## Laser applications in nanotechnology: nanofabrication using laser ablation and laser nanolithography

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<u>Abstract.</u> The fact that nanoparticles and nanomaterials have fundamental properties different both from their constituent

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Received 25 July 2012, revised 17 January 2013 Uspekhi Fizicheskikh Nauk **183** (7) 673–718 (2013) DOI: 10.3367/UFNr.0183.201307a.0673 Translated by Yu V Morozov; edited by A Radzig atoms or molecules and from their bulk counterparts has stimulated great interest, both theoretical and practical, in nanoparticles and nanoparticle-based assemblies (functional materials), with the result that these structures have become the subject of explosive research over the last twenty years or so. A great deal of progress in this field has relied on the use of lasers. In this paper, the directions followed and results obtained in laser nanotechnology research are reviewed. The parameters, properties, and applications of nanoparticles are discussed, along with the physical and chemical methods for their fabrication and investigation. Nanofabrication applications of and fundamental physical principles behind laser ablation and laser nanolithography are discussed in detail. The applications of laser radiation are shown to range from fabricating, melting, and evaporating nanoparticles to changing their shape, structure, size, and size distribution, through studying their dynamics and forming them into periodic arrays and various structures and assemblies. The historical development of research on nanoparticles and nanomaterials and the application of laser nanotechnology in various fields are briefly reviewed.

## 1. Introduction

Investigations into small-sized objects, nanoparticles (NPs) and nanomaterials, are currently a very rapidly developing field of the natural sciences. Colloidal chemistry and the science of colloids at large, formerly the realm of a few select researchers, have evolved for the past 20 years into an extensive interdisciplinary research area including nanoscience and nanotechnology. It deals with conceptual problems of nanoparticle fabrication and research, as well as the creation of nanoparticle-based assemblies (functional materials). A great variety of physical, chemical, physicochemical, and biological methods for nanoparticle fabrication and research have been developed, and nanotechnologies, including laser-assisted ones, are also widely available.

The enormous scientific and practical interest in nanoparticles and nanomaterials arises from the fact that many of their physical, chemical, and thermodynamic properties are fundamentally different from those of their constituent atoms and molecules or macroscopic matter. This opens up huge possibilities for the production of essentially new materials and the development of new technologies on their basis. It can be expected that nanoparticles and nanomaterials will play an important role in the economy, technology, and all other spheres of human life.

The unique properties of nanomaterials are due first and foremost to their structure at the atomic level, especially the structural properties of their interfaces and surfaces. The size and structure of nanoparticles is often as important as their chemical composition, which adds one more versatile and adjustable parameter for designing new materials (nanomaterials) and controling their behavior. Many of these unique properties are very important and promising for such future technological applications as nanoelectronics, nanophotonics, biomedicine, the storage of information, communication, defense, environmental surveys, and space exploration.

Rapid progress in nanoparticle and nanomaterial research is due to several reasons. First, the available nanotechnologies make it possible to synthesize nanoparticles of any shape and composition. Second, modern diagnostic techniques provide a deeper insight into the properties of NPs and nanostructures. Third, advances in computers and computational methods provide a basis for predicting and optimizing the properties of NPs and NP-based devices. Today, there are various methods for fabricating and studying NPs and nanostructures starting from metals, semiconductors, and other materials. The rapid development of experimental and theoretical methods has promoted the understanding of many properties of nanoparticles and nanomaterials.

Considerable progress in the science of nanoparticles and nanotechnologies has been achieved by using lasers. In certain cases, the unique properties of laser radiation are exploited, such as spatial and temporal coherence; not infrequently, lasers serve as convenient and easily operable sources of electromagnetic radiation. The present review is designed to analyze selected avenues and results of laser nanotechnology research. General definitions of NPs, their parameters, properties, and applications, and the physical and chemical methods of fabrication and research are briefly discussed. Much attention is given to the fabrication of NPs and nanostructures by laser ablation and nanolithography, with reference to the physical basis and principles of these techniques. Approaches to the creation of NP assemblies and functional nanostructures are considered. A brief excursion into the history of nanoparticle and nanomaterial research is presented. Laser nanotechnologies applied in various fields are described.

The review layout is as follows. Introductory Sections 2–7 contain the general characteristics of nanoparticles and nanomaterials, methods for their fabrication and study, and their applications. Section 2 is a brief excursion into the history of nanoparticle and nanomaterial research. Section 3 is focused on the size and dimension(ality) of nanoparticles and nanomaterials and their classification. Available methods for nanoparticle and nanomaterial fabrication are outlined in Section 4, and physical methods of their investigation in Section 5. The geometric structure and optical properties of metal and semiconductor NPs are considered in Section 6. Certain applications of nanoparticles and nanomaterials are described in Section 7.

Sections 8–13 are devoted to laser nanotechnologies. Section 8 contains a detailed analysis of the physical basis and principles of fabrication of nanoparticles and nanomaterials by laser ablation of solid targets in a vacuum and the surrounding gas or liquid. The current state of and prospects for the development of optical laser nanolithography are discussed in Section 9. Laser interference, nanosphere, nanoimprint, and near-field scanning nanolithography techniques are considered in Sections 10–13, respectively. Concluding Section 14 summarizes the results of the research reviewed in this report, along with the most important achievements and prospects of nanotechnology.

## **2.** Brief excursion into the history

The study of small-sized objects (powders, pigments, colloids, ceolytes, films, clusters, etc.) and quantum-dimensional phenomena has a long history, dating far back to 'prenanoboom' times (see Refs [1–7] and references cited therein). Archaeological finds give evidence of the extensive use of colloidal formulations even in the ancient world. Suffice it to mention that 'China ink' (colloidal aqueous soot solution mixed with gum arabica to stabilize dispersed soot particles and prevent their agglomeration and precipitation) appeared more than four thousand years ago in Ancient Egypt, while biological nanoobjects may be as old as life on Earth.

Metal nanoparticles appear to be of special importance among all micro- and nanoparticles [8] by virtue of their unique optical properties and ability to scatter and absorb light (see Section 6.2.1). People learnt how to utilize them long ago, e.g., for dyeing gemstones as objects of aesthetic, mystical, and commercial significance in human life [7, 8]. To this end, they used such small amounts of the admixtures of heavy metals and their oxides that they can be regarded as colloids or nanoparticles. Archeologists excavated fragments of colored glass for stained-glass windows dating back to the 2nd millennium BCE (Ancient Egypt) and the 1st century CE (Ancient Rome). The most beautiful specimen is the famous Lycurgus Cup (4th century CE, British Museum, London) made by craftsmen of Ancient Rome. Under ambient lighting it looks green until illuminated from a certain angle, whereupon the cup glows red. The cause of such variations has until recently been unknown; today, it is believed to be due to light scattering by tiny gold and silver nanoparticles embedded in the glass [9]. Metal NPs have been widely applied since the Middle Ages, lasted from the 5th to the 15th century, to make stained-glass windows in gothic cathedrals. Fine examples of using metal and semiconductor nanoparticles to dye glass and crystals are the colorful stained-glass windows of Notre Dame de Paris installed by great master glassworkers in 12th through 14th century, Saint Vitus Cathedral in Prague or the ruby stars fabricated and installed on the Kremlin towers in 1937 (submicrometer CdSe and CdS crystals were immersed into their glass to make them appear brilliant red, the color known as 'selenium ruby' [10]).

In Ancient Rome, citizens applied colloidal metals in fabric dyeing and as medicines for the treatment of arthritis. A purple-colored dye obtained in the reaction between stannic acid and gold chloride acid was very popular in ancient times [11]. It is the color of a colloidal solution of tin oxide particles and gold nanocrystals. As shown recently [12], the Maya blue paint used by Mayas around the 7th century contained metal and metal oxide nanocrystals added to indigo and silicon dioxide. Evidently, those who synthesized such nanoparticles had gone so far as to understood nanoscale processes.

Studies of nanoparticles were carried out in the 17th century [8] Antonio Neri, a Florentine priest and glassmaker, described the synthesis of colloidal gold in his treatise, *L'Arte Vetraria* (1612). John Kunckel revised Neri's work and translated it into German 1689. Therefore, Kunckel is often regarded as having discovered that glass can be colored red by adding gold. Indeed, he developed the method for making 'gold ruby glass' that looked like true rubies. It was believed that the secret died with him, because he left no basic technical specifications detailing the production of this highly valued, intensely colored glass. The secrets of gold ruby glass were re-discovered by M V Lomonosov, who developed the complete method for its production (the addition of small amounts (0.01–0.1%) of crushed gold particles 4–30 µm in diameter to ordinary glass) [7].

Despite the success of this early work, it did not go any further. Systematic investigations of nanoobjects started in the 19th century when M Faraday prepared and studied colloidal solutions of highly dispersed gold and its films (1856–1857). In 1857, he completed his landmark research on colloidal metals, which he termed 'divided' metals [13]. Faraday laid the basis of this discipline by demonstrating that colloidal metal sols lack thermodynamic stability and that individual particles must be stabilized to avoid their aggregation. To recall, sols are colloidal suspensions of solid particles in a continuous liquid medium. In addition, Faraday elucidated the nature of small (nanoscale) colloidal metal particles. He maintained that "part of the gold is reduced in exceedingly fine particles which, becoming diffused, produce a beautiful fluid" of various colors, depending on the particle size. Mie and Gans [14-16] laid a theoretical foundation for the description of the optical properties of nanoscale particles that are extensively used nowadays. Fröhlich and Kubo developed theories [17, 18] predicting that the electronic structure of colloidal metals has to differ from that of macroscopic bodies.

In the early 20th century, scientific studies of colloids were not very popular and attracted the research interest of only a few specialized groups [8]. The lack of attention to colloidal materials prompted Ostwald to entitle his book, published in 1915, The World of Neglected Dimensions [19]. At the same time, there were evidences of successful development of the methods for obtaining colloidal gold. Bredig [20] ignited an electric arc between two gold electrodes dipped in an alkaline solution, whereas Donau [21] suggested passing CO gas through a gold chloride acid solution. Zsigmondy [22] proposed the seeding method and utilized formaldehyde and a weak alkali for obtaining gold sol from gold salts. The award of the Nobel Prize in Chemistry 1925 to R A Zsigmondy partly for his work on colloidal gold as well did not arouse great enthusiasm among the scientific community and failed to give momentum to further developments in this research area.

Using methods of colloid chemistry for the nanoparticle fabrication from various materials became the subject of explosive research in the second half of the 20th century due to awakening interest in nanomaterials sparked in 1959 by Feynman's famous lecture [23] underscoring the importance of small-scale objects. In the lecture allegorically entitled "There's plenty of room at the bottom: an invitation to enter a new field of physics," R P Feynman, a future Nobel Laureate in Physics 1965, accentuated attention on the importance of research into 'squeezing of information,' 'miniaturizing the computer,' and designing materials and devices by molecular architecture methods taking into account the peculiarities of biological objects. Great expectations were placed on chemical synthesis; it was emphasized that the laws of physics do not forbid designing materials at the atomic and molecular level.

Certain Feynman's ideas were later developed by K E Drexler (Massachusetts Institute of Technology, USA). In 1986, he published the book, Engines of Creation: The Coming Era of Nanotechnology [24]. Based on biological models, the author introduced the notion of molecular phototechnical machines and proposed the 'bottom-up' strategy in conformity with the miniaturization of integrated circuits (atomic and molecular assembly mentioned earlier by Feynman), as opposed to the traditional 'top-down' technological principle (typical examples being fragmentation, etching, lithography). By that time, the most important instruments and devices crucial for the observation and investigation of micro- and nanoparticles had been invented (the electron microscope and scanning tunneling microscope), which gave impetus to the development of new methods for the investigation of small-scale objects; this, in turn, greatly promoted nanoparticle and nanostructure research (see Section 5).

The concepts of nanomaterials were elaborated in parallel [5]. They were formulated for the first time by H Gleiter in 1981 [25] with respect to metallic materials. This author coined the term 'nanocrystalline' materials. Thereafter, the terms 'nanostructured', 'nanophase', 'nanocomposite' materials, etc. came into general use [1, 25]. Moreover, Gleiter proposed a method for the fabrication of nanomaterials by evaporating-condensing ultradispersed powders with subsequent *in situ* vacuum consolidation under high pressure.

Other terms with the prefix nano- have received wide acceptance, e.g., 'nanotechnology', 'nanoelectronics', 'nano-

chemistry', and 'nanoplasmonics' [7, 26, 27]. The Japanese researcher Norio Taniguchi was the first to introduce the term 'nanotechnology' [28] to describe the fabrication of objects a few nanometers in size. The notion of nanotechnology implies the ability to deliberately create and use materials, devices, and systems with structural elements of size around 1–100 nm [3]. The science of small-sized objects is the body of knowledge about the properties of nanoscale substances and phenomena [5].

In 1989, D Eigler, who is associated with IBM, used a scanning tunneling microscope to move 35 individual xenon atoms into a pattern that spelled the letters 'IBM' (letter of height 5 nm) at the (110) edge of a nickel single crystal [29]; it was the world's smallest ever company logo. This result confirmed the reality of the idea of atomic architecture and demonstrated the unique potential of nanotechnology. General information about nanotechnology can be found in Refs [5, 7, 26, 30–34].

