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Nanostructural elements of some high temperature semiconductors

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Introduction

High-temperature semiconductors (HTS) with wide forbidden zones embody the very essence of materials for modern nano-electronics. Complex HTS materials based on carbon and boron provide unique structural properties. Technology for their preparation as films is emerging in order to have their desirable electrical and physico-chemical properties such as mechanical hardness and chemical resistance in convenient forms. Research conducted during the last decades of the 20th century has shown that carbon and boron crystals form clusters, of which the essential structural elements contain 4, 12, 60 or 84 atoms. The thermodynamics of these "nanoelements" decree their transformation to amorphous or crystalline films, layers and other deposits, which have some advanced properties.[1,2] Clusters having a stable configuration under equilibration conditions take the forms of different geometrical figures, from triangular to dodecahedral and icosahedral.[3,4] According to classical ideas of particle formation and growth, and in correspondence with the so-called atomistic process of nucleation, atoms as the 'germ' of the solid phase unite in aggregates (clusters) whose size is dependent on the atomic potentials.

Statistical calculations of the thermodynamic properties of small clusters carried out by means of computer modelling have shown that the potential energy of atomic cluster components is the main factor determining the chemical potential of the cluster. The elemental atoms in small aggregates can be packed according to the laws of

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[1] A.G. Mamalis, S.N. Lavrinenko, A.I. Grabchenko, L.G. Duebner & N.M. Kirjukhin. "Biomedical functional surface generation with control at the nanoscale". *Nanotechnology Perceptions* **1** (2005) 79–87.

[2] P. Kervalishvili. "Investigations of small particles growth". In: *Proc. Greek Natl Conf. Solid State Physics*, pp. 18–29. Ioannina Univ., Athens, Greece, September 1998.

[3] U.T. Petrov. *Small Particle Physics,* p. 356. Moscow: Nauka (1982).

[4] R. Kern. "The equilibrium form of a crystal". In: *Morphology of Crystals* (ed. I. Sunagawa), pp. 77– 206. Tokyo: Terra (1987).

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crystallography, together with packing of non-crystallographic pentagonal symmetry. However, the pentagonal symmetry of clusters, despite its small deviation from crystallographic packing, is energetically less advantageous. This becomes partially apparent when the crystal growth in the complex is accompanied by the corresponding increase in inter-atomic spacing.

The growth in the quantity N of atoms in the cluster results in an increase of the thermodynamic potential P (N), caused by the increase in the number of atoms at the surface. At the same time, the increase of surface energy accompanying the addition of atoms is not continuous, but discrete because of the differences between the energetic contributions of the atoms completing the formation of the co-coordinating sphere.[5] Further growth in the aggregate[6,7] leads to an increase in its volume by means of the gradual addition of atoms from the sides to the growing cluster—volume growth. Using both established and recent approaches to the mechanism of cluster formation, it is easy to show that the appearance of small particles analogous to so-called fractal clusters very often takes place. Following this, particle growth occurs not by the joining of new atoms to the existing aggregates, but by the conglomeration of aggregates with stable configurations, which tends to preserve their individual properties. Such 'volume clusters' consisting of smaller separate clusters have much lower density than the substance constituting the primary structural elements, which often have the shape of a regular solid (tetrahedrons, cubes, octahedra, etc.), one or more surface planes of which are stuck together.

The formation of small particles (clusters) is technically realized by various methods, including supersonic outflow of vapour into vacuum, thermo-, laser- and plasma-chemical modes of substance reduction from gas-phase precursor compounds, vapour precipitation upon cold substrates, reaction following molecular effusion from a cell, etc. These techniques are being used to study the process of small particle formation, volume growth and growth on specially prepared surfaces.

Boron structures

The production of elemental boron is presently being developed through various powder and film technologies.[8] The greatest interest is in modes of small particle production to provide high dispersion and purity as well as the study of the processes of cluster nucleation and growth.

Established theory and experiments have shown that the elemental boron atoms

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[5] V.K. Vainshtein, A.A. Chernov and L.A. Shuvalov. *Contemporary Crystallography. B: Formation of Crystals,* p. 408. Moscow: Nauka (1980).

[6] H. Brune, H. Roder, C. Bogarno and K. Kern. "Microscopic view of nucleation on surfaces". *Phys. Rev. Lett*. **73** (1994) 1955–1958.

[7] P. Kervalishvili and T. Jandieri. "Oxidation of crystalline boron". *Proc. USSR AN, Inorganic Materials* **27** (1986) 1115.

