

Carbon photonics

V.I. Konov

Abstract. The properties of new carbon materials (single-crystal and polycrystalline CVD diamond films and wafers, single-wall carbon nanotubes and graphene) and the prospects of their use as optical elements and devices are discussed.

Keywords: photonics, lasers, carbon, diamond, nanotubes, graphene.

1. Introduction

Natural diamond single crystals, which possess a number of unique characteristics [transparency in a wide range (from UV to microwave regions), unprecedentedly high hardness and thermal conductivity, high radiative and chemical durability, etc.], have long attracted attention of researchers due to the properties of this unique optical material. However, their wide practical application is limited, primarily, because of high cost, small size and poor reproducibility of properties even within one set of crystals. Among initial studies devoted to carbon photonics, we should note only the works on radiation detectors based on natural diamond single crystals [1] and application of natural diamonds as tools for profiling and polishing metal-optics elements for high-power IR lasers [2]. The other well-known and widespread carbon material – graphite – can be considered optical only rather conditionally: due to the high absorption (light absorption coefficient no less than 10^5 cm^{-1}), graphite is used only as an ideal absorber.

The technological progress in recent years has made it possible to synthesise both known carbon materials (e.g., diamond) with superior or even new properties and lower cost and previously unknown optical carbon materials. The latter are generally accepted to refer to as new carbon materials. They include, primarily, synthetic polycrystalline and single-crystal CVD diamond films and wafers [3, 4], single-wall carbon nanotubes [5] and graphene [6]. These materials have been intensively studied in the last years (several hundreds of publications per year); however, their commercial production and application have only been started. Currently, most attention is paid to the use of new carbon materials in treatment of materials and in micro- and nanoelectronics.

Nevertheless, their application in photonics also looks rather promising.

This paper is a review of the results of studying new carbon materials for photonics, which were performed at the Center of Natural Research, A.M. Prokhorov General Physics Institute of the Russian Academy of Sciences (GPI RAS). These studies are carried out in three interrelated directions:

(i) CVD synthesis of diamond films and wafers (CVD diamond), carbon nanotubes and graphene and study of their optical and other characteristics;

(ii) selection, modification and treatment of new carbon materials (using, in particular, lasers); and

(iii) development of the physical bases and methods for fabricating carbon elements and photonic devices and their analysis.

2. Fabrication of new optical-quality carbon materials

Chemical vapour deposition (CVD) of diamond films and wafers was performed using specially developed (in cooperation with Optosystems Ltd.) microwave plasma-chemical reactors [7]. A $\text{CH}_4\text{--H}_2$ mixture was mainly used. The substrate temperature (700–1000 °C), determined by the heat transfer from the plasma contacting with the substrate, is measured by a pyrometer. Depending on the substrate type, one of two basic synthesis regimes is implemented.

If the substrate is a diamond single crystal, epitaxial diamond layers grow under appropriate conditions; the thickness of grown layers may exceed 1 mm, and their transverse size is determined by the substrate size. Diamond single crystals synthesised under high pressures and temperatures are generally used in this case. As a rule, their transverse size does not exceed 5×5 mm. Having performed preliminary treatment of the substrate surface in Ar–O₂ plasma, one can carry out synthesis simultaneously on several such substrates with the (100) orientation. Then the grown layers of single-crystal CVD diamond are separated from the diamond substrate by laser cutting and subjected to polishing; thus, optical-quality diamond wafers are obtained.

The typical growth rates of CVD diamond single crystals are 5–10 $\mu\text{m h}^{-1}$; however, application of non-conventional deposition conditions (i.e., introduction of argon or nitrogen into the gas mixture) allows one to increase the deposition rate by an order of magnitude with conservation of high optical and even electronic quality of CVD diamond. Currently, the best samples synthesised by us are characterised by a Raman-peak width of $\sim 1.7 \text{ cm}^{-1}$ at a frequency of 1332.5 cm^{-1} and contain nitrogen and hydrogen in concentrations of

V.I. Konov A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, 119991 Moscow, Russia; National Research Nuclear University MPhI, Kashirskoe sh. 31, 115409 Moscow, Russia; e-mail: vik@nsc.gpi.ru

Received 10 June 2015; revision received 31 August 2015
Kvantovaya Elektronika 45 (11) 1043–1049 (2015)
Translated by Yu.P. Sin'kov

15–40 ppb and 0.3–4 ppm, respectively [8]. The synthesised diamond wafers exceed the best natural diamond single crystals in all aforementioned parameters. The thermal conductivity of single-crystal CVD diamond layers separated from substrate was measured by the laser flash method. This is a very important parameter, which determines to a great extent the possibility of using diamond optics in high-power systems (lasers and synchrotron radiation sources). The thermal conductivity of synthesised crystals was measured to be $\sim 19 \text{ W (cm K)}^{-1}$ [9]; this value is close to the best values obtained for natural diamond single crystals and exceeds the thermal conductivity of copper (the best of conventional heat-removing materials) by a factor of about 4.