The discovery of fullerenes (1985), carbon nanotubes (their structure was described in 1991), and graphene (it was created for the first time in 2004), their investigations, and the development of up-to-date powerful methods for nanoparticle and nanostructure fabrication and research were the most important events in the progress of the science of nanoparticles and nanotechnology (see Sections 5, 8–13).

The ever-increasing interest in nanoparticles and nanotechnology is due to a few circumstances [5, 26, 32–34]. First, nanotechnology approaches make it possible to create fundamentally new devices and materials with characteristics much better than those of macroscopic specimens, which is rather important for the development of many branches of technology, bioengineering, medicine, environmental protection, defense, etc. Second, nanotechnology is a broad interdisciplinary sphere attracting specialists in physics, chemistry, materials science, biology, medicine, technology, earth science, computer technology, etc. Finally, the solution to nanotechnological problems revealed many gaps in basic and technical knowledge, which made the scientific and engineering community focus attention on this line of inquiry.

At present, many countries (USA, European Union, Japan, China, Russia) have national programs for the intensive development of nanotechnological research and development. Also, much attention is being given to the training of research personnel [5–7, 30–34].

## **3.** Size and dimension. Classification of nanoparticles and nanomaterials

Nanoparticles designate small aggregates or ensembles of particles sized roughly between 1 and 100 nm (or from 10 to 1000 Å) [35–37]. In general, NPs include clusters or large molecules (consisting of at least 50–100 atoms and measuring around 1 nm) and particles composed of tens or hundreds of thousands of atoms and having a diameter from tens to hundreds of nanometers. Such particles have for a long time been called colloids [38–42], although this notion most frequently referred to aqueous suspensions of metal particles. Let us compare the size of clusters and nanoparticles. The radius of a spherical cluster comprising N atoms is given by

$$R_N = R_0 N^{1/3} \,, \tag{3.1}$$

where  $R_0$  is the monomer radius. At  $R_0 \approx 2-3$  Å, a cluster composed of  $N \approx 10^7$  atoms has radius  $R_N \approx 400-600$  Å, while the radius of a 50-atom cluster is  $R_N \approx 7.5-11$  Å. This means that clusters containing  $50 \le N \le 10^7$  atoms and NPs are identical particle aggregates or ensembles. Therefore, in what follows, we shall not distinguish between nanoparticles and clusters with  $N \ge 50$ .

There are three-, two-, one-, and zero-dimensional (3D, 2D, 1D, and 0D, respectively) nanoparticles and nanomaterials. Two-, one-, and zero-dimensional nanoparticles and nanostructures are termed quantum wells, quantum wires, and quantum dots, respectively. The free motion of charge carriers in 2D and 1D structures is two- and one-dimensional, respectively. The electron energy spectrum in quantum dots is 'quantized' in three dimensions and represents (as for an assemblage of individual atoms) a set of discrete levels spaced by forbidden bands. The size of quantum dots usually varies from roughly 3 to 20 nm, depending on the interval between electron energy levels and effective electron mass (see Section 6.2). Thus, nonspherical nanoparticles and nanomaterials are those whose smallest structural element measures 1–100 nm in at least one dimension.

Nanomaterials are categorized into a few main varieties [1, 5]: consolidated nanomaterials, nanosemiconductors, nanopolymers, nanobiomaterials, fullerenes and tubular nanostructures, catalyzers, nanoporous materials, and supramolecular structures. Nanocrystals and the recently discovered graphene (2004) are also referred to as nanomaterials. Graphene is an allotropic form of carbon having a hexagonal crystal lattice as thick as a single atomic layer that resembles a honeycomb structure. It represents a new class of unique nanomaterials. A Geim and K Novoselov were awarded the Nobel Prize in Physics 2010 "for groundbreaking experiments regarding the two-dimensional material graphene" [43, 44].

Metal and semiconductor NPs and NPs of metal oxides make up a large class of nanomaterials [8]. They are zerodimensional structures of nanometer size in all three dimensions. Their diameters can vary from one to several dozen and even hundreds of nanometers. The electron and atomic structures of such small NPs show unusual properties, essentially different from those of macroscopic materials [45]. Nanoparticles may be either amorphous or crystalline. The latter are small single-domain structures. Many nanoparticles of metals, chalcogenides, nitrides, and oxides are single crystals. Crystalline nanoparticles are referred to as nanocrystals [8]

Consolidated nanomaterials comprise compacts, films, and coatings from metals, alloys, and compounds fabricated by powder technologies, intense plastic deformation, controllable crystallization from the amorphous state, and various methods of film and coating deposition [5]. These materials consist of consolidated (rather than isolated or weakly bound) nanograins and have fairly strong intergrain layers.

Nanosemiconductors, nanopolymers, and nanobiomaterials occur both as isolated and as partly consolidated entities. They can give rise to hybrid (mixed) structures [5]. This class includes semiconductor heterostructures that have recently found rather wide application of utmost importance. In 2000, Zh I Alferov and H Kroemer were awarded the Nobel Prize in Physics "for developing semiconductor heterostructures used in high-speed- and opto-electronics" [46, 47].

Fullerenes, carbon nanotubes (CNTs), and other tubular nanostructures make up one more broad class of nanomater-

ials. They became subjects of extensive investigation beginning in 1985, when a new allotropic form of carbon,  $C_{60}$  and  $C_{70}$  clusters termed fullerenes, was identified (see the work of Nobel Prize laureates in Chemistry 1996 H Kroto, R Curl, and R Smalley), and especially commencing 1991 when the Japanese researcher S Iijima [51] revealed CNTs in products of the electric arc evaporation of graphite. Fullerene- and nanotube-like structures had been observed even before this work; the comprehensive history of their discovery and the results of research can be found in monograph [4].

Nanoporous materials have pores measuring, as a rule, less than 100 nm. Catalyzers also exemplify long-explored and widely applied nanoobjects. Supramolecular structures are nanostructures obtained by so-called noncovalent synthesis with the formation of weak (van der Waals, hydrogen, etc.) bonds between molecules or their assemblies [8].

The above-listed nanomaterials are significantly different both in fabrication methods and functional characteristics. Their sole common feature is the characteristically small size of particles, grains, tubes, and pores, which determines their structure and properties. The minimum size of the structural elements ranges 0.1–1.0 nm, i.e., commensurate with the size of individual atoms and molecules; the maximum size is conditionally established at 100 nm.

The reader interested in the technology, properties, and applications of nanomaterials and nanostructures is referred to numerous monographs and review articles, e.g., Refs [1–8, 26, 30–37, 45–50, 52–58].

# 4. Methods for fabricating nanoparticles and nanomaterials

The modern science of nanomaterials is developing in close interaction with physics, chemistry, and biology, as most clearly demonstrated by the methods of fabrication (synthesis) of nanoparticles and nanomaterials. Some methods are based on the so-called 'top-down' approach, i.e., fragmentation (grinding, structuring) of macroscopic materials. Others make use of the 'bottom-up' strategy (production of nanomaterials from their constituent atoms or molecules). The top-down approach is usually employed in physical methods, while the bottom-up strategy is for chemical synthesis. Moreover, there are a number of hybrid technologies. At present, a great variety of methods for the fabrication of nanoparticles and nanomaterials are available (see, for instance, Refs [5–8, 32–34, 53–59] and references cited therein). The most popular of them are considered below.

#### 4.1 Physical methods

Many physical methods take advantage of the evaporation of a solid material and the formation of oversaturated vapor from which nanoparticles emerge as a result of homogeneous condensation. In these methods, the particle size is controlled either by alternately switching the vapor source on and off or by reducing the atomic aggregation rate upon the admixture of neutral gas atoms to vapor that collide with hot metal atoms and cool them. A number of special methods have been developed in recent decades that can be classified either in terms of energy sources for evaporation or solid and liquid precursor composition (a substance whose atoms or molecules are synthesized into nanoparticles) [60]. The physical methods for fabricating nanoparticles and nanomaterials include the inert gas condensation technique, arc discharge, ion sputtering, laser ablation, laser or spray pyrolysis, the laser generation of nanoparticles in molecular beams, and plasma techniques [8].

**Condensation in an inert gas** is the most straightforward way of obtaining nanoscale clusters (usually metal ones). A metal foil or specimen is heated in a ceramic pot placed in a chamber filled with an inert gas (usually argon) under a pressure of several torrs. Metal vapors rapidly cool down and lose energy in collisions with argon atoms, thereby giving rise to nanoparticles. This method is widely used, for example, for the production of iron NPs 5–40 nm in size [61, 62], SnO [63], CdS [64], core-shell NPs of  $Fe-Fe_2O_3$  [65] and PbS-Ag [66], and nanoparticles of many other elements (see review [8] and references cited therein).

When applying the **arc discharge** technique, the material is evaporated by ignition of the electric arc between two metal electrodes in the presence of an inert gas, which gives rise to plasma; its cooling results in the emergence of nanoparticles. Arc discharge ignition in a proper gaseous medium with the use of electrodes containing the necessary precursors yields NPs of metal oxides, carbides, and nitrides. For example, Ref. [67] reports the synthesis of AlN nanoparticles of size 15– 80 nm by arc discharge ignition between the cathode from W and the anode from Al in a gas mixture of nitrogen and argon; the resulting particles had a cubic structure. The same method was employed to obtain NPs of Ni [68] and other elements [8].

In the **ion sputtering** method, accelerated ions, e.g., Ar<sup>+</sup>, bombard a target and knock atoms and small clusters out of its surface. The ions are incident on the target at a relatively high pressure of the inert gas (roughly 1 mTorr), which causes the particles released from the surface to aggregate into nanoparticles. This method was applied to obtain NPs of metals and alloys of semiconductor materials (see review [8]). Reference [69] reports on the fabrication of NPs of various metals by magnetron sputtering.

Laser ablation provides a simple and widely employed tool for preparing nanoparticles not only of metals, but refractory materials as well. An advantage of this technique is that the chemical composition of the resulting nanoparticles reflects the composition of the target material. See Section 8 for a detailed discussion.

In **laser pyrolysis**, a gaseous precursor is mixed with an inert gas and the mixture is heated by IR CO<sub>2</sub> laser generating continuous or pulsed beams. The laser energy is absorbed either by the precursor or by the added sensitizing inert gas, e.g., SF<sub>6</sub>. Intense heating of the gas causes precursor dissociation and formation of metal atoms that collide with the inert gas, cool, and aggregate, giving rise to clusters and nanoparticles. In this way, the authors of Refs [60, 70, 71] prepared Si nanoparticles from SiH<sub>4</sub>, and metal NPs [8]. The Co NPs were obtained by laser pyrolysis of  $Co_2(CO)_8$  vapors [72].

The **spray pyrolysis** technique produces nanoparticles from droplets of a precursor-containing solution injected into the hot zone of a furnace. The droplets are generated with the aid of a nebulizer. The size of the NPs depends on the nebulizer temperature, relative gas pressure, and furnace temperature. This method was employed to produce NPs of Cu [73] and TiO<sub>2</sub> [74]. The authors of Refs [75, 76] used Cdcontaining precursors to fabricate the CdS and CdSe NPs. Flame-spray pyrolysis is a modification of this method.

One more physical method for making nanoparticles is concerned with a **high-energy ball milling**, used extensively to obtain metastable phases of alloys and mixed metals [77], various oxides, and other nanomaterials.

Laser generation of clusters and nanoparticles in molecular beams has its origin in laser-induced evaporation of a material placed close to the nozzle channel and irradiated by intense laser pulses. Atoms, ions, and small clusters of the target material produced by laser ablation are captured by the carrier gas (usually helium) and cooled in the course of gasdynamic expansion, thereby giving rise to large clusters and nanoparticles. The method developed for the first time by Smalley and co-workers [78-80] makes use of an excimer or Nd:YAG laser to evaporate the specimen with a common pulse energy and duration of 30-50 mJ and 5-50 ns, respectively. The indicated method and its physical basis are considered at some length in review articles [81, 82]. Atomic and molecular clusters and nanoparticles [82-84], as well as superfluid helium nanodroplets [85], are also generated in molecular beams.

Metal clusters and nanoparticles may also be produced by **plasma techniques** using plasmatrons of moderate power (~ 1 kW) operated in a continuous regime. According to review [81], a metal in the form of metal-containing  $MX_k$ molecules (*M* is the metal atom, *X* is the halogen atom, and *k* is the number of halogen atoms) is introduced into the central part of the buffer gas plasma flow outgoing from the plasmatron. The buffer gas pressure is roughly 1 atm. The  $MX_k$  molecules dissociate in the plasma and the resulting metal atoms aggregate into clusters which remain in the center of the flow due to their low mobility. Thereafter, this cluster-containing part of the plasma passes through the nozzle into a vacuum chamber.

A different scheme [81] is applied in the pulsed regime, taking into account the high density of bound atoms in clusters and nanoparticles. A droplet composed of metalcontaining molecules and readily ionizable admixtures is introduced into a dense buffer gas filling a waveguide and rapidly heated by a high-frequency discharge. As a consequence, the droplet evaporates and the metal-containing molecules dissociate into atoms that fuse into clusters.

#### 4.2 Chemical methods

Chemical methods underlie the synthesis of nanoparticles from a variety of materials. These relatively straightforward methods are usually realized under moderate reaction conditions. The nanoscale materials in the form of diluted salts, liquids, and foams were also produced by chemical methods over rather a long period. In what follows, we briefly overview methods used to obtain isolated nanoparticles capable of dispersion in solutions (sols). The reader is referred to Refs [86–88] for details of chemical methods involved in NP fabrication.