[8] V. Matckovich, ed. *Boron and Refractory Bodies,* p. 485. Heidelberg: Springer-Verlag (1977).

group into an aggregate of icosahedral form consisting of 12 boron atoms (B_{12}).[9,10] These small icosahedra are then usually united in a flat cluster whose configuration depends on the thermodynamic conditions at formation. Designating the chemical potential of the structural element (in boron this is a 12-atom icosahedron, in carbon it is a 4-atom tetrahedron) as E, and the chemical potential of the flat cluster as P, it is apparent that equilibrium between the longitudinal dimensions and flat cluster thickness will be achieved when

$$\mu(E-P) = 2\alpha v/r,$$

where α is the specific surface free energy per structural element, v is the specific volume of the cluster per structural element (analogous to the Gibbs-Thomson expression), and r is the radius vector. Given that the equilibrium form is subordinated to the second order non-linear differential equation[11,12] and the difference $\mu(E-P)$ is constant over the whole surface of a particle, the solution of this equation represents the envelope of the cluster:

$$\mathbf{hr} = 2\alpha(\mathbf{h})\, v/(\mu(E-P)),$$

where **h** is the vector of the normal to the envelope (the surface) of the small particle as determined by the radius vector **r** of magnitude r (the expression is analogous to the Curie-Wulff formula[13]). From this equation it is possible to evaluate the geometric form and longitudinal dimension of the equilibrium state of the cluster of elemental boron in flat form (Fig. 1) under given thermodynamic conditions.

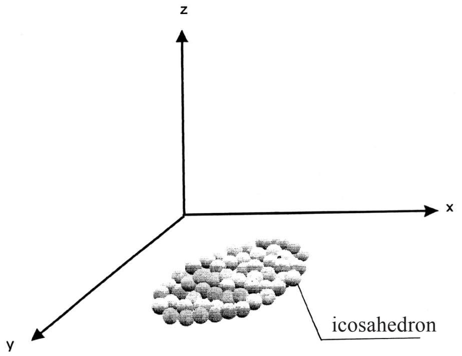

Figure 1. Schematic picture of a flat cluster of 12-atom icosahedra.

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[9] W.N. Lipscomb. “Borides and borates”. *Journal of Less-Common Metals* **82** (1981) 1–20.

[10] G. Abdushelishvili, T. Abzianidze and P. Kervalishvili. “Boron particles production in nonequilibrium laser-chemical radical reactions during the IR multiphoton dissociation”. *Laser Chemistry* **10** (1989) 81–87.

[11] L. Landau and V. Lifshits. *Statistical Physics, Part 1*, p. 584. Moscow: Nauka (1975).

[12] J. Bernholc, E.L. Briggs, M. Buongiorno Nardelli et al. In: *Multiscale Computational Methods in Chemistry and Physics* (eds A. Brandt et al.), pp. 65–89. Amsterdam: IOS Press (2001).

[13] P.J. Kervalishvili. “On the mechanism of elementary boron small particle growth”. *Solid State Physics* **28** (1986) 3218–3220.

In recent electron microscopic studies and testing of the structure of elemental boron produced by means of boron trichloride reduced with hydrogen and laser-chemical multi-photon dissociation of the dichlorborane molecule, the observed structural elements—boron icosahedra—have been found to be statistically distributed in both an amorphous form and in a crystalline form with rhombohedral symmetry.

Under Scherrer focus, the particularities of the initial structure of the specimen and its alteration under thermal absorption of the electron beam as well as under thermal treatment of the particles in deep vacuum were observed. Electron microscopy shows that the particle has an amorphous structure; boron icosahedra are placed irregularly in the plane.

Analysis of the microdiffractograms, consisting of three diffuse halos, yields values of the interplane distance consistent with the (111) interplane spacing of β-rhombohedral boron (7.962 Å). A number of boron particles partly overlapping each other are shown in Fig. 2. The particles are indeed planar structures with a diameter 20–40 times their thickness, which corresponds to the linear size of a 12-atom boron cluster.