Silicon substrates are used to synthesise polycrystalline diamond. Here, the deposition area is determined by the size of the plasma region and substrate; it is $\sim 30 \text{ cm}^2$ for the microwave reactors (power 6 kW) used by us. The thickness of the grown diamond films and wafers varies from 50 nm to 1.5 mm. They have a columnar structure, characteristic of polycrystals; the maximum crystallite size is 0.1–0.2 of the film thickness. After the synthesis, the silicon substrate can be completely or partially removed by chemical etching; thus, a polycrystalline diamond membrane or wafer is obtained. Optical elements with a smooth surface and specified shape and size can be prepared from them using laser cutting and mechanical (or mechanochemical) polishing.

Polycrystalline CVD diamond has a much larger size than the single-crystal one; however, its optical characteristics and thermal conductivity are somewhat worse. However, it was shown in [10] that, using methane with monoisotopic carbon, one can grow polycrystalline CVD films with high thermal conductivity (despite the presence of grain boundaries): $\sim 24 \text{ W (cm K)}^{-1}$ (0.05% C^{13}). This value even exceeds the thermal conductivity of the best diamond single crystals of natural isotopic composition. One should expect even larger values of thermal conductivity for monoisotopic CVD diamond single crystals. Typical deposition rates of polycrystalline diamond range from 1 to $10 \mu\text{m h}^{-1}$; reducing the deposition rate, one can increase the optical quality of crystals grown. We should note also another property of diamond, which is important in fabrication of optical elements for high-power IR lasers. This is a very weak temperature dependence on its refractive index: $1.3 \times 10^{-6} \text{ K}^{-1}$.

Diamond can be transformed into graphite (specifically, into graphite-like phases) by local laser irradiation and heating (to $\sim 800^\circ\text{C}$ on the surface and to $\sim 2000^\circ\text{C}$ in the bulk). The graphitised diamond becomes opaque and conducting (the difference in the light absorption coefficients for optical-quality diamond and graphite is 7 to 8 orders of magnitude; the difference in their electrical conductivities is even larger). This effect is basic for the formation of surface and volume diamond micro- and nanostructures using laser radiation [11]. Graphitised material can be removed by chemical etching (in particular, from the volume, if the graphitised structure outcrops on the sample surface) or by a laser beam. Heating a graphitised material to a temperature of $\sim 4000^\circ\text{C}$ by laser pulses with durations from several femtoseconds to several microseconds implements its evaporative ablation with rates from 10 nm pulse^{-1} to $10 \mu\text{m pulse}^{-1}$. Irradiating a graphitised surface by a less intense laser pulse in a chemically active medium (e.g., air), one can initiate local etching of this surface. Under these conditions, ultrathin ($\sim 1 \text{ nm}$ thick) layers are generally removed during a pulse. Even thinner diamond layers can be removed at low radiation intensities in the

absence of any pronounced graphitisation of the diamond surface. In these cases, photoprocesses dominate over heat processes, and, on average, separate carbon atoms (atomic clusters) are removed during a pulse. This regime was referred to as nanoablation.

Single-wall carbon nanotubes were most often synthesised in an electric-arc plasma reactor [12] filled with a neutral gas (He). An electric arc is ignited between two graphite rods, one of which (anode) is filled with catalyst nanoparticles. The output of this system is $\sim 10 \text{ g}$ of product per day. The product consists of single-wall carbon nanotubes with a diameter of 1–1.5 nm and a length of 1–10 μm (15% in total), soot and catalyst particles. In addition, some nanotubes assemble into bundles, where they are held by van der Waals forces; the bundles contain both metal and semiconductor nanotubes, the properties of which are determined by their diameter and chirality. Special methods are applied to select monodisperse phases of individual nanotubes; the main of them are dispersion of bundles into aqueous suspensions using high-power ultrasound and bonding of individual nanotubes by surfactant molecules with subsequent removal of soot and nanocatalysts in a ultracentrifuge (acceleration up to 200000g). In addition, gradient centrifugation and some other methods are used to separate fractions into metal and semiconductor ones.

One can measure nanotube diameters using Raman spectroscopy and determine the energy spectrum of optical transitions by spectral-luminescence diagnostics. Application of these methods allows one to obtain aqueous suspensions of single nanotubes with pronounced and controlled light absorption lines, characteristic of metal and semiconductor tubes in the visible and near-IR (up to $\lambda \approx 2 \mu\text{m}$) ranges [13]. Technologies of incorporation of single nanotubes into water-soluble polymers have been developed. As a result, researchers can work with three types of nanotube-containing media: aqueous suspensions, free polymer films and coatings on optical substrates (e.g., quartz wafers). It was shown that nanotubes can be selected by a laser beam and that resonant irradiation of nanotube-containing suspensions by femtosecond laser pulses makes it possible to remove ('burn out') both semiconductor and metal fractions [14].