Any chemical reaction leading to sol formation consists of three steps: seeding, particle growth, and growth arrest as a result of particle's shell formation. An important process involved in colloidal particle synthesis has come to be known as Ostwald ripening, i.e., the mechanism of growth in which smaller particles rapidly dissolve to supply monomers and ions for the growth of larger particles. This phenomenon is attributable to the poorer solubility of large particles. Given that particles grow under equilibrium conditions, the Ostwald ripening restricts the final particle size distribution to approximately 15% of the particle diameter. However, the employment of high concentrations of monomers and particle-coating substances creates conditions for particle growth in the transient regime. The stages of seeding, particle growth, and growth arrest are frequently indivisible; therefore, NP fabrication is usually started using a mixture of a material for making nanoparticles, a substance for coating nanoparticles, and a solvent. The most common chemical methods include: reduction; solvothermal, photochemical, and electrochemical syntheses; arrested precipitation; thermolysis and a number of other methods [8].

**4.2.1 Fabrication of metal nanocrystals by the reduction method.** Nanoclusters and nanocrystals are produced by this technique from various metal salts. Metal nanoparticles are formed due to the restriction of crystal growth by suitable surfactants or ions. Some of these methods are briefly considered below. A few old methods for the purpose were considered by Turkevich et al. back in 1951 [89].

**Boron hydride reduction**, known since the 1950s, was investigated in the framework of the Manhattan Project [90, 91]. The main reaction of boron hydride hydrolysis proceeds with the release of hydrogen:

$$BH_4^- + 2H_2O \to BO_2^- + 4H_2.$$
 (4.1)

Nanocrystals of many metals were obtained by this method [8, 89].

A two-phase method for the reduction of noble metals was devised in work [92]. It is frequently referred to as the Brust method and is widely applied to obtaining organic sols. Metal ions in an aqueous solution are transferred onto a toluene layer in the presence of tetraoctylammonium bromide, a catalyzer and stabilizer utilized in phase transformation processes [8]. The gold-containing complex is transferred to toluene, where it reacts with alkanethiols, giving rise to polymeric thiolates. An aqueous boron hydride solution is added to the mixture to initiate the reduction reaction that is driven by processes at the toluene–water interface [8].

**Reduction of citric acid salts** for the synthesis of colloidal Au particles was described for the first time in monograph [93]. This method is widely applied to produce gold hydrosols. The synthesis of nanoparticles by this method [89] is based on the addition of tetrachloroauric acid (HAuCl<sub>4</sub> solution) to a boiling sodium citrate solution (sodium salt of citric acid —  $Na_3C_6H_5O_7$ ). Development of the characteristic color of red wine indicates the onset of the reduction reaction. The method was used to synthesize Pt and Au nanoparticles [94, 95].

Reduction with alcohols and other substances. Alcohols, including high molecular weight alcohols (polyols) with a high boiling point, e.g., ethylene glycol, are widely used to reduce metal particles [96, 97]. Polyols serve therewith as reducing and stabilizing agents. The method based on their application constitutes a convenient chemical synthesis of nanoparticles ranging in size from 100 nm to a few micrometers [8]. The employment of hydrogen and gases as reducing agents, e.g.,  $CO/H_2O$  (water gas) and diboran (B<sub>2</sub>H<sub>6</sub>), has an advantage over the application of other substances. By way of example, water gas found its use in work [98] to reduce PtO<sub>2</sub> to Pt.

**4.2.2 Solvothermal synthesis.** This method proceeds from the use of a salt solution containing the desired element at temperatures much above the solvent boiling point. The reaction runs in a sealed vessel. The pressure created in the vessel by evaporation of the solution increases the boiling point of the system. The most common solvents are ethanol, toluene, and water. High pressure allows ultrahard materials

to be synthesized [8]. The method is employed to produce zeolites, nanocrystals of inorganic materials, nanocrystalline powders, and nanocrystals dispersed in liquids [99].

**4.2.3 Photochemical synthesis.** Synthesis of nanoparticles by this method has its origins in light-induced decomposition of metallic complexes or reduction of metal salts by photogenerated reducing agents, such as solvated electrons. The former is called photolysis, exemplified by the well-known reaction in AgBr photographic films, and the latter is designated radiolysis. Photolysis and radiolysis were first applied to produce metal nanoparticles by Henglein, Belloni and their colleagues [100]. Photolysis made it possible to synthesize Cd and Tl NPs. The Au nanocrystals coated with polyvinyl pyrrolidone (PVP) were fabricated in the process of HAuCl<sub>4</sub> reduction in formamide (formic acid amide) under UV irradiation.

**4.2.4 Electrochemical synthesis.** This method [8, 101–103] actually constitutes an improved classical electroprocessing technique and includes the following main stages: anode oxidative degradation, migration of metal particles to a cathode, ion reduction to the zero-valent state, particle formation via nucleation and growth, growth arrest by capping agents, and particle precipitation. The method of interest was used to synthesize metal NPs of various sizes (starting from approximately 1–5 nm), viz. Pd, Ni, Co, Fe, Ti, Ag, and Au [8]. Also, it can be applied when obtaining bimetallic particles. By way of example, Pd–Ni, Fe–Co, and Fe–Ni nanoparticles were obtained in work [102] with the use of two anodes made from the respective materials.

4.2.5 Synthesis of semiconductor nanocrystals and other materials by an arrested precipitation method. Nanocrystals can be obtained by precipitation from a solution. For example, precipitation of metal salts in the presence of chalcogens can be discontinued by increasing pH levels. This approach yielded CdS nanocrystals some 5 nm in diameter in the reaction between CdSO<sub>4</sub> and  $(NH_4)_2S$  in water at high pH [104, 105]. The CdS and ZnS nanocrystals can also be produced using H<sub>2</sub>S and Na<sub>2</sub>S or other solvents (methanol, acetonitrile) instead of water [8, 106].

**4.2.6 Thermolysis.** This method has its origins in chemical vapor deposition (CVD) for preparing thin films. It allows obtaining nanocrystals of various elements in high-boiling point solutions in the presence of capping agents. The thermal decomposition process underling this method makes it possible to control nanoparticle size and scale up the reaction to synthesize nanoparticles in gram amounts. The method was used to produce NPs of various metals, their oxides, bimetals, and semiconductors (see, e.g., Ref. [8] and references cited therein).

**4.2.7 Other methods.** It is worth mentioning some other chemical synthesis methods for nanoparticles and nanostructures, such as ultrasonic (US, sonochemical) method [107], those in which micelles [108, 109] and microemulsions [109, 110] are used, and nanoparticle synthesis at the liquid–liquid interface [8, 111–113]. Microemulsions prepared from water and supercritical liquids, such as  $CO_2$ , found their use to synthesize Ag, Ir, and Pt NPs. The synthesis of NPs in reverse micelles for commercial applications has been described. Laser photochemical synthesis [114] is applied to produce

relatively large amounts of metal nanoparticles and composite materials. For the same purpose, selective laser photolysis of liquids containing a desired precursor was recently developed [115, 116]. It was employed to manufacture C:WO<sub>3</sub> nanoplates and C:VO<sub>2</sub> nanocapsules [115], as well as iron-platinum preparations for medical applications [116].

Worthy of note is the well-known Langmuir–Blodgett method [117, 118] providing a technically simple tool for the production of very thin films (mono- and polylayers) on a substrate and the currently widely employed methods with the use of DNA [59, 119–122] and RNA [123] matrices for the synthesis of nanoparticles and various nanostructures.

#### 4.3 Biological methods

Biological methods for the production of nanocrystals and nanostructures are based on the use of biological matrices and systems. Microbes may be regarded as a promising system for the purpose. The innards of microorganisms are known to function as tiny reactors or containers. Such elementary reactions as reduction are usually catalyzed by enzymes. This means that nanoparticle synthesis can be driven simply by adding a metal salt solution to the selected microbial culture.

The ability of microorganisms to accumulate particles of inorganic elements and substances, such as Au [124, 125], CdS [126–128], ZnS [129], and magnetite (FeO  $\cdot$  Fe<sub>2</sub>O<sub>3</sub>) [130] is an established fact. It is equally well known that microorganisms utilize nanoparticles, e.g., CdS, to protect themselves against UV radiation or as indicators of direction (magnetite). The possibility of utilizing microorganisms for nanoparticle synthesis has been demonstrated in recent studies [8, 131, 132]. Biological synthesis methods for the gold nanoparticles are comprehensively discussed in Refs [133, 134].

## 5. Physical methods for studying nanomaterials

## 5.1 General considerations

Considerable progress in nanoscience and nanotechnology has been achieved in the few past years thanks to the presence and development of rather sophisticated high-precision physical methods for deeper insight into the properties of nanomaterials [135, 136]. Modern methods include electron microscopy and scanning probe microscopy, besides traditional techniques (X-ray and neutron diffraction, X-ray scattering, some other spectroscopic methods). Studies of nanomaterials include not only determination of their size and shape but also their atomic and electronic structure and many other important characteristics. Some methods find their use when examining the size, shape, and morphology of nanostructures, while others are used to obtain structural information at the molecular or atomic level. Detailed knowledge of the nanoparticle structure is needed not only to understand their fundamental properties but also to estimate their functional and technical potential for practical applications. The structure of materials can be investigated at different levels of complexity, including crystalline structure, microstructure, and atomic and electronic structures.

There is a diversity of rather powerful experimental tools for the direct or indirect investigations of the structural and surface properties of nanomaterials. They include X-ray diffraction (XRD), scanning tunneling microscopy (STM), atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (EELS), infrared (IR) absorption, Raman scattering (RS) of light, and photoluminescence (PL) [137– 141]. Some of these methods are more sensitive to the particles' surface structure, others to the structure and elemental composition of the material of particles. The choice of the method depends largely on the type of information sought. The main physical methods applied in nanoparticle and nanomaterial research are briefly described below.

## 5.2 X-ray and neutron diffraction

The X-ray and neutron diffraction techniques are most commonly employed in studying the crystalline structure of nanomaterials [142, 143]. The use of synchrotron radiation in combination with Rietveld analysis [144] made this method more efficient and universal. The crystal structure of nanomaterials depends on the arrangement (packaging) of the atoms spaced approximately 0.1 nm apart. An analysis of the diffraction pattern makes it possible to identify the crystalline phase of the material. Small-angle scattering is involved to estimate the mean distance between particles, whereas large-angle diffraction allows elucidating their atomic structure [145-148]. The width of diffraction lines is closely related to the size itself and size distribution of the particles, as well as to nanocrystal defects and deformities. The width of diffraction lines increases with decreasing nanocrystal size due to the loss of long-range order, in contrast to the bulk material. The width of diffraction lines permits estimating the nanoparticle size with the help of the Debye–Sherrer formula

$$a = \frac{0.9\lambda}{B\cos\theta} \,, \tag{5.1}$$

where *a* is the particle size,  $\lambda$  is the X-ray wavelength, *B* is the full width (in radians) at half maximum of the peak of scattered X-rays, and  $\theta$  is the Bragg angle. However, broadening of diffraction lines leads to an error in the structural analysis of particles less than 1 nm in size. The XRD phenomenon is also the basis for the powder X-ray diffraction technique, taking advantage of the well-known Bragg's law

$$\lambda = 2d\sin\theta, \qquad (5.2)$$

where *d* is the distance between the scattering centers (atoms). Neutron diffraction is more frequently employed in studies of ceramic nanomaterials, e.g., metal oxides.

#### 5.3 X-ray spectroscopy

X-ray spectroscopic techniques are applied to determine the chemical composition of nanomaterials and perform elemental analyses. These methods include XAS, X-ray fluorescence (XRF) spectroscopy, energy-dispersive X-ray spectroscopy (EDS), and XPS [149, 150]. They rely on the detection and analysis of radiation absorbed or emitted by the sample after it is excited by X-ray radiation.

**5.3.1 Energy-dispersive X-ray spectroscopy.** The EDS method is based on sample excitation by an electron beam with subsequent detection of emitted X-ray radiation [151]. The specific atomic structure of each material makes characteristics of its X-ray radiation easy to distinguish from those of

other materials. In this method, an electron beam incident on the sample excites an electron in the inner atomic shell, which causes its ejection and leaves a hole in the shell. The hole is filled by an electron from the outer shell, and the difference between the energies of higher- and lower-energy shells turns into X-ray radiation measured by an energy-dispersive spectrometer. Such spectrometers are frequently used in combination with scanning and transmission electron microscopes.

5.3.2 X-ray photoelectron spectroscopy. XPS is a quantitative method allowing the determination of the elemental composition, empirical formula, and chemical and electron states of the elements present in nanomaterials [142, 143]. The method is as follows. The study sample is excited by X-ray radiation, and emitted photoelectron spectra are detected. Simultaneously, the kinetic energy and the number of electrons knocked out of its upper surface layers (from the depth of about 1-10 nm) are measured. In other words, XPS is a surface-sensitive analytical method requiring ultrahigh vacuum to be applied [149]. XPS permits detecting, e.g., boron and nitrogen in B-C-N nanotubes and even determining the BC<sub>28</sub>N nanotube composition [152]. This technique can be divided into two subgroups depending on the spectral characteristics of radiation employed to excite the samples. Thus, soft X-rays (with quantum energy of 200-2000 eV) are used to study electrons in the inner shells, and UV radiation is harnessed to analyze them in the outer valence shells (UV photoelectron spectroscopy).

