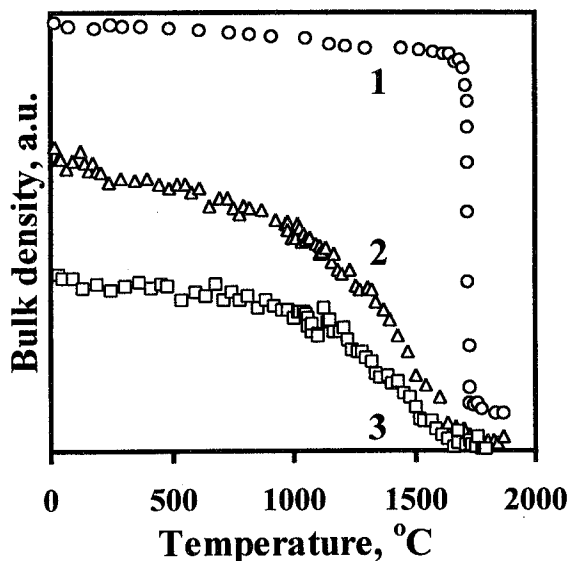


Figure 1. Bulk density change on diamond annealing. 1 - ASM; 2 - UDD, $d \sim 4.7$ nm; 3 - UDD, $d \sim 4.0$ nm.

layer of CCGS at the surface of the micron size diamond (for example see Fig.2).

So, Figure 2 demonstrates the formation of short 2 - 4 layers nanotubes on the natural diamond surface. The further annealing leads to the formation of highly defective large graphite particles covered with CCGS (nanotubes, nanofolds and structures of conical form).

At the interfaces between diamond and evolving graphite-like structures two curved graphite sheets are found to form from three (111) diamond planes. CCGS (nanotubes, nanofolds) build the surface mosaic structures (see Fig. 2, B).

TEM results and molecular mechanics simulations allow us to conclude that the CCGS formation during the diamond annealing is a self-assembling process. The self-assembling ability of CCGS can be considered in terms of a shrinkage along the graphite network (relative to the (111) diamond plane), a simultaneous increase of the distance between graphite-like sheets and a sufficient decrease in the carbon particle surface energy due to the closure of the graphitic shells and elimination of their dangling bonds.

Conclusions

The annealing of micron size diamond leads to the formation of surface self-assembled CCGS such as nanotubes, nanofolds. Graphite-like species start to form after hydrogen, and oxygen containing groups quit the diamond surface. The activation energy of UDD annealing is equal to 42 ± 3 kcal/mol at 1150-1550 °C.

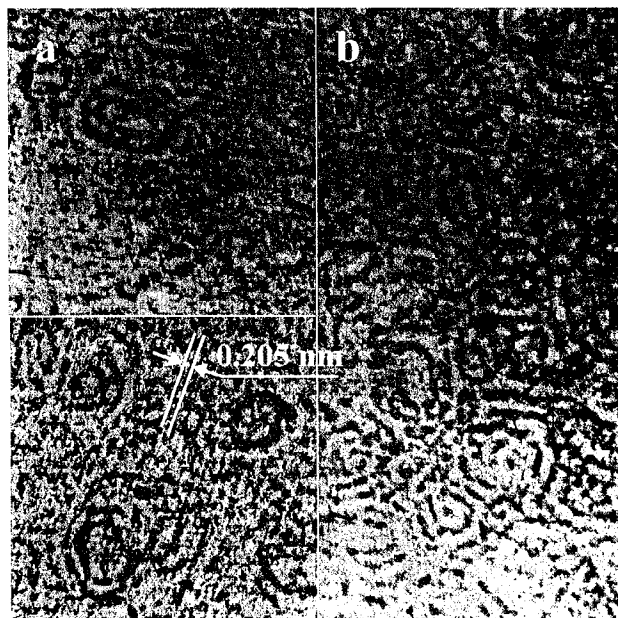


Figure 2. HR TEM micrograph of natural diamond annealing product. The dark contrast closed circles enclosed each to others (a) correspond to the top view projection of surface nanotubes. The distance between nanotube layers (~ 0.35 nm) is closed to that of graphite (0.34 nm). Side view of those nanotubes (images do not presented here) allows to estimate the height of nanotubes as 1.5-2.0 nm. CCGS on diamond surface form mosaic structures (b).

Acknowledgments

The work was supported by the program "Fullerenes and atomic clusters" (project 96122), Russian Foundation for Basic Research (Grant No. 95-03-08912) and Civilian Research and Development Foundation for the Independent States of the Former Soviet Union (Award # RC1-251).

References

1. Kuznetsov, V.L., Malkov, I.Yu., Chuvilin, A.L., Moroz, E.M., Kolomiichuk, V.N., Shaichutdinov, Sh.K., Butenko, Yu.V., *Carbon*, 1994, 32, p. 873.
2. Kuznetsov, V.L., Chuvilin, A.L., Butenko, Yu.V., Malkov, I.Yu., Titov, V.M., *Chem. Phys. Lett.*, 1994, 222, p. 343.
3. Kuznetsov, V.L., Chuvilin, A.L., Butenko, Yu.V., Malkov, I.Yu., Gutakovskii, A.K., Stankus, S.V., Khairulin, R.A., in *Science and Technology of Fullerene Materials*, eds. P.Bernuer, D.C.Bethune et.al., *MRS Symposium Proceedings*, MRS, Pittsburgh, Pennsylvania, 1995, 359, p. 105