Graphene is a unique optical material, which is transparent (as well as diamond) in a wide spectral range: from visible light to THz radiation. Graphene can be either single- or multilayer (its transition to graphite occurs at a number of layers exceeding 5–10). Each graphene layer absorbs only 2.3% of incident radiation energy; hence, one has a unique possibility of determining the number of layers in a graphene sheet from its optical transmission. Another reliable way for determining the number of graphene layers and the quality of the material is Raman scattering. Initially, graphene was obtained in a purely mechanical way (by detaching it from single-crystal graphite). Later on, the main method for obtaining this material became chemical vapour deposition, with subsequent separation of graphene sheets and their transfer from the growth substrate to the working substrate (a polished transparent plate in optical studies). In our experiments, we performed CVD of graphene from a methane–hydrogen mixture onto a hot metal substrate (nickel or copper foil), heated by electric current. This approach makes it possible to obtain graphene sheets with different numbers of layers (from one to five), with an area up to $10^4 \mu\text{m}^2$ or even larger.

Thus, we can conclude that similar technologies are applied to synthesise all three materials under consideration:

synthetic diamond films and wafers, carbon nanotubes and graphene.

Graphene may have derivatives: quantum structures of lower dimension. An example is graphene strips (ribbons), which can be fabricated by different methods. If the strip width is small (less than 10 nm), it is no longer a two-dimensional carbon nanoobject (as a graphene sheet) but a one-dimensional one. A band gap arises in its spectrum, which can be controlled by changing the strip width. Cutting out a structure with a size less than 10 nm in both coordinates from a graphene sheet, one obtains another interesting nanoobject: a carbon quantum dot. In addition, there are combinations of single-wall carbon nanotubes and graphene strips. For example, graphene strips, composed of hydrocarbon molecules (in particular, coronene $C_{12}H_{24}$) penetrating into nanotubes, can be synthesised in the latter. As a result, peculiar luminescence bands in the visible range can be obtained in this combined carbon nanomaterial [15].

3. Development of optical elements and devices

Diamond optics for high-power IR lasers. The development and wide application of fibre and CO_2 lasers with wavelengths of 1 μm and $\sim 10 \mu m$, respectively, and average powers up to 10 kW (or even more) in materials processing industry (for welding, cutting and surface hardening) initiated a search for new optical materials. On the one hand, these materials should be sufficiently high transparent in the IR range; on the other hand, they must remove (with a maximum possible efficiency) the thermal power released in them, which constitutes a relatively low fraction but is rather high in magnitude. In this context, polycrystalline diamond CVD wafers look very promising, because they provide a unique combination of high optical quality, efficient heat removal, large aperture and low (especially in comparison with natural single crystals) cost. Joint experiments performed at the GPI RAS and NPO Astrofizika [16] clearly demonstrated advantages of high-power diamond IR optics. The experiments were carried out on polycrystalline diamond CVD wafers (GPI RAS), which were 25 mm in diameter, 1.3 mm thick, and polished from both sides. The thermal conductivity, measured across the wafer growth surface, was found to be $19.7 \text{ W (cm K)}^{-1}$ (the thermal conductivity measured along the growth surface is generally lower by 20%–30% because of the influence of grain boundaries). The wafers were placed in a water-cooled copper housing, serving as a heat sink. The radiation source was a 10-kW ytterbium-doped fibre laser ($\lambda = 1.07 \mu m$). The optical damage threshold of the diamond wafer at a beam spot diameter of 0.33 mm was 11.7 MW cm^{-2} , which exceeds significantly the radiation resistance of other known IR-transparent materials.

Note that high-quality CVD diamond has unprecedentedly high transparency in the microwave range. For example, the polycrystalline diamond wafers synthesised by us had a dissipation factor at a level of 10^{-5} [17]. Therefore, it is no wonder that CVD diamond windows with an aperture up to 10 cm turned out to be absolutely unique as elements for extracting super-high-power THz radiation of gyrotrons, produced at the Institute of Applied Physics, RAS.

Diamond is also transparent for synchrotron radiation. Thus, it can be used to release this radiation into atmosphere and as a material for refracting X-ray lenses. An X-ray lens is a wafer in which an array of holes with a successively decreasing transverse size is formed by laser cutting. Each hole is gen-

erated by two parabolas, and the lens quality depends on the verticality and defects of hole walls; these characteristics are determined by the conditions of ablation removal of the diamond material by an intense repetitively pulsed laser beam.

Diamond diffraction optics. Another important and wide range of applications of CVD diamond is the diffraction optics for high-power radiation sources. To fabricate a transparent diffraction element, one must develop a specified profile on one of its surfaces; the depth of this profile for diamond is on the order of the radiation wavelength (specifically, smaller by a factor of $n - 1$, where n is the refractive index of the material). Less stringent requirements are imposed on the spatial resolution of diffraction structures along the element surface. Two approaches are used to make diamond surface microstructured: photolithography and laser writing. The former technique provides a high spatial resolution and makes it possible to form structures for the visible and near-IR range with a high efficiency and accuracy. The drawbacks of this method are necessity of using photomasks and difficulties in forming deep profiles in diamond.