#### 5.4 Electron microscopy

Electron microscopy yields atomic-resolution imaging of matter due to the tapping of electrons with a shorter wavelength than photons for probing matter. For electrons with energies from 1 to  $10^4$  eV, the de Broglie wavelength ( $\lambda_{dB} = h/mv$ , where *h* is the Planck constant, *m* and *v* are the particle's mass and velocity) lies in the range from ~ 1 to  $10^{-2}$  nm, i.e., in the X-ray wavelength range. There are two types of electron microscopy: transmission (TEM) and scanning (SEM) microscopies.

5.4.1 Transmission electron microscopy. TEM is characterized by a rather high spatial resolution of the sample structure and chemical composition [153]. In a transmission electron microscope, an accelerated high-energy ( $\sim 50-100$  keV) electron beam is passed through a thin sample; its changes due to electron scattering in the sample are recorded [142, 143, 154]. The electron wavelength under these conditions is roughly  $(5.5-3.9) \times 10^{-3}$  nm. Modern TEM produces images of atoms in crystal samples with a resolution close to 0.1 nm (this value is less than the interatomic distance). An electron beam can be focused to less than 0.3 nm in diameter to enable quantitative chemical analysis of nanocrystals. The difference in the contrast between the sample and the background contains direct morphological information about nanomaterials. The results of such an analysis are of utmost importance for the characterization of nanomaterials on a length scale from atomic size to hundreds of nanometers. TEM provides information on the size, shape, and crystal structure of nanoparticles and the interaction between them [140, 155]. A microscope having high enough spatial resolution for the sample properly oriented relative to its axis yields a high-resolution image. High-resolution electron microscopy enables new insights into the atomic structure and growth direction of nanomaterials [156, 157]. TEM is extensively applied to studying different types of carbon nanotubes [158, 159] and graphene [160, 161].

5.4.2 Scanning electron microscopy. SEM constitutes a powerful tool for the visualization of the surface of practically any material with a resolution of up to 1 nm [140, 141]. In a scanning electron microscope, an electron beam with an energy of  $\sim 50$  keV is scanned over the sample surface with simultaneous detection of backscattered electrons [151]. Interaction between the incident electron beam and the sample results in the emission of secondary electrons typically having energies below 50 eV. The efficiency of emission depends on the surface geometry and properties, and the chemical composition of the material under consideration [162]. The spatial resolution of SEM (1-10 nm) is much lower than that of a transmission microscope. But it has an advantage of yielding images for large surface areas of the sample. The resolution of SEM images depends not only on the electron probe properties but also on the probe-sample interaction force.

#### 5.5 Scanning probe microscopy

Scanning probe microscopy (SPM) includes scanning tunneling microscopy, atomic force microscopy, and chemical force microscopy [139, 163, 164]. All these methods are based on the same principle: the sharp tip of an atomic-thickness needle (with a vertex radius of  $\sim 10$  nm) is scanned along or across the sample surface and the image is formed by measuring either the current passing through the needle or the force acting on it.

5.5.1 Scanning tunneling microscopy. STM makes use of the quantum tunneling effect [165]. The electron wave function decays exponentially with distance from the solid-vacuum boundary. When the probe tip approaches the solid surface, electron wave functions of tip atoms and surface atoms overlap, which results in electron tunneling from the surface to the probe under the action of a low applied electric field. The images are taken due to the detection of tunneling current at a low constant voltage of roughly 0.01-10 V between the surface and the probe. The tunneling current is highly sensitive to both the gap size between the surface and the probe and the surface chemical composition. Measuring voltampere characteristics also yields information about the surface electronic structure. This information is usually supplemented by the results of spectrometry. Taken together, these data characterize the topological, chemical, and electronic properties of the surface. In other words, STM is both a visualization and a spectroscopic method. It is used largely to study conductive specimens or specimens placed on a conductive substrate.

Studies with an aid of STM make it possible not only to characterize the surface structure of materials with high accuracy but also to move individual atoms over the surface using the probe [29], i.e., to modify the surface. STM yields images of the surface of inorganic materials and organic molecules placed in various liquids and gases under different ambient conditions. The invention of STM is of fundamental significance for nanotechnology because it is the first facility that markedly enhanced the potential of nanotechnological research. STM was proposed by G Binning and H Rohrer in 1981 [165]. These authors were awarded the Nobel Prize in Physics 1986 "for their design of the scanning tunneling microscope" [166]. In the same year, the Nobel Prize in Physics was awarded to E Ruska "for his fundamental work in electron optics, and for the design of the first electron microscope" [167].

5.5.2 Atomic force microscopy. Atomic force microscopy is the method of choice for the analysis of nonconductive nanomaterials [163, 168]. The mechanism of AFM operation is similar to that of STM, but the parameter being detected is the force acting between the probe and the solid surface. The interaction potential between two atoms is repulsive at small distances and attractive at large ones. The force acting on the probe depends on the spacing between the atoms (atom) of the probe and the surface atoms. Scanning reveals variations in the tip-sample force interaction. The probe is attached to the end of a cantilever beam bending under the action of weak van der Waals forces emerging between the probe and the surface being studied. Deformation of the cantilever is recorded by sensitive sensors, which allows the high-resolution reconstruction of the topography of the surface under study following relevant transformation. Scanning atomic-force microscopy is an extension of AFM applications designed to measure magnetic, electrostatic, and frictional forces, as well as intermolecular interaction forces that need to be known for nanomechanical measurements. AFM makes it possible to study both conductive objects and dielectrics.

*Chemical force microscopy* permits exploring the local surface chemical structure of various materials [169]. The foundation of this method is the measurement of variations of the intermolecular interaction force between the probe and surface particles.

#### 5.6 Electron energy loss spectroscopy

In this method [170, 171], the sample of interest is exposed to an electron beam with a known kinetic energy and narrow energy distribution. Its interaction with the sample is accompanied by inelastic scattering of some electrons. The related energy loss is measured by an electron spectrometer, and the causes behind the loss are elucidated. Characteristic electron energy losses fall into a wide range from  $10^{-3}$  to 10<sup>4</sup> eV and may result from various processes, such as deep energy level excitation  $(10^2 - 10^4 \text{ eV})$ , the excitation of plasmons and electron interband transitions (1-100 eV), and the excitation of surface atom oscillations  $(10^{-3} - 1 \text{ eV})$ . Deep level excitation (internal ionization) is frequently used to determine the elemental composition of a sample. EELS allows determining, for example, the electron density in plasmon oscillations and the frequencies of acoustic and plasmon oscillations [172].

#### 5.7 Optical spectroscopy methods

Optical methods, i.e., IR and Raman spectroscopy, can give more direct information on material structure than electron absorption and photoluminescence in the visible and UV spectral regions. Suffice it to say that high crystallinity and large particle size are responsible for sharper peaks and more intense Raman scattering signals. Disordering or a high density of defects account for low PL output and emission from the acceptor states [137, 173]. In general, optical spectroscopy is sensitive to the structural properties of materials but fails to yield direct information about structural details.



**Figure 1.** (Color online.) (a) Optical absorption spectra of a series of monodispersed CdSe nanocrystals 1.7–15 nm in diameter. Progressive displacement of the absorption edge to the high-frequency region occurs with decreasing particle size. (b) Size-dependent changes of the first absorption maximum in CdS, CdSe and CdTe nanocrystals. The curves allow estimating the mean NP diameter from the position of the marginal optical absorption peak. (c) PL spectra of CdSe nanoparticles 2.4–4.4 nm in diameter. PL band edge shifts toward higher energies as diameter decreases [146]. (d) Fluorescence of CdSe quantum dot solutions of various sizes irradiated with UV light. (Figure taken from Ref. [136].)

5.7.1 Electron absorption spectroscopy. This technique has its origins in the measurement of light beam attenuation after passage through the sample or reflection from its surface [142, 143]. Attenuation may be due to absorption, scattering, reflection, and interference. Transmissivity and reflectivity are the most commonly measured parameters of the sample material. Transmissivity in the wavelength range from 150 nm (UV region) to 3000 nm (near-IR region) is usually measured with double-beam spectrophotometers. Measurement of the position, width, and shape of the absorption band of surface plasmons in the UV and visible spectral regions yields information on the size and shape of metal nanocrystals. Electronic spectra of semiconductor nanocrystals are directly related to the energy gap width in the materials of interest. For example, the absorption band edge becomes displaced to the blue as nanoparticle diameter decreases [146, 147] (Fig. 1).

**5.7.2 Photoluminescence.** PL spectroscopy constitutes a highly efficient method for studying the electronic structure of both undoped and doped semiconductor nanomaterials

[142, 143]. PL spectra provide information on the quality of the samples studied and allow one to determine the concentration of impurities, to identify the defects, and to measure the energy gap width of the semiconductor. If a semiconductor is excited by light with the energy of a photon in excess of the bandgap energy, subsequent electron-hole recombination results in photon emission; the wavelength of this photon and the emission probability (quantum yield) are characteristics of both the material and the radiation emission process (see Fig. 1). Very useful information about nanomaterials (processes of charge carrier relaxation and recombination of electron-hole pairs) can be deduced from measurements of the time dependence and efficiency of the pulsed laserinduced luminescence of nanomaterials.

The potential of some of the above spectroscopic methods for the diagnostics of nanomaterials is illustrated in Fig. 2 [136] by the example of graphene, viz. a plane monolayer of carbon atoms packed into a two-dimensional honeycomb crystal structure. Graphene has been investigated by a variety of microscopic and spectroscopic methods [175]. AFM gave information on the number of layers in the sample (Fig. 2a)



Figure 2. (a) AFM image of single-layer graphene. The single layer is quite apparent at the  $\sim$  4 Å high bent edge. (b) TEM images of bent edges of single- and double-layer graphene. Bent sheet of graphene is locally parallel to the electron beam. The folded single layer displays up as only one dark line (left panel) similar to the TEM image of one-half of the single-layer CNT. For comparison, the right panel displays the bent edge of double-layer graphene exhibiting two dark lines as in the case of a double-layer CNT. (c) STM image of single-layer graphene in an area of 1 nm<sup>2</sup>. Regions identified as containing single-layer graphene show up as a honeycomb-like structure. (d) XRD spectrum of many-layer graphene. Wide peak near 25° is due to (002)-reflection of graphene. Inset shows double Lorentzian fitting of graphene (002)-reflection spectrum. Mean number of layers is four. (e) Raman spectrum of graphene with an increasing number of layers (n = 1-19) on SiO<sub>2</sub>-Si substrate and the spectrum of highly oriented pyrolytic graphite (HOPG)  $(n = \infty)$  [160, 161, 175-179]. (Figure taken from Ref. [136].)

[160]. TEM allowed one to determine the number of layers and the structure of graphene (Fig. 2b) [161]. The same data were also obtained by STM (Fig. 2c) [176], XRD (Fig. 2d) [177, 178], and Raman spectroscopy (Fig. 2e) [179].

#### 5.8 Laser scanning confocal microscopy

Laser scanning confocal microscopy (LSCM) yields highresolution and depth-selective focused optical images (optical sectioning) of the sample being studied [180–182]. In this method, a laser beam passed through the aperture is focused by the objective lens onto a small spot inside or at the surface of the study specimen. The same lens collects scattered and reflected laser radiation and fluorescence radiation from the irradiated volume; then, the light is directed by a beam splitter (through which the exciting laser beam passes) to a filter and



**Figure 3.** (a) The number of surface atoms vs total number of atoms in a particle. Calculation of the number of surface atoms is based on relation (6.1); it holds true for metal particles [8]. (b) Schematic representation of size-dependent NP properties. Figure demonstrates specific property domains [8].

further on to a photodetector, where the light signal is converted into an electric one and finally fed into a computer. The method is frequently applied to obtaining micrometer- and submicrometer-resolved images in biological and medical research, and possibly with the use of fluorescent labels.

## 6. Geometric structure and optical properties of nanoparticles

### 6.1 Geometric characteristics of nanoparticles

NPs being small, most atoms of the particles are located on their surfaces [8]. The proportion of surface atoms ( $P_s$ , in percent) can be calculated [183] from the simple relation

$$P_{\rm s} = 4N^{-1/3} \times 100\,,\tag{6.1}$$

where N is the total number of atoms in a particle. Figure 3a shows the number of surface atoms plotted versus their total

number in the particle. Evidently, the surface proportion is less than 1% only when the total number of atoms reaches  $10^7$ . For a typical metal, this value corresponds to an NP diameter of approximately 150 nm.

Many believe nanoparticles to be spherical. However, there is a relationship between their morphology and packaging structure; this is especially true of small crystals. If the structure of nanocrystals is assumed to exactly reproduce the crystalline structure of macroscopic matter, its highest stability can be achieved by simple restriction of the number of surface atoms. Many nanoparticles exhibit a polyhedral structure [8]. Polyhedrons, such as tetrahedrons, octahedrons, and cuboctahedrons, can be constructed based on the assembly scheme for a face-centered cubic structure [184, 185]. Small clusters not infrequently have an amorphous icosahedral structure [186].

