Large man-made diamond single crystals: manufacture, properties and application

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Diamond is a material possessing a unique complex of physical and chemical properties which potentially allow using it, besides traditional application in the processing industry, in Hi-Tech branches also. Such use of diamond restrains by insufficient quantity of natural perfect raw material of so-called "device" quality. Single crystals of diamond grown up in laboratory conditions differ from natural, first of all, in high reproducibility of physical properties (impurities level, an optical transparency, heat conductivity, specific electric resistance, etc.).

Creation of technologies for cultivation a high purity «nitrogen free» (IIa type) and semi-conductor (IIb type) large diamond single crystals, which are extremely rare among natural diamonds and very expensive, is of the great interest and simultaneously of the greatest difficulty. Technologies for manufacture of both IIa and IIb diamond single crystals 0.5 to 5.0 carat in weight (characteristic size 3÷8 mm) from solvent/catalyst melt of transitive metals at high static pressures and temperatures (based on a temperature gradient growth technique) have been developed by Dr. Terentiev's research team some years ago and successfully introduced in industrial department of TISNCM.

Man-made IIa type single crystals are characterized by an optical transparency in a less than 25 μm wave lengths region and have fundamental absorption edge at 225 nanometers. Their thermal conductivity reaches 2000 Wt/m•K. Nitrogen concentration (a basic impurity element) level does not exceed 2 ppm (usually less than 1 ppm). Specific electric resistance of such crystals is 109 ÷ 1013 Ohm•cm.

A perspective scopes for such crystals are: anvils for research of materials properties at ultrahigh pressure; sensitive elements of radiation detectors (UV, X-ray, α, β, γ, high-energy particles, nuclear and synchrotron radiation) and also optical windows for lasers, probes for tunnel microscopes and heat spreaders/sinks of powerful electronic devices.

The semiconductor diamonds doped by boron are characterized by P-type electric conductivity. Thermal conductivity of such crystals is within the limits of 1000 ÷ 2000 Wt/m•K. Nitrogen concentration is less than 1 ppm, and boron concentration can reach value 300 ppм (estimate). Specific electric resistance of this material is 0.1÷109 Ohm•cm.

The most perspective applications of semiconductor diamond will be high-speed temperature sensors for medicine, the automobile and aviation industry, liquids and gases flow meters (including aggressive environments), vacuum gauges, low inertia heating elements.

Another and most perspective application of both types diamond single crystals is enough big area substrates manufacturing from them for the subsequent homoepitaxial deposition of diamond single crystal layers by CVD technique to create planar structures. Such approach will allow creating the technological base for next generation high-temperature electronics.

CVD diamonds and their applications.

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Diamond is a material that shows a wide range of exceptional properties making it a very promising material for electronics and instrument making. Diamond is the hardest material with excellent chemical resistance. The electrical, thermal and optical properties of diamond are unique. It is a large band gap semiconductor with very high carrier mobility, exceptionally high breakdown field and extremely high thermal conductivity. Owing to its mechanical properties, diamond is perfect material for cutting tools. It is also very promising material for micromechanics and microsystems. Light, very rigid and wear-resistant parts of microsystems could be made of it. The electrical properties of diamond make it an unsurpassed material for high power and high voltage electronics. Having extremely high radiation resistance, diamond is the best material for particle and high-energy radiation detectors. Due to its unique optical properties diamond is also excellent material for different windows and UV detectors.

Despite the fact that single nature diamonds can show very good properties to be used in electronics and instrument making, they cannot be used in these fields of application. Nature diamonds are very rare, small and expensive. And they have very wide property spread. The properties of HPHT diamonds can be controlled much better. However such diamonds are also restricted in size and they have inclusions and additions, the eliminating of which is very difficult if possible at all. CVD diamonds are the most promising candidate to be used in electronics. CVD diamonds are very pure. The restriction in size is much less. However the growth rate is relatively low.

Last years TISNCM also conducts works on CVD diamonds. The more so as our institute produces its own high-quality diamond substrates with unique properties. We grow high-quality monocrystalline epitaxial diamond films, and try to build prototypes of different detectors and electronic elements on their base. Using boron-containing IIb-type monocrystalline diamond plates produced in TISNCM as substrates for the deposition of epitaxial monocrystalline IIa-type diamond layers with the thickness from a fraction of a micrometer to hundreds micrometers, we obtain two-layer IIa/IIb-type monocrystalline diamond plates. Such plates have great potential to be used as a base for electronic components and bulk sensors. Using such plates we have built the prototypes of Schottky diodes and radiation detectors (α-particles and UV).