The other method, used by us in [18], is based on laser ablation of diamond by a scanning laser beam. A focused beam of a repetitively pulsed laser causes heating, graphitisation and evaporation of the modified surface layer of diamond. Each surface area (with the size determined by the beam spot) is exposed to laser pulses, the number of which is chosen so as to remove a layer of specified thickness. Different diffraction structures can be formed on a diamond surface scanned by an excimer KrF laser beam ($\lambda = 248 \text{ nm}$, pulse duration 20 ns) with a square cross section ($50 \times 50 \mu m$) in the surface plane. The main diffraction element under study was a Fresnel lens for a CO_2 laser beam ($\lambda = 10.6 \mu m$). The time of processing a wafer 1 cm in diameter with a frequency $f = 50 \text{ Hz}$ was several hours. After the laser ablation processing, a graphitised layer remained on the wafer surface; it was removed by thermal oxidation. Finally, the efficiency of the thus fabricated diamond lens was measured; it exceeded 90% for the best samples. A number of different diamond diffraction elements have been developed and fabricated in cooperation with the Institute of Image Processing Systems, RAS. An example is an element transforming a Gaussian beam into a 'frame' with a uniform energy distribution along the laser beam cross section at a specified distance from the focuser [19].

In our opinion, the laser technology of diffraction optical elements (DOEs) is most promising in two spectral ranges: mid-IR and THz ($\lambda \sim 100 \mu m$). In these ranges, one can easily obtain a desired spatial resolution, while the structure depth ($\sim \lambda$) is provided by multipulse laser ablation (this is a very difficult problem of photolithography). A laser-processed diamond wafer remains sufficiently thick to retain high mechanical strength. The main problems in laser-based production of diamond DOEs are insufficiently high efficiency of this process and quality of surface structures (determined by the deviation of real profiles from calculated). It is believed that both these problems can be solved by applying lasers with an ultrahigh ($f \geq 1 \text{ MHz}$) repetition rate of intense ultrashort pulses, each of which causes thermal graphitisation and ablation of diamond.

Another promising way to fabricate surface diamond structures is the replica method. The essence of this technique is as follows. In the first stage, a microstructure is formed on a planar silicon substrate, after which a layer of polycrystalline diamond is grown on it. Thus, a diamond wafer with a

surface microstructured from the substrate side is prepared. Then the silicon substrate is removed by chemical etching. As a result is, one has a diamond wafer with a relief that is a mirror reflection ('negative') of the structure formed on the silicon surface. An additional advantage of this method is that the photolithography of a silicon surface is a well-developed technique. At the same time, the most problematic point in this case is the necessity of providing a high concentration of diamond nucleation centres to form high-quality micro- and nanostructures on the substrate surface [20]. Particles of ultrafine-grained diamond (3–5 nm in diameter) are used in this case. Applying ultrasonic treatment, these particles can be deposited in concentrations up to 10^{10} – 10^{12} cm⁻².

3D diamond structures. The replica method turned out to be fairly efficient for preparation of three-dimensional diamond nanostructures. To this end, opal crystals, composed of closely packed spherical SiO₂ particles 200–300 nm in diameter, were used as a matrix. These crystals served as a substrate for CVD growth of diamond. It turned out possible to fill opal with diamond nanoparticles under corresponding conditions of heating and seeding the surface of crystal pores with these particles. Post-growth chemical etching of the samples made it possible to remove silicon dioxide and form 'inverse opal' from CVD diamond [21]. Recently an even more complex (two-stage) version of preparation of diamond opal structures was implemented in [22]. In the first stage, an opal structure is filled with silicon by CVD, after which silicon dioxide particles are removed by chemical etching to leave silicon inverse opal. In the second stage, it serves as a substrate for depositing diamond, which can fill several (to date, up to 10) rows in the opal structure. Then silicon is removed, and diamond opal, containing spherical shells, remains. Note that each hollow nanodiamond can be separated from the opal structure; it has no analogues and is of independent interest for research and applications.

Laser processing methods provide even more possibilities to form three-dimensional diamond microstructures. First, laser ablation allows one to remove locally diamond layers to obtain, for example, periodic structures of channels of specified and variable depth, including through channels. In particular, application of such channels with a depth $\lambda/4n$ (n is the diamond refractive index) in the experiments performed in [23] made it possible to reduce significantly the reflectance of the CO₂ laser beam from a diamond wafer. Second, using tight focusing of ultrashort laser pulses in the diamond bulk, one can transform diamond into graphite-like carbon with a much higher electrical conductivity. Moving the focal volume along a specified trajectory (for example, by placing a sample on a translation stage), one can form various conducting graphitised structures in diamond, including curvilinear structures. This technology was used in [24] to fabricate diamond photonic crystals in the form of parallel graphite filaments 200 μ m long, which form a square matrix with a period of 4 μ m in a diamond single crystal. The results of measuring the crystal transmittance in the spectral range of 2–12 μ m are in good agreement with the numerical simulation data. Note that, if graphitised structures outcrop on the diamond sample surface, they can be chemically removed (for example, using wet etching), as a result of which cavities of complex shape and structure can be formed in the diamond bulk. Third, a combined technology of forming conducting metal structures in the CVD diamond bulk was developed in [25]. Here, the first stage is the synthesis of a polycrystalline CVD diamond wafer of specified thickness. Then the areas of the diamond

surface that must be metallised are subjected to laser graphitisation. The next stage is thermal deposition of metal (Ni, Cu) from a metal-containing liquid; the deposited metal film has good adhesion only on previously laser graphitised areas. Finally, the sample is placed again in the plasma-chemical reactor, and its entire surface is coated with a new layer of CVD diamond. As a result, the metal structures are encapsulated in diamond, and this procedure can be multiply repeated.