The properties of clusters and nanoparticles also strongly depend on the formation of filled geometric shells, which occurs when the cluster contains a definite number of particles [187, 188]. Such a number, called magic, ensures the perfect stability of clusters and nanocrystals, which can be understood from purely geometric considerations. The magic number of particles in a cluster carries information about its morphology. An equal number of atoms is needed to form the filled shells for the two most common forms (icosahedron and cuboctahedron) [8].

In the case of icosahedral and cuboctahedral structures, the number of atoms needed to form a cluster with L geometric shells is given by the relation [189]

$$N = \frac{10L^3 + 15L^2 + 11L + 3}{3} . \tag{6.2}$$

Particles having as many atoms as is deduced from formula (6.2) exhibit a closed-shell configuration. The number of atoms needed to completely fill up an individual coordination shell,  $n_L$ , is given by the relationship

$$n_L = 10n_{L-1}^2 + 2\,,\tag{6.3}$$

where  $n_0 = n_{L=0} = 1$ . Thus, the first shell is filled with 12 atoms, the second one with 42, etc. This property is inherent in large clusters, too. Configuration with the filled shell confers stability to giant clusters consisting of smaller clusters and to clusters made up of giant ones [8].

Small NPs a few nanometers in diameter are commensurate with molecules. Accordingly, the electronic and atomic structures of such particles have unusual properties significantly different from the properties of bulk materials. At the same time, large NPs of size  $\geq 20-50$  nm must show the properties of macroscopic bodies [8, 45]. The properties of small nanoparticles undergo irregular variations specific for each size [190]. For bigger particles, this dependence is smooth, which makes it possible to derive similarity laws as a basis on which to describe changes in the properties within given limits. Size-dependent NP properties include electronic, optical, magnetic, chemical, and some other characteristics (Fig. 3b).

## 6.2 Optical properties

## of metal and semiconductor nanoparticles

The most surprising features of nanomaterials are exhibited in their optical properties, including linear and nonlinear absorption, photo- and electroluminescence, and light scattering. For instance, metal nanoparticles show quite apparent size dependence of absorption, while semiconductor nanomaterials with a spatial structure of a few nanometers in size exhibit a strong size-dependence of optical properties due to the quantum confinement effect [135, 191, 192]. The particle shape and interparticle interactions are equally important [86, 146, 193]. This means that the optical properties of particles can be modulated for specific applications by varying their size and shape.

**6.2.1 Optical properties of metal nanoparticles.** The electronic spectra of metal nanoparticles are dominated by absorption bands of surface plasmons resulting from excitations of collective coherent oscillations of free conduction electrons [7, 8, 39, 194–197]. The electric field of an incident light wave induces polarization of free electrons. It corresponds to dipole excitation of the mode mostly responsible for radiation absorption in particles much smaller in size than the optical wavelength. However, higher-order excitations are equally possible and acquire significance in the case of nanocrystals a few dozen nanometers in size.

In 1908, Gustav Mie developed the theory of light absorption [14] and applied it to small particles (see also Refs [15, 16, 198–200]). This theory, based on the electrodynamic approach to the problem of light interaction with small-sized particles, implies a solution of Maxwell equations with suitable boundary conditions. According to this theory, the absorption cross section of a small particle ( $R \ll \lambda$ , where R is the nanoparticle radius, and  $\lambda$  is the light wavelength) is given by the expression [8, 14]

$$\sigma_{\rm ext} = \frac{24\pi^2 R^3 \varepsilon_{\rm m}^{3/2}}{\lambda} \frac{\varepsilon_2}{\left(\varepsilon_1 + 2\varepsilon_{\rm m}\right)^2 + \varepsilon_2^2}, \qquad (6.4)$$

where  $\sigma_{ext}$  is the absorption cross section,  $\varepsilon_m$  is the dielectric constant of the surrounding medium, and  $\varepsilon_1$  and  $\varepsilon_2$  are the real and imaginary parts of frequency-dependent dielectric constant of nanoparticle material. Dielectric constants can be deduced either from the Drude model for free electrons [8] or from experimental data [201]. It follows from relationship (6.4) that NP absorption maximum is accomplished when

$$\varepsilon_1 = -2\varepsilon_m \,. \tag{6.5}$$

Thus, metal NPs (nanocrystals) of different size exhibit characteristic colors depending on their diameter and dielectric constant  $\varepsilon_m$  of the ambient medium. Typical sizerelated changes in nanoparticle optical spectra are shown in Fig. 4. Mathematical methods were developed for the accurate calculation of high-order terms in the Mie theory [7, 202, 203].

**6.2.2 Optical properties of semiconductor nanoparticles.** *Linear absorption and emission.* A surprising property of semiconductor nanoparticles or quantum dots consists in the strong size dependence of light absorption and photoluminescence [8, 45, 135, 204, 205] (Fig. 5b) especially when the particle size is commensurate with the exciton Bohr radius for nanoparticle material. Such dependence was demonstrated experimentally by the observation of absorption and PL spectra displacement in UV and visible frequency regions with decreasing particle size. Such behavior is due to quantum confinement effect that can be qualitatively explained based on the quantum-mechanical model of a particle residing in the



Figure 4. Optical absorption spectra of gold NPs 22, 48, and 99 nm in diameter [194].

square potential well: the smaller the well, the wider the energy gap between electron states. The quantitative definition of quantum confinement for spherical particles is given by the relation [191, 192]

$$E_{\rm g,eff}(R) = E_{\rm g}(\infty) + \frac{\hbar^2 \pi^2}{2R^2} \left(\frac{1}{m_{\rm e}} + \frac{1}{m_{\rm h}}\right) - \frac{1.8e^2}{\varepsilon R} , \qquad (6.6)$$

where  $E_{g}(\infty)$  is the bandgap energy of macroscopic matter,  $m_{\rm e}$  and  $m_{\rm h}$  are the effective electron and hole masses, respectively, and  $\varepsilon$  is the optical dielectric constant of macroscopic matter. The second term on the right-hand side of the last formula suggests that the effective energy gap width is inversely proportional to  $R^2$  and increases with decreasing size. On the other hand, the third term on the right-hand side of Eqn (6.6) shows that the band gap narrows as R decreases due to Coulomb interaction. Also, since the second term becomes predominant at small R, it can be expected that the effective energy gap width will increase with decreasing R, especially when R is small. This effect is schematically illustrated in Fig. 5a. Relation (6.6) disregards the influence of the solvent or the surrounding medium, but it is usually insignificant in comparison with the quantum confinement effect.

The quantum confinement effect shows its worth most essentially when the particle size is comparable to or smaller than the excitonic Bohr radius  $a_{\rm B}$ . The Bohr radius is defined as

$$a_{\rm B} = \frac{\varepsilon_0 \varepsilon h^2}{\pi \mu e^2} \,, \tag{6.7}$$

where  $\varepsilon_0$  and  $\varepsilon$  are the dielectric constant of the vacuum and relative dielectric constant of the semiconductor, respectively,  $\mu$  is the reduced mass of an electron and a hole,  $\mu = m_{\rm e} m_{\rm h} / (m_{\rm e} + m_{\rm h})$ , and e is the electron charge. For example, the exciton Bohr radius in CdS is roughly 2.4 nm [206], and particles with a similar or smaller radius exhibit a strong quantum confinement effect, manifested as a noticeable shift of their optical absorption to the blue spectral region, in contrast to macroscopic matter [207-209]. Similarly, the absorption spectrum of CdSe nanoparticles is characterized by a strong blue shift with decreasing particle size [210, 211] (see Fig. 1). Typically, emission spectra also exhibit shift to the blue region with decreasing particle size. Figure 5b displays the luminescent colors of CdTe nanoparticles. Differently sized particles have different central wavelengths of emission spectra, bigger ones emitting redder luminescence.

The efficiency (quantum yield) of quantum dot PL can be increased by surface modification [212–215] and/or using coated structures [216–219]. It was established in experiments that many nanoparticles, such as CdSe, CdS, and ZnS, are capable of producing rather intense PL [220]. Some others either weakly luminesce or do not luminesce at all at room temperature, e.g., PbS [221], PbI<sub>2</sub> [222], CuS [223], and Ag<sub>2</sub>S [224]. Low PL efficiency may be due either to indirect band-to-band transitions in a semiconductor or to the high density of bulk and surface acceptor states effectively quenching luminescence. The efficiency of luminescence usually increases at low temperatures due to suppression of electron–phonon coupling and the resulting increase in the lifetime of the excited electronic state.

Surface modification due to the employment of capping agents (organic, inorganic, biological molecules, and even ions) effectively eliminates acceptor states and enhances PL. This effect is very important for many applications with the use of strongly luminescent nanoparticles (e.g., in lasers, light-



Figure 5. (Color online.) (a) Illustration of a quantum confinement effect in different systems, from atoms to macroscopic matter. (b) Photograph of quantum dots of different size in UV-irradiated CdTe [205].

emitting diodes, and optical sensors, and for fluorescence imaging).

Interestingly, measurements of PL from individual nanoparticles excited by continuous light have revealed an intermittent (blinking) character of radiation [225-227] (see also review [228] and references cited therein). PL intermittence may be related to Auger photoionization associated with the excitation of two or more excitons in a nanocrystal [225–228]. Ionization causes the ejection of one charge carrier (electron or hole) out of the particle or, for example, into the surface acceptor state or the shell. The 'dark exciton' state has been ascribed to such an ionized nanocrystal whose emission is suppressed by the presence of an excess charge. The nanoparticle begins to luminesce again after neutralization. Spectroscopy of individual NPs appears to be a powerful tool for the study of the properties and dynamics of shell-coated and doped semiconductor NPs, including doping homogeneity, the location and state of dopant ions, and dopant-host interaction [135, 228].

Nanomaterials possess other important optical properties, besides light absorption and emission, such as chemiluminescence [229, 230] and electroluminescence [231–233], of interest for technological applications, e.g., sensing and biochemical detection. Chemiluminescence has been described for CdTe particles [229, 230], and electroluminescence for Si [231], ZnO [232], and CdSe/CdS [233].

Nonlinear optical absorption and emission. Nanoparticles also exhibit nonlinear optical properties, such as multiphoton absorption or emission, generation of harmonics, and up- or down-conversion (see paper [135] and references cited therein). Absorption saturation and bleaching are the most common nonlinear optical effects in semiconductor NPs [234–236]. Nonlinear absorption has also been observed in GaAs nanowires [237] and porous silicon [238]. Nonlinear absorption and induced bleaching may find applications for optical confinement and all-optical switching [239].

Another nonlinear optical effect interesting and important for practical applications and known as charge carrier multiplication involves the generation of several (two or three) excitons per absorbed photon in narrow bandgap  $(\sim 0.3-1.2 \text{ eV})$  semiconductors, such as PbSe, PbS [240-245], and Si [246]. This phenomenon may be of value for solar energy conversion and other applications [246-251]. However, further studies assessing the efficiency of the process and its optimization are needed, because electronic relaxation in nanocrystals proceeds very fast ( $\leq 100$  fs) and multiexciton generation strongly depends on particle's surface quality and composition [248–251]. Impact ionization is supposed to be a mechanism of multiexciton generation in quantum dots after single-photon absorption [240-244]. Impact ionization lasts as long as several femtoseconds and leads to the relaxation of hot charge carriers as a result of exciton generation. If a lowenergy irradiation is used under quantum confinement conditions, impact ionization produces only a few excitons rather than avalanche photoionization [242]. The 'instantaneous' mechanism of multiexciton generation involving a series of virtual single-exciton states was postulated from an analysis of generation dynamics for several excitons in CdSe and PbSe crystals [252, 253]. The foundation of this mechanism is the strong Coulomb coupling between single excitons under quantum confinement conditions and the high spectral density of single- and many-exciton resonances in quantum dots [252].

# 7. Certain applications of nanoparticles and nanomaterials

The unique optical and dynamic properties of nanoparticles and nanomaterials find applications in such fields as optics, electronics, photocatalysis, chemical sensing, photoelectrochemistry, conversion of solar energy, biomedical detection and therapy, and environmental protection (see, e.g., Refs [5, 8, 135, 254-257] and references cited therein). These applications take advantage of such features of nanomaterials [8, 135, 258] as their size comparable with the scattering length (it significantly decreases the scattering rate and increases the efficiency of charge carrier collection), strong optical absorption and possibility of rearranging the absorption band by modulating nanoparticle size to the desired range and thereby covering the entire solar spectrum (Fig. 6) [258], and the possibility of modifying the particle surface for specific applications and simply integrating nanoparticles into large and complex systems. Nanoparticle-based devices can be mounted on flexible substrates, and they can be lightweight and relatively cheap.

At the same time, the use of nanomaterials in certain specific applications is limited [135]. For example, the large surface area makes them vulnerable to surface defects and acceptor states having an adverse effect on their optical and other properties. The same factor accounts for the high reactivity of NPs due to the large number of free bonds. The acceptor state density, even in thoroughly fabricated high-



**Figure 6.** (Color online.) Absorption and emission spectra: (a) rhodamine red and genetically encoded protein (DsRed2), and (b) six different ZnS-CdSe quantum dot solutions. (c) Photograph showing size-adjusted fluorescent properties of quantum dot dispersed solutions [258].