We also grow polycrystalline diamond films on silicon substrates with diameter of up to 50 mm. The silicon substrate can be easily etched, and then a diamond film remains, which can serve as a material for the manufacture of diamond tools, heat-spreaders and optical, microwaves or x-ray windows. At present time we conduct works on heat-spreaders and electronic component packaging.

Mutual consistency of mechanical testing at micro- and nanometer scales as investigated with scanning nano-hardness tester NanoScan

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To a considerable degree hardness is an empirical value which depends on many details involved in the measuring process, like equipment design, technique, indentor type, measuring conditions, range of applied loads, etc. When a hardness value is mentioned, one should always keep in mind that it is not a physical constant, but some experimental value obtained with known method and depending not only on the material, but on conditions and methods as well.

Two competing techniques for measuring hardness at the nanometer scale are instrumented nanoindentation and scratch hardness test. Due to easy and fast obtaining of a numerical result, nanoindentation has become the most common way to measure hardness, which is studied carefully in many aspects. This technique underlies an international standard on measuring hardness ISO 14577.

At the same time, the scratch hardness testing is used more rarely. However, this technique has several apparent advantages, especially when applied at the nanometer scale. Some of them are less influence of roughness, less effect of elastic recovery of scratch width compared to indentation imprint perimeter, the effect of averaging along the scratch length, variation of attach angle if scratching face forward or edge forward, the possibility of variable load scratch test, easier pile-ups analysis, and the possibility to study the anisotropy of hardness.

Scanning nano-hardness testers of NanoScan series are intended for investigation of the surface topography, elastic modulus mapping and for measuring the mechanical properties (including hardness and elastic modulus) of bulk materials and thin films on a submicron and nanometer scale. NanoScan has been developed on principles of scanning probe microscopy (SPM). The main characteristic feature of NanoScan is the use of piezoceramic probe sensor having high bending stiffness of the cantilever ($\sim 2*10^4$ N/m). High bending stiffness of the cantilever permits to go through the viscous contamination layer when working in an ambient environment until the contact with rigid surface and to make a modification of surface (indentation and scratching). The probe design allows using diamond indentors of different type.

For investigation of mechanical testing consistency the hardness values measured on different depth scales (from microscopic down to nanometer), with different techniques (microhardness test, nanoindentation and scratch hardness test) on the materials of different structure (fused silica, steel and sapphire) were compared to each other.

Some critical aspects of both scratch hardness and nanoindentation applications were considered. The scratching was made it constant load mode, the scratch traces were carefully imaged in SPM mode. The resulting plastic deformation around the scratch perimeter was studied in dependence of most critical scratch parameters such as maximum normal load, loading velocity, relaxation time, attack angle, etc. For the particular material the suggestions are made on the optimal scratching conditions which make it possible to produce a scratch free from such artifacts as fracture and cracking. The transition between ploughing and cutting and its effect on measured hardness value is observed and discussed as well.

It is shown that scratch hardness test is a powerful and informative test not only for bulk materials but also for thin films and superhard materials.

Quick-response single crystal semiconductor diamond temperature sensors.

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The high-temperature function of semiconductor sensors is limited by crystal lattice stability. The critical temperature value roughly equals to 2/3 of the melting point. Doped diamond is the most temperature stable crystal with semiconductor properties. Besides high temperature stability diamond possesses high radiation strength, chemical inertness and mechanical strength. Therefore open-frame use of diamond sensors is possible. This is particularly important for the quick time response applications, because diamond is the best thermal conductive material. Thus diamond is an advanced material for temperature sensors design. However semiconductor natural diamonds are very rare and their electrical properties different. Only synthetic diamonds are suitable for scaled sensor production.

TISNCM developed the technology of synthetics single crystal semiconductor diamond growth and the technology of making temperature sensors. Boron doping at growth process is used. Boron acceptor level locates at 0.37 eV above the valence band top and the activation energy of charge carriers (holes) varies in the range of 0.2 –0.37 eV depending on boron concentration.

The typical B concentration in diamond sensors is 1018-1019 cm-3, that provides good electrical conductivity and temperature sensitivity. The dimensions of sensor crystals are 0,5´0,5´0,2 mm3. The golden or platinum wires are attached to contact plates deposited on the one of the square faces by magnetron sputtering of Mo and Pt which provide ohmic contacts after special vacuum annealing.

The working temperature range of thermistor type sensors is (–196) ¸ (+500)oC. Their electrical resistance changes several orders of magnitude in this range. The sensitivity is highest at low temperatures. At upper limit temperature 500oC the sensitivity is about 0,1oC.