Diamond detectors. Wide-gap semiconductors have been used for a long time in radiation detectors. Initiation of inter-band transitions; absorption by impurity centers and multiphoton absorption of light, X rays and shorter wavelength radiation; and the effect of high-energy particles make it possible to implement bulk ionisation of the detector material. Placing a sample between electric contacts and applying an electric field to it, one can detect a signal proportional to the concentration of generated charge carriers. Note important advantages of diamond detectors: high radiation resistance, high breakdown voltage and low dark currents.

A key parameter in designing a detector is the ratio L_0/L , where L is the distance between electrodes, $L_0 = \mu E \tau$ is the charge collection distance, μ is the carrier mobility, E is the applied electric field, and τ is the carrier lifetime. The condition $L_0/L \geq 1$ must be satisfied to provide efficient operation of the detector. This criterion is fulfilled either by improving the diamond quality and, correspondingly, increasing the L_0 value or by reducing crystal thickness L . However, in the latter case, the detector diminishes in size, as a result of which its sensitivity deteriorates.

In experimental study [26], diamond detectors with metal electrodes were successfully applied to detect light. It was shown that the recorded signal intensity in the UV spectral range, where the quantum energy exceeds the diamond band gap (~5.6 eV), is 4 to 5 orders of magnitude higher than in the visible range, where the key mechanism determining ionisation is light absorption by defects and impurities. Thus, the so-called solar-blind detector can be designed.

The application of laser processing methods has opened new prospects for developing diamond detectors. First, it was shown that contacts (both point and large-area) having low resistivity and weakly absorbing radiation can be formed by laser graphitisation of thin surface diamond layers. The diamond-graphite sandwich open for incident high-intensity beam consists of carbon only and, correspondingly, has an enhanced radiation resistance.

Another promising approach implies the so-called 3D detector architecture. It is based on the laser-assisted fabrication of detecting electrodes in the detector body. In this case, having preserved the volume and sensitivity of the diamond crystal, one can significantly increase the charge collection efficiency by reducing the distance between the electrodes of 3D structure in the crystal. Indeed, the current record L_0 values for single-crystal and polycrystalline diamond wafers are, respectively, 480 and 350 μ m, and the crystal thickness L is generally close to 1 mm, i.e., $L \geq L_0$. At the same time, due to the close location of electrodes in the 3D detector, the distance L between them can be as small as several tens of micrometers [27]. In this way, the condition $L_0 \geq L$ is fulfilled even for crystals of moderate quality (e.g., polycrystalline diamond wafers). The main problem in forming this electrode structure is the choice of laser radiation parameters that would allow one to obtain graphitised material with a structure providing high electrical conductivity and, at the same

time, avoid formation of microcracks during carbon transformation in the diamond matrix.

The works in this field are carried out in cooperation with First University of Rome (Italy), National Research Nuclear University MEPhI and Troitsk Institute for Innovation and Fusion Research (TRINITI).

Diamond luminescence radiation visualisers. A promising application of colour centres [nitrogen–vacancy (N–V) and silicon–vacancy (Si–V) defects] in diamond are visualisers of high-power synchrotron radiation beams. Intense and stable photoluminescence is observed at the wavelength $\lambda = 575$ nm for neutral N–V centres with zero-phonon electronic transition, at $\lambda = 637$ nm for negatively charged N–V centres and at $\lambda = 738$ nm for Si–V centres. The most attractive way to form these colour centres is to perform co-deposition during CVD synthesis, for example, by adding N_2 or SiH_4 to a conventional CH_4-H_2 gas mixture. It was shown that the concentration of Si–V centres in single-crystal diamond may reach ~ 450 ppb [28], and the maximum nitrogen concentration in CVD diamond single crystals in the saturation regime is estimated to be ~ 10 ppm [29]. In the latter case, such high concentrations of colour centres are obtained using additional irradiation by high-energy particle beams, which can generate vacancies in sufficiently large amounts.

Two problems must be solved to make a significant progress in the design of diamond scintillators. First, it is necessary to improve the techniques used to generate colour centres in diamond with high and reproducible concentrations; this factor determines the sensitivity and resolution of luminescence radiation detectors. Second, ultrathin and strong diamond membranes or thin films must be fabricated using developed techniques (e.g., laser ablation). With allowance for the diamond transparency in the X-ray range and unprecedentedly high thermal conductivity of this material, the use of these elements will make it possible to develop unique through detectors of high-power synchrotron radiation.