**Figure 7.** Fluorescence wavelengths of typical semiconductor quantum dots and their applications in biology. Specific materials used to form magnetic quantum dots are listed in the inset [258]. FRET—Fortser resonance energy transfer.

quality specimens, is usually much greater than in bulk materials, which leads to a low mobility of charge carriers undesirable for applications requiring effective carrier transport. Some of these limitations can be overcome by scrutinous design and engineering of all elements of the device being developed.

In Sections 7.1–7.5 below, we shall consider certain currently essential applications of nanoparticles, nanomaterials, and nanostructures. Some of them are illustrated in Fig. 7 [258]. Worthy of note among other numerous applications of nanoparticles and nanostructures is their use for surface modification with the aim of SERS research [259–261] and the investigation of various nonlinear optical effects and light-pulse converters [262, 263]. A large number of applications are considered in Sections 8–13.

#### 7.1 Energy transformation:

#### photovoltaics and photoelectrochemistry

One of the most promising applications of the optical properties of nanomaterials deals with conversion of solar energy into electric or chemical energy, e.g., the employment of solar energy in hydrogen production processes [264–269]. Dye-sensitized solar cells have attracted much attention since the first report on the high effectiveness ( $\sim 12\%$ ) of such conversion, published in 1991 [264]. Semiconducting nanostructured materials, nanotubes (including CNTs), nanowires, various quantum dots, metal nanoparticles, and fullerenes are most frequently involved in manufacturing solar cells [255]. Inherent in all these nanomaterials are quantum-dimensional effects and unique optoelectronic properties making them suitable for designing photoelectric cells. Extensive studies to evaluate the principal possibility and practical expedience of utilizing such materials in high-quality and effective solar energy converters are mainly focused on two types of such devices: dye- or quantum dot-sensitized solar cells (Grätzel solar cells) [255, 268, 270], and hybrid organic/inorganic nanocomposite photoelectric cells [255, 256]. The main difficulty encountered in studies designed to optimize the cost-effectiveness ratio of such devices arises from the necessity of utilizing relatively pure materials to ensure the high mobility and effective collection of charge carriers. Zerodimensional nanomaterials are characterized by the highest surface area-to-volume ratio, which sometimes gives an advantage to designers of solar cells based on these materials. A drawback of such devices comes from the slow transport and low mobility of charge carriers that are captured by surface acceptor states or other defects. In this

respect, one- and two-dimensional nanomaterials have better transport properties than zero-dimensional ones.

As of now, the best single-junction solar cells have an energy conversion efficiency on the order of 20–25% [255]. Wide bandgap (bandgap energy ~ 3.2 and ~ 3.4 eV, respectively) TiO<sub>2</sub> and ZnO nanoparticles, CNTs, and fullerenes, as well as combinations of TiO<sub>2</sub> with SnO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> nanoparticles, are most widely relied on by the developers of solar cells [255]. Single- and many-layer CNTs attract much attention as offering ample possibilities of improving many characteristics of organic solar cells due to their unique structure, high electric conductivity, and high mechanical strength. The high electron affinity of CNTs makes them excellent materials for electron collectors and enhances the mobility of charge carriers in conjugate polymer films.

Much interest has recently been generated in solar cells based on one-dimensional structures, including CdSe and dye-sensitized nanowires, nanorods, and nanotubes from semiconducting TiO<sub>2</sub> and ZnO [271–275]. In many cases, they have an advantage over zero-dimensional materials [135]. However, these nanostructures usually lack the proper orientation or ordering needed in solar cell engineering. Manufacturing well-oriented one-dimensional nanostructures with improved characteristics requires sophisticated methods of synthesis, such as glancing angle deposition [276, 277].

#### 7.2 Photoelectrochemistry and photocatalysis

Photoelectrochemistry and photocatalysis comprise processes related to the direct conversion of solar energy into electricity. Photoelectrochemistry makes it possible to transform solar energy into chemical fuel, as exemplified by hydrogen reduction from water — a process attracting increasing attention in recent years [135]. Nanoparticles play a key role in many important chemical reactions as reactants, catalyzers, or photocatalyzers. Their reactivity is frequently enhanced by virtue of size-dependent changes in the redox potentials and the high density of active surface states due to the large surface area-to-volume ratio. It has been shown that photooxidation of some small molecules in the presence of semiconductor NPs may lead to the formation of biologically important molecules, such as amino acids, peptide oligomers, and nucleic acids [278, 279].

An important area of semiconductor NP applications is photoelectrochemical reactions. For example, structurally governed photocurrent generation was described for photoirradiated double-stranded DNA cross-linked by an assembly of CdSe nanoparticles [280]. The photoelectrochemical effect has been observed in a number of semiconductor films, including CdS and CdSe [281, 282], ZnO [283], TiO<sub>2</sub> [284, 285], Mn-doped ZnS [286, 287], WO<sub>3</sub> [288], SnO<sub>2</sub>/TiO<sub>2</sub> [289] and TiO<sub>2</sub>/In<sub>2</sub>O<sub>3</sub> [290] composites. Semiconductors with a wide band gap, e.g., TiO<sub>2</sub> and ZnO, need to be sensitized by dye molecules in order to extend phosphorescence to the visible spectral region [286, 291].

Photocatalysis with the employment of semiconductor NPs plays an important role in chemical reactions involving small inorganic molecules or large organic and biological molecules. Photocatalytic reactivity strongly depends on the chemical nature and properties of photocatalyzers, including the pH value of a solution, and the size and characteristics of the particle surface [292]. Photocatalytic oxidation of organic and biological molecules is of great interest for nanoparticle applications in environmental protection, and, in particular, for dangerous waste degradation. Various metal oxide-based semiconductors, e.g.,  $TiO_2$  and ZnO, are utilized as photocatalyzers. They promote disintegration of alkanes, halogenalkanes, aliphatic alcohols, carboxylic acids, alkenes, aromatic compounds, polymers, surfactants, herbicides, insecticides, and dyes [293]. The elimination or degradation of harmful impurities is the most important application of photocatalytic reactions for water treatment and purification [254, 294] (see Section 7.5 below).

# 7.3 Application of nanoparticles and nanomaterials in chemistry, biology, and medicine

The unique optical properties of nanomaterials allow extensively applying them as diversified optical sensors and for detecting chemical and biological specimens. The optical luminescence of quantum dots frequently serves as an indicator of the study sample [295-300]. For example, the luminescence of a CdSe/ZnS core-shell quantum dot coupled to a biological tissue is intended for immediately stimulating proteolytic enzyme activity due to resonance fluorescence energy transfer [301]. The modular architecture of the peptide structure was designed to control the distance between fluorescence donors and acceptors. High PL sensitivity makes it possible to detect individual molecules and complex systems, e.g., viruses [302]. The plasmonic properties of metal NPs (especially gold nanoparticles) make them suitable for use in biology and medicine as optical sensors and contrast agents for tumor (diseased cells) diagnostics and photothermal therapy [257, 303]. Gold-plated CNTs were harnessed as contrast agents for the visualization of diseased tissues [304].

#### 7.4 Photonics and solid-state illuminators

Nanomaterials are extensively applied in photonics (fiberglass optics) as lasers, photodiodes, solid-state illuminators, and luminophors. Doping (especially of luminophors) is essential in many of these applications. Thin-film lasers and photodiodes are commercially available. In the case of oneand zero-dimensional nanomaterials, the laser effect was obtained in optical pumping; such lasers are shown to be suitable for technical applications [305, 306]. Generation in electrical pumping constitutes a problem partly related to the high density of surface acceptor states in one- and zerodimensional nanomaterials compared with two-dimensional ones.

Regarding the application of nanoparticles as lasers, the good point should be noted that lasers with the tunable generation wavelength can, in principle, be created by simple variation of the particle size. Realization of this idea encounters two difficulties. First, most NPs have a rather wide spectrum due to homogeneous and inhomogeneous line broadening. Second, the high density of acceptor states leads to rapid relaxation of excited charge carriers, which hampers achieving the population inversion necessary for generation. Generation can be realized when the particle's surface is rather perfect and has only few defects. This was demonstrated using nanoparticles obtained in a clean environment by molecular beam epitaxy (MBE) [307-310] or metalloorganic chemical vapor deposition (MOCVD) [311]. Examples of quantum dot-based lasers are InGaAs [307], InAs [309], AlInAs [308, 310], and InP [312]. Stimulated optically pumped emission was also observed in GaN quantum dots [311]. In most cases, the laser effect was apparent at low temperatures [310, 312], but generation proved possible at room temperature as well [307, 308].

Laser generation in the UV range at room temperature was revealed in a ZnO nanowire system [305]. ZnO nanowires grown on a sapphire substrate were synthesized directly by vapor condensation and particle deposition onto the substrate. Nanoparticles with a diameter from 20 to 150 nm and a length of up to 10  $\mu$ m form by themselves a natural laser resonator. In optical pumping at a wavelength of 266 nm, laser generation from the substrate surface occurs at 385 nm with the radiation linewidth near 0.3 nm. Such miniature lasers may find application in many fields, e.g., for the development of optical memory storage devices and integrated optical communication systems.

Nanoparticles find dual application in light-emitting diodes: they serve as radiation amplifiers in diodes made from other materials, e.g., conjugate polymers forming the active medium, and as active materials for light generation [218, 313–315]. In the latter case, an electron and a hole are injected directly into conduction and valence bands of the nanoparticle, respectively, and their recombination results in light emission. Injection and transport of charge carriers was studied in CdS [315] and CdSe [313, 314] nanocrystals to optimize the functioning of such devices.

To conclude this section, it is worthwhile to note that charge transport is the main factor limiting effective light generation in photodiodes based on quantum dots, because the mobility of charge carriers in NPs is usually much lower than in macroscopic monocrystals. New nanostructures, viz. nanowires [305, 316], nanorods [317, 318], and nanoribbons [319], make up interesting alternative materials with better transport properties than those of quantum dots.

# 7.5 Application of nanoparticles and nanotechnologies for environmental protection

Nanotechnology is greatly contributing to the development of innovative methods for the environmentally friendly production of new materials and chemicals with improved characteristics requiring lower expenditures of energy and matter. The use of nanomaterials provides ample opportunities for environmental protection, both by their direct application to detect, isolate, and eliminate pollution and through indirect effects mediated via the introduction of environmentally sound nanotechnologies meeting current ecological standards. By way of example, iron nanoparticles may be utilized to remove radionuclides from the soil and groundwater, while nano-sized sensors can find application in detecting and monitoring such impurities [254].

The treatment of polluted and contaminated water and air in living quarters and production areas are of special importance among the numerous applications of nanoparticles and nanotechnologies for environmental protection. There is an increasingly emerging tendency toward converting seawater into drinking water and, thereby, eliminating the fresh water deficit in the world; hence, the necessity of water desalination. However, it is thus far an expensive and energyconsuming procedure. The use of CNT-based membranes can significantly reduce expenses [254]. Similarly, nanofilters can be used to remediate and purify groundwater and surface water chemically polluted and contaminated with harmful impurities. Filtration techniques may also be employed for air cleaning. It is hoped that sensitive nanosensors for detecting deleterious impurities in water and extremely low-grade toxic gas leaks will be developed.

One of the most serious concerns is the presence of heavy metals (mercury, lead, cadmium) and organic compounds (benzene, chlorinated solvents, creosote, phenol, toluene) in the soil, sediments, and groundwater. Reducing the amount and influence of harmful impurities is one of the main goals of environmental protection. Nanotechnology may be crucial for achieving this [254, 320].

Water treatment for the removal of harmful impurities is performed with the aid of iron and titanium dioxide nanoparticles, bimetallic and magnetic NPs, CNTs, micelles, dendrimers, nanosponges, membranes, nanosieves, and nanocrystal- and nanopowder-based catalyzers (see paper [254] and references cited therein). Phenols are the most widespread toxic compounds in tap water and groundwater. Phenol oxidation by the hydrothermal purification technique was studied with the use of TiO<sub>2</sub> nanoparticles [321]. Zerovalent iron can be applied to purify water from many pollutants [322], removing them from chlorinated solvents by means of reductive dechlorination and reducing metal ions in water to insoluble compounds.

Carbon nanotubes can serve as effective adsorbents used to purify water and air from heavy metals and organic pollutants. The unique adsorption properties of CNTs [323] are due to the fact that the atoms and molecules being adsorbed enter the cylindrical pores of these nanostructures and strongly interact with the surrounding carbon atoms resided on the tube walls, depending on pore size and geometry. Single- and multilayer CNTs can remove heavy metals, such as lead [324] and zinc [325], from air and water. CNTs coated with amorphous Al<sub>2</sub>O<sub>3</sub> particles were used to remove fluorine, the most common pollutant in drinking water [326].

# 8. Fabrication of nanoparticles and nanostructures by laser ablation

#### 8.1 General considerations.

### Advantages and disadvantages of the method

One of the most popular laser-assisted techniques for producing nanoparticles and nanostructures is pulsed laser ablation (PLA) of solid targets placed in a vacuum, gas, or liquid [327-332]. To this end, NPs are assembled in the form of either a nanopowder or thin film, or colloidal solution. Laser ablation provides a relatively simple, direct, and rapid means of NP synthesis, yielding different types of nanoparticles, such as metal, semiconductor, and polymer nanostructures, as well as NPs of complex many-element metal and semiconductor alloys. In this case, chemical reaction time is short, neither high temperature nor high pressure is needed, and multistep processes characteristic of chemical synthesis are absent; nor is there a necessity to utilize toxic or explosive chemical precursors. NP generation in water yields ultrapure colloidal solutions containing no reaction co-products. These features promote in vivo biological and biochemical applications of NPs.