The characteristic time response value of the developed temperature sensors is about 20ms.

Carbon nanotubes and nanofibres for construction materials and functional applications

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Carbon science and technology is one of the most vividly developing branches of materials science. Great promises are related with carbon fibers based on long aligned strands of carbon nanotubes as described in our earlier work [1] in detail. The high-strength and high-modulus carbon nanotubes can become a cheaper alternative to carbon fibers based on traditional technology of carbonization/graphitization of fibrous precursors (PAN, viscose, pitch, lignin, etc.). Indeed, the tensile strength of an individual nanotube may exceed 30 GPa while the best fibrous precursor-based fibers never show tensile strength higher than 7 GPa. Moreover, the carbon fiber production based on catalytic growth of nanotubes would include simpler technological chain and no annealing at the temperatures of around 2000°C, which imply very complex and expensive equipment and extraordinary energy expense.

Another prospective way is the development of prepregs for composite materials on the basis of those same longer carbon nanotubes or nanofibres. Shorter carbon nanotubes application future is related with filling various composites based on polymer, metal or ceramic matrix for improvement of their properties such as strength, modulus, wear resistance, fire resistance, heat and electricity conduction etc. The chief problem for realization of unique properties of nanotubes as filler is their high cost and low yields reached at present time. The yields of lower than 300 g/g, which were typical for earlier catalytic growth works reported before 2003, are no longer interesting for future development. The future of higher-yield nanotube growth is related to satisfaction of three major requirements, i.e. (a) yield higher than 1000 g/g; (b) impurities of non-nanotube as low as possible for easier purification; and (c) cheaper catalyst.

It is important to note that the requirements for the nanotubes for functional applications differ drastically from those for construction materials.

Here we consider prospective ways for high-yield production of shorter or longer carbon nanotubes. Several research groups throughout the world have started research and development in this area recently. Approaches of making carbon nanofibers via long single wall carbon nanotubes “smoke” or via multiwall carbon nanotube/nanofiber strands or via multiwall carbon nanotube forests are analyzed. The problems of providing proper quality of the future materials such as length, morphology, crystallinity of individual fibrils are presented. The transition from as-grown nanotubes to ready material such as spun fibers by spinning threads is shown to be as important as the growth itself.

[1] V.Z.Mordkovich, Ultra-high strength carbon nano-fibres. Khim. Prom. Segodnya (2) 12 (2003)

Novel carbon nanomaterials based on a low-density graphite foil.

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High chemical and thermal stability, ability to be pressed without binder, low thermal conductivity – the unique properties combined in exfoliated graphite (EG) provide its application for multi-purpose materials creation. EG covered by PC could be used to produce high-temperature heaters and thermal insulators. Traditionally, pyrolitic carbon (PC) is applied for carbon composites strengthening [1].

Herein we report physicochemical investigation of low-dense carbon materials modified with pyrolitic carbon. EG obtained by nitrate expandable graphite thermal destruction was pressed into low-dense graphite materials (LDGM) with densities of 0.045-0.500 g/cm^3. LDGM were saturated with PC by impact CVD technique included methane decomposition at 1060 ^{o}C and pressure of 100 mbar.

LDGM density growth from 0.045 g/cm^3 to 0.5 g/cm^3 leads to 15 times saturation degree diminution. PC deposition also causes specific area and pore volume lessening, for example, LDGM with density of 0.045 g/cm^3 is characterized by surface area of 50 m^2/g that dramatically decrease down to 8 m^2/g after PC deposition. According to scanning electron microscopy data, low-ordered anisotropic pyrolitic carbon uniformly drifted on LDGM forming layers with average thickness of 8 nm (for LDGM with density of 0.045 g/cm^3). Composites mechanical strength is significantly higher than that of initial LDGM, for example, compression strength for samples with density less than 0.2 g/cm^3 grown up for 2 times after PC saturation.

Laser flash analysis shows that temperature conductivity increases via EG modification by PC. Temperature shift in higher values causes composites temperature conductivity reduction that is advantageous in comparison with other known thermal insulators. Composites thermal conductivity is about 1.0-2.5 Wt/m·K.

Thus, exfoliated graphite modification by pyrolitic carbon allows obtaining composites with relatively high strength and low thermal conductivity that makes them promising materials for high-performance high-temperature thermal insulators production.

Keyword: exfoliated graphite, pyrolitic carbon, composites

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Diamond treatment from new viewpoint.