Single and matrix quantum-sized carbon light sources. Currently, two approaches to design nanosized carbon light sources are under study. The first implies formation of single-photon sources based on N–V and Si–V centres in diamond. Matrices and arrays of these emitters are of great importance for quantum metrology and quantum informatics. Here, an important problem is to develop special CVD techniques that would make it possible to control the concentration of single-photon centres and their location in the surface layer of a CVD diamond film. In particular, one can apply micro- and nanostructuring of the surface, e.g., form single emitters on nanospikes or in microcavities [30]. This can be done both by modifying the CVD technology and combining it with the surface processing by nanoprobe and laser beams. Another important problem to solve is to provide addressing to individual luminescent centres using near-field microscopy. Finally, it is necessary to determine the basic parameters of single-photon diamond emitters: threshold optical pump power, photon emission rates, excited-state lifetimes and the dependence of these characteristics on the concentration of centres.

The second line of research is the formation of graphene-based quantum nanostructures (strips and quantum dots) and matrices of these elements. In our opinion, the most promising method for their formation is probe nanolithography of graphene sheets transported onto substrates. We have obtained graphene strips 10-nm wide [31] by combining ‘soft’ mechanical effect of a probe tip with application of electric

pulses between the conducting probe and graphene. The luminescence characteristics of these nanoobjects must be studied, and prospects of their use as miniature emitting devices should be estimated. Collective effects are also expected to manifest themselves in matrices of these elements with a decrease in the distance between them to the de-Broglie wavelength. Note another interesting feature: the matrix may consist of nanoelements of different dimensions.

Diamond lasers. An important problem of laser technology is to expand the spectral range in which high-intensity laser radiation can be generated. For example, the overwhelming majority of pulsed solid-state lasers generate in the vicinity of $\lambda \approx 1$ μm . At the same time, high-power laser beams in the spectral ranges of 550–700 nm and 1.2–1.5 μm are required in many cases. There is much interest in the possibility of converting the lasing wavelength. Many researchers believe that a promising way to solve this problem is to pass to diamond lasers based on stimulated Raman scattering (SRS), the so-called SRS (Raman) lasers. The scheme of the SRS laser is rather simple. A pulsed laser with $\lambda \sim 1$ μm (pump source) irradiates a diamond crystal, in which the pump beam interacts with the crystal lattice vibrations. When the intensity is sufficiently high, the nonlinear SRS mechanism is switched on, and a significant fraction of laser energy (up to several percent of even several tens of percent) can be converted into radiation with smaller (anti-Stokes component) and larger (Stokes component) wavelengths; the frequency shift modulus is multiple of 1332 cm^{-1} . An advantage of diamond over many other known materials is the largest frequency shift, high conversion efficiency (gain 15 $\text{cm}^{-1} \text{GW}^{-1}$) and high thermal conductivity. Six anti-Stokes lines (wavelength range $\Delta\lambda = 0.57$ – 0.93 μm) and three Stokes lines ($\Delta\lambda = 1.24$ – 1.49 μm) were obtained for a diamond single crystal $3.8 \times 2 \times 0.62$ mm in size, pumped by picosecond laser pulses ($\lambda = 1.06$ μm) with intensity $I = 2.8$ GW cm^{-2} , in one of our recent joint studies with the Shubnikov Institute of Crystallography, RAS, devoted to diamond SRS laser [32]. Note that one must use laser pulses of higher intensity to increase the SRS conversion efficiency. In addition, it is necessary to increase the single crystal sizes (and, correspondingly, the SRS length) in order to increase the SRS pulse energy with conservation of high radiation resistance. Note also that the main mechanisms of degradation and fracture of diamond SRS crystals are ionisation and photooxidation in air (nanoablation regime), which are stimulated by high-intensity radiation.

Carbon elements of nonlinear optics. An urgent problem of laser technique is generation of ultrashort laser pulses. It is solved by introducing elements characterised by nonlinear absorption of light and fast switching into the laser cavity. Soon after the discovery of single-wall carbon nanotubes, it was shown that extraction of these tubes from bundles with their subsequent selection over diameter make it possible to obtain the ‘antireflection’ effect for intense radiation and extremely short relaxation times of electronic excitations on optical semiconductor transitions of these one-dimensional objects. Generally, the nanotube diameter is ~ 1 nm, due to which nonlinear absorption effect can be observed for IR lasers (radiation wavelength $\lambda = 1$ – 2 μm). Correspondingly, ultrashort subpicosecond pulses were obtained in this spectral range for a number of solid-state and fibre lasers [33, 34].