The PLA technique is applicable to a practically unlimited combination of materials, targets, and liquids, which enables NP synthesis in the desired medium. The properties of the NPs being generated, namely, shape, size, size distribution, composition and structure for each target material, depend on the laser characteristics adjusted for ablation (radiation wavelength, pulse length and repetition rate, and pulse energy) and surrounding conditions (vacuum, fixed gas pressure, or liquid). Moreover, NP generation in liquids allows another advantage to be realized, i.e., the possibility of controling NP size distribution by varying ablation duration or additional irradiation of synthesized NPs in a colloidal solution. Finally, PLA permits forming so-called colloidal alloys, i.e., colloidal solutions composed of identical NPs or a mixture of different NPs.

The main drawback of pulsed laser ablation of targets for the production of nanoparticles and nanostructures consists in its relatively low efficiency compared with traditional chemical methods [327] (see Section 4.2). Another disadvantage is high dispersion of synthesized particles by shape and size (roughly between 1–5 nm and 100–150 nm) [328].

#### 8.2 Effect of laser pulse duration on ablation mechanisms

The interaction of intense laser radiation with matter in terms of ablation (removal) of the material largely depends on pulse duration as opposed to electron-phonon coupling time [329]. PLA of a solid target produces a plasma cloud or plume near its surface. Condensation of this cloud directly yields ablation products. Thus, there are three main processes involved in plasma plume evolution during PLA of solid targets: generation, transformation, and condensation. Ablation mechanisms underlying the formation of a plasma cloud are different for nano-, pico-, and femtosecond laser pulses [329]. They depend on the relationship between pulse length  $\tau_{\rm p}$ , electron relaxation time  $\tau_e$ , and target lattice (ionic subsystem) heating time  $\tau_i$ . It is these three parameters that determine three different regimes of interaction between laser radiation and a solid target: nano-, pico-, and femtosecond [329].

**8.2.1 Femtosecond pulses.** In this case, a laser pulse is much shorter than electron relaxation time,  $\tau_p \ll \tau_e$ . Electron–lattice interaction during the pulse can be neglected and lattice temperature remains unaltered. After an exciting pulse ceases, electrons undergo thermalization (over roughly 100 fs), whereupon they rapidly cool down due to energy transfer to the target lattice and its heat conductivity. The lattice temperature depends therewith on the electron cooling time and amounts to [329]

$$T_{\rm i} \simeq \frac{F_{\rm a}\alpha}{C_{\rm i}} \exp\left(-\alpha z\right),\tag{8.1}$$

where  $F_a = I_a \tau_p$  is the absorbed energy,  $I_a$  is the radiation intensity,  $C_i$  is the heat capacity of the lattice subsystem (per unit volume),  $\alpha$  is the absorption coefficient of the target material, and z is the distance from the surface downward. The initial lattice temperature is assumed to be negligible and does not enter relation (8.1).

The electron relaxation dynamics in metals excited by femtosecond laser pulses are well known [333, 334]. It was found that the time of fast electron cooling and appreciable energy transfer from electrons to the lattice is roughly 1 ps. A characteristic feature of the PLA of metallic targets with femtosecond pulses is the logarithmic dependence of the ablation depth on laser radiation energy density [329, 335], as in the PLA of organic polymers. Under these conditions, the ejection of target material and formation of a plasma cloud occur well after the cessation of the laser pulse.

Due to very short times, PLA with femtosecond pulses can be regarded as being a direct solid body–vapor or solid– plasma transition. In this case, lattice heating takes picoseconds and results in the formation of vapor and plasma phases that rapidly extend to the surrounding space. In all these processes, heat conduction in the target material can be



**Figure 8.** Schematic of nanosecond (a) and femtosecond (b) PLA and holes drilled in a 100-µm thick steel foil by laser pulses at wavelength  $\lambda = 780$  nm with the following parameters: (c) pulse length  $\tau_p = 3.3$  ns, pulse energy E = 1 mJ, energy density F = 4.2 J cm<sup>-2</sup>, (d)  $\tau_p = 80$  ps, E = 900 µJ, F = 3.7 J cm<sup>-2</sup>, and (e)  $\tau_p = 200$  fs, E = 120 µJ, F = 0.5 J cm<sup>-2</sup> [329].

neglected in the first approximation. These advantages of laser femtosecond pulses make possible high-precision surface finishing of metals and other solid materials [329] (Fig. 8).

**8.2.2 Picosecond pulses.** Ablation process with picosecond laser pulses proceeds under the condition  $\tau_e \ll \tau_p \ll \tau_i$  imposed on the aforementioned times. In this case, electron temperature  $T_e$  for times  $t \ge \tau_e$  becomes quasistationary, while lattice temperature  $T_i$  [329] remains much lower than the electron temperature:

$$T_{\rm i} \simeq T_{\rm e} \left( 1 - \exp\left(-\frac{t}{\tau_{\rm i}}\right) \right) \simeq \frac{t}{\tau_{\rm i}} T_{\rm e} \,.$$
 (8.2)

When the condition  $t \ll \tau_i$  is satisfied, lattice temperature is determined by electron cooling time, as in the femtosecond regime, and reaches the value given by relation (8.1) near pulse cessation [329]. In this case, the threshold energy density and ablation depth are roughly equal, too. Also, the picosecond regime is characterized by a logarithmic dependence of the ablation depth on laser pulse energy density. PLA is accompanied by electron heat conduction and the formation of a molten zone inside the target. Despite the possibility of considering the evaporation process on the target surface as a direct solid body–vapor or solid–plasma transition, the presence of the liquid phase inside the target compromises the accuracy of laser metal treatment in the picosecond regime, as opposed to the femtosecond one [329] (see Fig. 8).

**8.2.3 Nanosecond pulses.** Ablation in the nanosecond regime proceeds under the condition  $\tau_p \ge \tau_i$ . In this case, electron and target lattice temperatures are equal:  $T_e = T_i$ . The absorbed laser energy first heats the target surface to the melting point and then to the vaporization temperature [336, 337]. To recall, metal evaporation requires much more energy than melting. Heat transfer to the target depths is the main source of energy loss during pulse–target interaction. The threshold energy density  $F_{th}$  needed to evaporate the target by

a long laser pulse increases as the square root of pulse duration ( $F_{\rm th} \sim \tau_{\rm p}^{1/2}$ ) [329]. Ejection of the target material is now largely accomplished due to thermal processes [338], because there is enough time for the thermal wave to propagate deep into the target and for a thick layer of molten material to form. In this case, evaporation occurs from the liquid metal, which makes difficult high-precision treatment of metallic targets or other materials with nanosecond laser pulses in a vacuum [329] (see Fig. 8).

# 8.3 Mechanisms of nanoparticle formation by laser ablation

8.3.1 Target ablation in a vacuum or surrounding gas. PLA causes the ejection of highly excited particles and neutral atoms from the target material surface in the form of a strongly nonequilibrium high-energy and very dense plasma cloud. The gas temperature in the cloud amounts to  $(3-4) \times 10^3$  K, pressure to a few dozen atmospheres, and particle velocity to  $10^6$  cm s<sup>-1</sup> [327]. Evaporated particles (atoms, ions, electrons, clusters) move outward the target surface. Particles of the plasma cloud and the surrounding (background) gas interact with one another. Intense thermal diffusion of particles in the cloud leads to their collisions, aggregation, and condensation, and thereafter to phase transitions, such as the formation of new molecules. Temperature, pressure, and composition of particles in the cloud are essential for the activation of transformations in the plasma. At the same time, we note that pressure has less influence on plasma transformation, when PLA of a target occurs in a vacuum or a gas, because it is rather low during cloud expansion compared with that in the case of PLA in a liquid (see Section 8.3.2).

Chemical reactions of two types proceed at the interface. The first includes ionization of ambient gas molecules by virtue of a high cloud plasma temperature near the interface, followed by a reaction between gas and cloud ions giving rise to new molecules. In reactions of the second type, plasma ions diffuse into the surrounding gas and induce chemical reactions due to the plasma density gradient at the interface. Thereafter, the diffused high-energy ions cool down in chemical reactions with the ambient gas and give also rise to new molecules. For this reason, oxide and nitride films are often fabricated by PLA with the use of oxygen or nitrogen as the surrounding gas [327, 328, 339].

The last stage in plasma cloud evolution covers cooling and condensation in a vacuum or surrounding gas. The mature plasma cloud expands adiabatically, cools down as it expands over the nanosecond time scale, and exerts pressure on the surrounding background gas. This leads to shock generation at the cloud–gas interface. As particles slow down at the interface, shock waves are formed inside the cloud itself and propagate from the interface to its center [327, 328]. Such internal shock wave cycles are responsible for thermalization and cooling of gas components in the cloud interiors. The gas undergoes condensation, nucleation, and clusterization inside the cloud during cooling, giving rise to the formation of nanoparticles

The extremely high cooling rate of the cloud (roughly  $10^{10}$  K s<sup>-1</sup>) results in the strong nonlinear dependence of gas density and pressure on this parameter, which accounts for a rather wide particle distribution by size [327]. Taken together, cloud slow-down and the influence of the particle concentration gradient at the interface bring about diffusion transfer of cloud particles and NPs into the surrounding gas. Various condensation conditions are used differently in the production of materials. Plasma cloud condensation on a substrate gives rise to thin films [327, 328, 339, 340]. This process is called pulsed laser deposition (PLD) [339]. Another process is free condensation of a plasma cloud by cooling in the surrounding gas with the formation of nanoparticles. Naturally, the substrate state and temperature, as well as the ambient gas characteristics (temperature and degree of ionization), exert a marked effect on the formation and crystal structure of the resulting products.

8.3.2 Ablation of solid targets in liquids. When the target is submerged in a liquid, the generated NPs give rise to a colloidal solution. The main difference between PLA of a target in a vacuum (or gas) and a liquid consists in the fact that the liquid hampers cloud expansion to a greater extent, which strongly affects the thermodynamic and kinetic characteristics of cloud evolution. This limitation transfers the laser-induced plasma to a thermodynamic state substantially different from that established as a result of PLA in a vacuum or gas. As a consequence, the processes of formation, transformation, and condensation of the plasma cloud are also different. Significantly more chemical reactions (four instead of two types in the case of target ablation in gas) occur in the laser-induced plasma and the boundary region during its transformation [327]. In these reactions, plasma particles interact with superheated liquid particles.

The limiting effect of the liquid accounts for the significantly higher temperature, pressure, and density of the plasma cloud formed than the same characteristics during PLA in a gas or vacuum. The laser-induced plasma exhibits unique characteristics, including very high temperature (4000–5000 K), pressure (2–10 GPa), and particle number density  $(10^{22} - 10^{23} \text{ cm}^{-3})$  [327, 341, 342]. Moreover, PLA in a liquid creates different surrounding conditions for plasma cloud particle expansion, cooling, and condensation. The liquid at the plasma–liquid interface is heated almost to the plasma temperature, which results in its evaporation and the generation of so-called 'liquid' plasma. It mixes subsequently



**Figure 9.** Comparison of plasma lifetimes during laser ablation of targets in air and liquid. Images of plasma radiation in the visible region, generated upon ablation of a graphite target by a pulsed Nd:YAG laser ( $\lambda = 1064 \text{ nm}, \tau_p = 20 \text{ ns}, F = 10 \text{ J cm}^{-2}$ ) in air (a) and water (b) [346].

with the parent plasma cloud, giving rise to chemical reactions between cloud particles and between particles of the cloud and the liquid plasma at the interface or inside the liquid. For example, PLA of metallic targets in water results in the formation of metal oxide nanoparticles, as shown in a number of studies. Reference [343] reports the formation of iron oxide NPs by the PLA of iron in water, whereas the PLA of pure graphite in an ammonia solution yields carbon nitride nanocrystals [344] and the PLA of silver or gold targets in chloroform or tetrachloride of carbon yields nanoparticles of silver or gold chlorides [345].

Another important difference between NP generation in a vacuum or gas versus liquid is that the plasma cloud cooling time in the latter medium is much shorter because of more rigid boundary conditions during ablation [327, 346] (Fig. 9). They account for the generation of NPs having a smaller average size. The shorter cooling time of the cloud accounts for the 'freezing' of metastable phases of the material till the formation of stable phases. By way of example, Refs [347–349] report the fabrication of diamond nanocrystals by the PLA of graphite targets in various liquids.



Figure 10. (a) Experimental setup for NP generation by PLA of a target in the surrounding gas, when the particles thus formed are transported to the solvent. (b) TEM image of GaAs NPs obtained in this apparatus using an Nd:YAG laser ( $\lambda = 266 \text{ nm}, \tau_p = 7 \text{ ns}, f = 5 \text{ Hz}$ ) [350].

A detailed description of the mechanisms underlying the formation of nanoparticles and nanostructures by the PLA of solid targets in a vacuum (or an ambient gas) and in liquids is presented in review articles [327, 328]; a comprehensive bibliography of the PLA of a target in liquids can be found in Ref. [332].