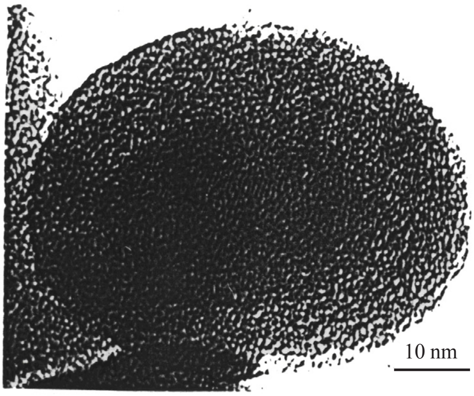

Figure 2. Electron microphotograph of overlapping planar boron particles. Freely-poured ultra-dispersed amorphous boron powder[14] produced by plasma-chemical reduction of boron trichloride with hydrogen was observed in an EM-100/OR "OPTON" electron microscope (electron acceleration voltage = 100 kV). The additional phase displacement caused by spherical aberration between non-dispersed and diffracted beams defocused the pictures but was compensated by defocusing of the lens.

Thermal treatment of the boron powder in a 1×10^{-6} Pa vacuum at a temperature of 800 °C for a period of 30 min leads to the partial crystallization of the inner clusters (stripe contrast, typical of the crystalline condition) while the amorphous structure of the outer clusters is preserved. Analysis of the corresponding electron microphotographs shows that the increase of the particle diameters under thermal treatment occurs because

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[14] P.J. Kervalishvili, E.R. Kutelia and V.S. Petrov. "Electron-microscopic structure of amorphous boron". *Solid State Physics* **27** (1985) 1414–1418.

of the joining of the lamellar clusters formed from boron icosahedra, with initial diameters in the range 20–50 Å and the thickness of a B_{12} icosahedron.

Thus, the direct observation of small particles of elemental boron using high-resolution electron microscopy shows that the boron clusters (20–50 Å) are amorphous planar compounds in which the ratio of the thickness to the diameter varies from 1:10 to 1:40. These clusters proceed to crystallization, which at first occurs in the centre of a particle, then advances to the edges, there is stratification, and finally volume crystallization.

Ultra-disperse amorphous boron powder clusters consisting of statistically (nonregularly) distributed icosahedra have also been found. These clusters have an elliptic or ellipsoidal configuration and longitudinal dimensions whose value is some ten times the diameter of the B_{12} structural element.[15] The cause of this is unknown.

Thermal treatment of the elemental boron powder consisting of planar clusters in a vacuum furnace as well as in the electron beam of the microscope resulted at first in the transition of icosahedra from a statistical into a regular arrangement and then their grouping into a rhombohedral configuration of β-type crystalline boron (Fig. 3). At the second stage a crystalline phase was formed. The observation of elemental boron structural elements gathered in flat clusters characterized only by local order is direct experimental corroboration of the energetic advantage of the existence of small particles with a flat geometry, and of the existence of spaces during the growth of solids from atoms to a cluster and further to a massive specimen.

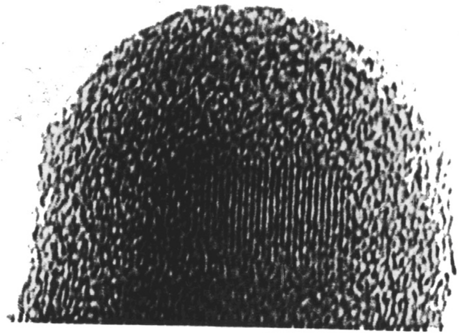

Figure 3. Electron microphotograph of a small particle of boron at the first stage of ordering.

Carbon structures

Similar results have been observed in the case of ultra-dispersed carbon powders. Electron microscope studies show that the carbon powder consists of small structural elements in the forms of tetrahedral disks. Upon adsorption of a very small amount of energy they organized themselves into bigger clusters, sometimes fullerenes. Upon

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[15] P. Kervalishvili. Some investigations of small particle growth. In: *Proc. XIV Pan-Hellenic Conf. Physics,* pp. 75–88. Ioannina Univ., Athens, Greece (1998).

prolonged exposure in the electron beam they became crystalline and under suitable thermodynamic conditions, diamond.[16]

Other structures

The further study of small particles, their nucleation and growth will doubtless explain a number of natural phenomena associated with the formation of small solid structures. The practical importance of these investigations resides in the possibility of creating new technologies for the production of ultradisperse materials with given crystalline or amorphous structure and their requisite properties.[17] Recent experimental studies of a plethora of small solids, including carbon, cobalt, etc. and biological systems (biomolecules) have provided new data regarding the nature of the kinetics of their formation.

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[16] A. Gippius. Semiconducting diamond: properties and applications. In: *Proc. X Pan-Hellenic Conf. Physics,* pp. 54–59. Delphi, Greece (1994).

[17] Ch. Lieber. In: *Proc. Korea–USA Forum on Nano Science and Technology*, pp. 83–96. Cambridge, Massachusetts, September 2000.