There are two approaches to designing a saturable absorber based on nanotubes. One of them is pyrolytic synthesis of nanotubes on optical substrates. Its significant drawback is low radiation resistance of elements, because nano-

tube synthesis is initiated by metal catalyst nanoparticles. After the formation of nanotubes, some of these particles remain on the substrate surface. They much better absorb radiation, are evaporated and cause destruction of the working surface layer of a nonlinear element. In addition, it is rather difficult to obtain nanotubes of the same diameter and chirality under these conditions. The other approach, which was applied in our studies, is as follows. First, carbon nanostructures (with a large fraction of single-wall nanotubes) are synthesised in a reactor. Then they are subjected to several stages of purification and selection in order to obtain suspensions of single semiconductor nanotubes of specified geometry. These suspensions can be processed in two ways: either fill an optical cell with a suspension and place it in a laser cavity or insert nanotubes into a polymer matrix, based on which thin-film coatings or membranes can be fabricated. This approach ensures high radiation resistance of elements and make it possible to introduce them into high-power laser systems, e.g., fibre lasers with an average power of 1–10 W or more.

Another optical carbon nanomaterial – graphene – was discovered about 10 years ago. With regard to photonics, graphene opens new unique possibilities for designing ultrafast nonlinear optical elements in practically unlimited spectral range (from near-IR to THz). The point is that, due to the linear dispersion of electron energy in dependence on the wave vector, graphene can be used at any wavelength, whereas nanotubes are efficient only upon excitation by light with wavelengths corresponding to peaks of their optical absorption. Mastering new spectral ranges for mode-locked lasers using graphene technologies has already begun. In particular, saturable optical losses at a wavelength of 10.6 μm (working wavelength of CO₂ lasers, which are widely applied in various fields) were detected and measured in [35].

4. Conclusions

The interest in carbon photonics has been growing very rapidly in the last years. This concerns both fundamental studies and various practical applications. Correspondingly, the number of publications in this subject area constantly increases. Therefore, it is expedient to supplement the list of references with some more reviews and monographs, which should help the reader to be better oriented in the tendencies of development of carbon photonics and the results obtained in this field by different scientific centres.

First of all, the recently published collective monograph ‘Optical Engineering of Diamond’ [36] should be mentioned. Many issues interrelated with the content of our review and supplementing it (e.g., diamond optical waveguides, cavities, and other microstructures) are considered in this book. One more important application of new carbon materials (nanodiamonds as optical biomarkers) was considered in [36]. Useful data on the nature and characteristics of optical centres in diamond can be found in review [37]. The prospects of using diamond detectors to record hard radiations and high-energy particles are discussed in [38, 39]. Finally, reviews [40, 41] contain useful information about the optical properties of single-wall carbon nanotubes and graphene and their applications in lasers optics.

Acknowledgements. I am grateful to many researchers of the Natural Sciences Centre GPI RAS (I.I. Vlasov, V.V. Kononenko, T.V. Kononenko, E.D. Obraztsova, S.M. Pimenov, V.G. Ral’chenko, V.D. Frolov, etc.) and our

colleagues from Russian and foreign scientific organisations, who were involved in the statement and performance of studies within the ‘Carbon Photonics’ line of research. This work was supported by the Russian Science Foundation (Grant No. 14-22-00243).