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It is known that only about 20-25% of gained diamonds may be used in jewelry according to their colour and quality characteristics. The remaining 75-80% of diamonds are used in industry and different technical devices.

It is hard to expect any revolution innovations and new technological solutions in industrial use of diamonds (abrasives, cutting instruments, drills, chisels, borers, saws, discs, etc.). There are other prospects in use of diamonds in new fields of technology. According to the authors of the monograph [1] "Application of natural diamonds in new fields of technology is done in two ways. The first is an attempt to use in practice (in transducers, heat sinks and other devices) the most outstanding properties of a diamond by replacing already used materials. The second is the search of new phenomena, new functional opportunities and device ideas that allow to realize the heuristic potential of diamond as a material of future technology. This way is developing fast and is based on optoelectronic properties of natural diamonds…".

A widening field of use of diamond will require an improvement of the known or the development of the new methods of diamond crystal treatment and study of the interaction of the diamond with adjoining materials and the environment.

In 1975 in the laboratory of experimental mineralogy of the Institute of geology in USSR was done a research of the interaction of the diamond with transitional metals in different gas environments in high temperatures and atmosphere pressure [2]. During one of the experiments a metallic plate (in particular – iron plate) began to penetrate into a diamond crystal. This result become a base of development of new methods of diamond treatment called "thermochemical treatment". The first application for the invention "The way of dimension diamond treatment" was given in May of 1975. More than 20 certificates of recognition (of USSR and of Russia and patents of Russia, seven foreign patents are given on thermochemical methods of diamond treatment. Dozens of articles in scientific magazines are written about them. Technological opportunities of thermochemical methods of diamond treatment are described in popular scientific magazines.

The essence of thermochemical methods of diamond treatment is a solution of the diamond by the metals of a transitional group (Fe, Co, Ni) and alloys of these metals at temperature of 650 ^{0}C in hydrogen environment.

In this temperature of treatment the diamond does not react with hydrogen itself but the latter reacts well with dissolved in the metal diamond carbon forming methane.

Therefore the diamond crystal is saved in areas that are not meant to be treated and there is constant regeneration of the used metal.

With the help of the described method one can cut items from diamond and make holes of complicated stencil forms in diamond products.

During diamond treatment with a motionless instrument the treated surface of the crystal is shaped compliance with the surface shape of the metal. For extension the number of treating operations and to increase the speed of the process, the diamond was used to be treated by a moving instrument. New results are achieved in polishing. In a traditional mechanical way of polishing the removal of the mass of a diamond is done during a mechanical blow with particles of abrasive when a diamond disk rolls fast. During the thermochemical way a diamond contacts with minimal loading with a slowly rolling heated disk. The removal of the mass of a diamond is done by dissolution of diamond carbon by metal. All that permit to get high surface-finish using the thermochemical way of polishing.

It is important to mention that one of the main disadvantages of thermochemical methods of diamond treatment is a low speed of the treatment. The search of the ways to increase the speed of thermochemical polishing lead to diamond treatment by melted metals [3]. The main problem during polishing by melted metals is getting the required forms and sizes of diamond products. If the methods of high-speed polishing by melted metals are not developed up to the end then high-speed sawing of a diamond by use an Fe-C-eutectic is already used in practice.

A technology of precision sharpening of blades of monocrystal diamond instruments based on thermochemical treatment of diamond was developed. The first Russian diamond microblade was successfully tested in Moscow institute of eye microsurgery in March 14, 1983. In a short term in experimental technical production of Moscow Institute of Eye Microsurgery was opened a department producing diamond microblades, later such departments were open in six cities of USSR including Barnaul.

The company “Krystalin” offers microsurgery ophthalmologic scalpels with diamond blade. In 1986 in Altai started the production process of this instrument. Hard work at upgrading of the holder construction, advancing sharpening of different forms of the blade considering leading Russian ophthalmologists requests made the production of this instrument possible.

Diamond microsurgery scalpels fit perfectly for any operations (ophthalmologic microsurgery, vessel and neurosurgery, cosmetology and plastic surgery). The sharpness of the cutting edge allows to pull apart tissues on molecular level which lead to fast recovery.

Recently we have developed the manufacture of microsurgery scalpels from synthetic diamond. The use of opaque synthetic diamond blades facilitate microsurgeon work significantly.

This good acquisition will let you make operations on a new higher level. The company “Kristalin” is the only Russian producer of these unique scalpels with diamond blades. Our scalpels are of great demand of all leading ophthalmologic centers in Russia and abroad (USA, Germany, France, Israel, India and Switzerland).