References

1. Kvaskov V.B. (Ed.) *Prirodnye almazy Rossii* (Natural Diamonds of Russia) (Moscow: Polyaron, 1997) p. 304.
2. Apollonov V.V. *High Power Optics*. Springer Series in Optical Sciences (Switzerland: Springer, 2015) Vol. 192.
3. Sussmann R.S. (Ed.) *Radiation Sensors. CVD-Diamond for Electronic Devices and Sensors* (Chichester, UK: John Wiley & Sons, 2009) pp 185–276.
4. Balmer R.S., Brandon J.R., Clewes S.L., et al. *J. Phys.: Cond. Matter.*, **21** (36), 364221 (2009).
5. Dresselhaus M.S., Dresselhaus G., Avouris Ph. (Eds.) *Carbon Nanotubes – Synthesis, Structure, Properties, and Applications*. Topics Appl. Phys. (Berlin, Heidelberg: Springer, 2001) Vol. 80.
6. Cooper D.R., D’Anjou B., et al. *ISRN Condensed Matter Phys.* Article ID 501686 (2012); doi:10.5402/2012/501686.
7. Konov V.I., Ral’chenko V.G., Sergeichev K.F., et al. RF Patent No. 2299929 (May 27, 2007; priority August 11, 2005).
8. Bol’shakov A.P., Ral’chenko V.G., Pol’skii A.V., et al. *Russ. Khim. Zh.*, **56** (1–2), 70 (2012).
9. Inyushkin A.V., Taldenkov A.N., Ral’chenko V.G., Konov V.I., Khomich A.V., Khmel’nitskii R.A. *Zh. Eksp. Teor. Fiz.*, **134** (3), 544 (2008).
10. Inyushkin A.V., Ral’chenko V.G., Taldenkov A.N., et al. *Kratk. Soobshch. Fiz. FIAN*, (11), 36 (2007).
11. Konov Vitaly I. *Laser & Photon. Rev.*, **6** (6), 739; doi:10.1002/lpor.201100030. Nov. (2012).
12. Obraztsova E.D., Bonard J.-M., Kuznetsov V.L., et al. *Nanostruct. Mater.*, **12**, 567 (1999).
13. Chernov A.I., Obraztsova E.D. *Phys. Status Solidi B*, **246** (11–12), 2477 (2009).
14. Arutyunyan N.R., Komlenok M.S., Kononenko V.V., et al. *Laser Phys.*, **25**, 015902 (2015).
15. Chernov A.I., Fedotov P.V., Talyzin A.V., et al. *ACS Nano*, **7**, 6346 (2013).
16. Rogalin V.E., Ashkinazi E.E., Popovich A.F., et al. *Mater. Elektron. Tekh.*, **3**, 41 (2011).
17. Garin B.M., Kopnin A.N., Parshin V.V., et al. *Pis’ma Zh. Tekh. Fiz.*, **25** (7–8), 85 (1999).
18. Kononenko V.V., Konov V.I., Pimenov S.M., et al. *Kvantovaya Elektron.*, **26** (1), 9 (1999) [*Quantum Electron.*, **29** (1), 9 (1999)].
19. Kononenko V.V., Konov V.I., Pimenov S.M., Prokhorov A.M., et al. *Proc. SPIE Int. Soc. Opt. Eng.*, **4426**, 128 (2002).
20. Ralchenko V., Vlasov I., Frolov V., Sovyk D., Karabutov A., Gogolinsky K., Yunkin V. In: *Nanostructured Thin Films and Nanodispersion Strengthened Coatings* (Netherlands: Kluwer Acad. Publ., 2004) pp 209–220.
21. Zakhidov A.A., Baughman R.H., Iqbal Z., et al. *Science*, **282**, 897 (1998).
22. Sovyk D.N., Ral’chenko V.G., et al. *Fiz. Tverd. Tela*, **55** (5), 1035 (2013).
23. Kononenko T.V., Kononenko V.V., Konov V.I., Pimenov S.M., et al. *Appl. Phys. A*, **68** (1), 99 (1999).
24. Kononenko T.V., Dyachenko P.N., Konov V.I. *Opt. Lett.*, **39**, 6962 (2014).
25. Pimenov S.M., Shafeev G.A., Konov V.I., Loubnin E.N. *Diamond Rel. Mater.*, **5**, 1042 (1996).
26. Ral’chenko V.G., Savel’ev A.V., Konov V.I., et al. *Kvantovaya Elektron.*, **36** (6), 487 (2006) [*Quantum Electron.*, **36** (6), 487 (2006)].
27. Kononenko T., Ralchenko V., Bolshakov A., Konov V., Allegrini P., Pacilli M., Conte G., Spiriti E. *Appl. Phys. A*, **114**, 297 (2014).
28. Bolshakov A., Ralchenko V., Sedov V., et al. *Phys. Status Solidi A*; doi: 10.1002/pssa.201532174 (2015).
29. Khomich A.A., Kudryavtsev O.S., Bol’shakov A.P., Khomich A.V., et al. *Zh. Prikl. Spektrosk.*, **82** (2), 248 (2015).

30. Sovyk D., Ralchenko V., Komlenok M., Khomich A.A., et al. *Appl. Phys. A*, **118**, 17 (2015).
31. Konov V.I., Frolov V.D., Zavedeev E.V., et al. *Kratk. Soobshch. Fiz. FIAN*, (12), 11 (2012).
32. Lux O., Ralchenko V.G., Bolshakov A.P., Konov V.I., et al. *Laser Phys. Lett.*, **11**, 086101 (2014).
33. Il'ichev N.N., Obraztsova E.D., Pashinin P.P., Konov V.I., Garnov S.V. *Kvantovaya Elektron.*, **34**, 785 (2004) [*Quantum Electron.*, **34**, 785 (2004)].
34. Solodyankin Max A., Obraztsova Elena D., Lobach Anatoly S., et al. *Opt. Lett.*, **33**, 1336 (2008).
35. Sorochenko V.R., Obraztsova E.D., Rusakov P.S., Rybin M.G. *Kvantovaya Elektron.*, **42** (10), 907 (2012) [*Quantum Electron.*, **42** (10), 907 (2012)].
36. Mildren Richard P., Rabeau James R. (Eds). *Optical Engineering of Diamond* (Wiley-VCH, 2013) pp 1–520.
37. Pezzagna S., Rogalla D., Wildanger D., Meijer J., Zaitsev A. *New J. Phys.*, **13**, 035024 (2013).
38. Sussmann R.S. (Ed.). *CVD-Diamond for Electronic Devices and Sensors* (Wiley-VCH, 2009) pp 85–276.
39. Berdermann E., Pomorski M., de Boer W., Ciobanu M., Dunst S., Grah C., Kis M., Koenig W., Lange W., Lohmann W., Lovrincic R., Moritz P., Morse J., Mueller S., Pucci A., Schreck M., Rahman S., Trager M. *Diamond Related Mater.*, **19**, 358 (2010).
40. Sun Z., Hasan T., Ferrari A.C. *Physica E*, **44**, 1082 (2012).
41. Martines A., Xu Bo, Yamashita S. *IEEE J. Sel. Top. Quantum Electron.*, **20** (5); doi: 10.1109/JSTQE. 2014. 2310652 (2014).