## 8.4 Design of laser ablation experiments

Nanoparticles produced by the target ablation in a vacuum or a gas scatter in the surrounding medium, necessitating the use of closed vessels to collect them. In many setups, the ablation chamber is connected with another chamber or a container where NPs are collected for further manipulation. A typical setup is depicted in Fig. 10 [350]. A flux of gaseous nitrogen moving largely parallel to the target surface draws in NPs and carries them into the vessel containing a liquid solution, where they make up a colloidal solution. Ablation of the target in a vacuum or an ambient gas is frequently used to sputter films over various substrates and produce nanostructures and nanomaterials (see Sections 8.6 and 8.7).

There are quite a few schemes of nanoparticle synthesis by PLA in liquids. The simplest and most widely applied one is presented in Fig. 11a [351]. The target is placed in a beaker or Petri dish filled with a liquid and fixed on a support movable along XYZ-axes. The laser beam irradiates the target vertically. Another, up-to-date scheme proposed by Semaltianos [328] is shown in Fig. 11b. Here, the target is fixed within a quartz cuvette  $(10 \times 10 \times 50 \text{ mm}^3)$  with a teflon ring that functions as a spring pressing the target against the wall. The cuvette is filled with a liquid, sealed, and placed on a movable stand. The target is irradiated horizontally. Such a configuration makes it possible to easily focus radiation on the target surface. A magnetic or electromagnetic stirrer is usually placed in the vessel for mixing liquid. One more scheme, presented in Fig. 11c, makes use of a rod-shaped target rotating during ablation process [351].

# **8.5** Size control of nanoparticles and nanostructures fabricated by the laser ablation technique

**8.5.1** Ablation in liquids. The newly formed nanoparticles generated by PLA in liquids happen to be in the path of the laser beam and interact either with the 'tail' of the nanosecond pulse that triggered their formation or with the next pulse (in the case of high-repetition-rate pico- and femtosecond pulses). This interaction narrows NP size distribution width, thus providing control over this parameter.

Reduction of nanoparticle size resulting from the particle interaction with the laser beam is underlain by two mechan-



**Figure 11.** Schematics of NP generation experiments with PLA of a target submerged in liquids: (a) laser beam vertically irradiates the target placed in an open Petri dish; (b) horizontal irradiation in a closed cuvette, and (c) irradiation of a rotating target [328, 351].

isms. The one of importance for strongly charged particles is the so-called Coulomb explosion. Large electron-free or deficient particles formed by ablation disintegrate into smaller ones [352]. This mechanism is essential when highintensity and short-wavelength laser radiation is involved in ablation [328]. The other mechanism is responsible for particle heating by a laser pulse to a temperature higher than the melting or vaporization point, which results in ablation of the nanoparticles themselves [353]. This effect is especially important when the exciting laser radiation frequency is close to the NP plasmon resonance frequency [354].

The universal method for controling NP size distribution consists in additional laser irradiation of the resulting colloidal solution after target withdrawal [355]. In this case, the NP size distribution width can be reduced by laser wavelength-dependent plasmon absorption of NPs and their subsequent heating, melting, and fragmentation (evaporation, dissociation). Finally, NP size can also be controlled by varying the laser parameters (radiation wavelength, pulse intensity, duration, and repetition rate) [354, 356–361]. It was revealed by Mafune et al. [360, 361] that small nanocrystals predominantly form at low energy flux densities. A decrease in the laser beam size also results in small (2– 3 nm) nanoparticles [362]. Similar nanocrystals are produced by PLA using ultrashort femtosecond pulses [363] or shorter radiation wavelengths [364].

8.5.2 Ablation in a vacuum or a gas. When nanoparticles are produced in a vacuum or a gas by PLA of solid targets, their size can be varied in situ by annealing. A so-called differential mobility analyzer (DMA) is used for particle size selection [328, 365]. It operates on the following principle. The newly formed NPs are swept away by the carrier gas (helium) to the charge chamber. The latter contains the radioactive isotope Am<sup>241</sup> that emits  $\alpha$ -radiation and ionizes helium atoms, converting them into doubly-charged ions. The ions next become associated with nanoparticles and thereby charge them. External voltage applied across the chamber creates an electric field in which trajectories of charged particles depend on their mass (diameter). NPs with a rather narrow size distribution are extracted from the chamber through a small orifice and are deposited onto a substrate. Moreover, the size of nanoparticles generated by PLA of a target in a vacuum or a gas is possible to control, similar to PLA in a liquid, by varying laser parameters and ambient gas pressure and composition [327, 328].

**8.6 Nanotechnological applications of pulsed laser ablation 8.6.1 Film deposition and nanoparticle synthesis.** PLA of solid targets has been extensively used in processing materials after this technique was developed in the early 1960s for ruby lasers. There are two well-known methods for manufacturing and processing materials with the help of PLA. One covers pulsed laser deposition (PLD) mentioned in Section 8.3.1 for producing thin solid films [339, 340]. The other implies PLA of solid targets in ambient gases for the synthesis of NPs [194, 366–370]. Moreover, PLA is employed in the formation of new micro- and nanostructures on polymer surfaces, the production of wide bandgap semiconductors, and cleaning the surfaces of various materials [338, 371, 372].

PLA of solid targets in liquids is largely used to produce nanoparticles and nanocrystals or to sputter films and coatings over various substrates [327, 328]. Many studies are devoted to the synthesis of three types of nanoparticles (diamond nanocrystals and carbon-containing materials, metal NPs, and nanostructures based on metal alloys, oxides, and nitrides) and deposition of diamond-like carbon coatings over oxide and nitride surface layers [327]. Moreover, the PLA of solid target surfaces in liquids is the basis of



**Figure 12.** Schematic diagram of the LIBWE apparatus for backside etching of silica wafers with the use of KrF-laser ( $\lambda = 248 \text{ nm}, \tau_p = 20 \text{ ns}, f = 2 \text{ Hz}$ ). Pyren is added to acetone to enhance absorbance of the solution at 248 nm [377].

the steam laser cleaning technique designed to remove micrometer- and submicrometer-sized particles from metal and semiconductor surfaces [373–376]. This method has good prospects for microelectronics and microprocessing (creating patterns on the surface of a liquid-submerged solid, making use of the novel etching kinetics under laser irradiation of the solid–liquid interface [377–379]). This method is essentially different from nanoscale pattern creation on a solid surface under laser irradiation in a gas [371, 372] (see Section 8.6.2).

8.6.2 Creating patterns on a surface. The continuous miniaturization of modern devices requires new etching techniques for semiconducting and optical materials. References [376-378, 380, 381] report a recently developed unique method of wet etching based on the PLA of materials submerged in a liquid, referred to as laser-induced backside wet etching (LIBWE) [327, 377]. A schematic of the method is presented in Fig. 12 [377]. It makes possible to fabricate crystalline or fused quartz wafers with a well-defined pattern of micrometer-sized lines and stripes during a single laser irradiation session [377]. Experimental data obtained in Refs [382, 383] suggest that the etching effect in this case is due to laser irradiation of the solution rather than laser-assisted quartz ablation. The laser pulse overheats the solution due to light absorption and continues to heat the wafer-liquid interface. For example, the temperature of the fused silica surface may be as high as 2000 K and exceed the softening point of this material (1700 K [377]). This gave reason to predict that the LIBWE mechanism consists in laser energy absorption by the solution, resulting in its heating. Heat is further transferred to the wafer surface and causes melting and evaporation of its material. Moreover, high-temperature/pressure vapor bombards the softened quartz surface and knocks small SiO<sub>2</sub> clusters out of it. The irradiated area of the surface rapidly cools down after the cessation of the pulse, which prevents destruction of the wafer. PLA of a target in liquids occurs at lower radiation energy densities but with a higher etching rate than in gases [327].

Compared with conventional pattern transfer techniques, such as electron beam lithography, LIBWE has advantages [377, 378], including a low energy threshold and high etching rate, simplicity (one-step process under normal conditions), easy control of the pattern creation process due to the linear dependence between laser fluence and etching depth, and a high resolution allowing one to obtain contrast patterns with clear-cut edges. This method was applied in an in-depth study of quartz surface irradiation with femtosecond laser pulses in Refs [384–388]. **8.6.3 Surface cleaning.** Surface cleaning of optical and semiconductor devices from micrometer and submicrometer particles is a serious issue challenging materials processing technology. There are several methods for the purpose, including ultrasonic and plasma cleaning. However, laser-assisted cleaning has certain advantages over traditional methods unsuitable for the removal of small-sized particles [389]. Laser cleaning is usually performed in two ways [390], one being dry laser cleaning (direct irradiation of surfaces or particles in an ambient gas), the other steam laser cleaning liquid transparent at the laser wavelength).

The latter method was proposed for the first time by Zapka et al. [391] who showed that the solid surface-adhered particles can be effectively removed by laser cleaning through depositing a thin liquid film. Consequently, this mechanism is totally different from dry laser cleaning in which laser energy is directly absorbed by surface particles. The mechanism proposed in Refs [374–376] includes film deposition onto the solid surface and overheating the solid–liquid interface due to thermal diffusion under the effect of laser-induced high temperature. Next this leads to the formation of numerous bubbles at the interface that rapidly expand and explode, causing the pressure to rise appreciably. Therefore, the elevated pressure built up by exploding bubbles creates a force at the interface that removes particles from the solid surface and thereby cleans the surface.

The efficiency of this method has been demonstrated by removing Au,  $SiO_2$ ,  $Al_2O_3$ ,  $Fe_2O_3$ , Si, polystyrene, and other particles [375, 376] from the surfaces of Au, Mo, Si, membranes, photoresist films, polymers, etc. (see review [327] and references cited therein).

#### 8.7 Certain results of nanoparticle fabrication

Aggregation-resistant nanoparticles are fabricated by PLA of the targets in aqueous solutions of surface active agents (SAAs) or surfactants. Sodium dodecyl sulphate (SDS,  $C_{12}H_{25}SO_4Na$ ) and cetyltrimethylammonium bromide [CTAB,  $C_{16}H_{33}N(CH_3)_3Br$ ] are anionic and cationic SAAs, respectively, finding most extensive application. The authors of Ref. [351] (see also Ref. [328]) used the scheme shown in Fig. 11c to obtain silver NPs with the help of the Nd:YAG laser second harmonic (wavelength  $\lambda = 532$  nm, pulse length  $\tau_p = 5$  ns, pulse energy E = 120 mJ, pulse repetition rate f = 10 Hz, and the duration of irradiation  $t_{exp} = 10$  min). It was revealed that NPs rapidly aggregated in distilled water at a small surfactant level. Well-separated and almost spherical Ag nanoparticles were made at high SAA concentrations.

A Nd:YAG laser ( $\lambda = 1064$  nm, f = 10 Hz) was used in Ref. [392] to produce gold NPs. Thereafter, colloidal solutions were irradiated by the 2nd harmonic of this laser ( $\lambda = 532$  nm) at a wavelength close to the plasmon resonance of Au nanoparticles (520 nm), thus enhancing radiation absorption efficiency. It has been found that irradiation of the colloidal solution results in fragmentation of large particles; after this, the particle size increases due to fragment coagulation. SDS particles ceased to coagulate at a certain SAA concentration, which allowed obtaining small NPs (with a mean diameter of 1.7 and 3.4 nm).

Generating NPs of complex multicomponent alloys by PLA technique under usual conditions in the air was performed in Ref. [393]. Ablation of a nickel-based superalloy (C263) applied in aerospace technologies was realized using a femtosecond laser ( $\lambda = 775$  nm,  $\tau_p = 180$  fs,

f = 1 kHz). It was recognized that the resulting NPs have a stoichiometric composition close to that of the target material. It was shown in Ref. [394] that both the structure and the composition of  $TiO_x$  nanoparticles generated by PLA of a titanium target (copper vapor laser:  $\lambda = 510.6$  nm,  $\tau_{\rm p} = 20$  ns) depend on the composition of solution in which the ablation occurs. For example, ablation in water yielded  $TiO_x$  nanoparticles, while ablation in dichloroethane and ethanol gave TiC nanoparticles. A rise in the SDS concentration caused the shape of NiO nanoparticles generated by target ablation with the aid of a continuous wave fiber laser to change from spherical (prevailing after ablation in water) to tetragonal with a decrease in NP size from roughly  $12.6 \pm 9$  to  $10.4 \pm 6$  nm. Moreover, nanoparticles obtained in an SDS aqueous solution were two-phase and exhibited cubic and rhombohedral structures.

Mixed Au/Ag nanoparticles were obtained in Ref. [396]. PLA (Nd:YAG laser,  $\lambda = 532$  nm,  $\tau_p = 10$  ps, f = 10 Hz) yielded two colloidal solutions mixed in a definite proportion. The resulting solution was irradiated by the same laser at higher energy densities. Similarly, mixed Au/Ag and Ag/Cu NPs were obtained with the use of a copper vapor laser in work [397]. Synthesis of a binary alloy of semiconductor CdSe and CdTe nanoparticles using a femtosecond laser ( $\lambda = 387.5$  nm,  $\tau_p = 180$  fs, f = 1 Hz) for ablation of targets submerged in liquids was demonstrated in Ref. [398]. NPs possessed the same crystal structure as the starting material, and roughly identical stoichiometry.

Core-shell Zn/ZnO NPs were generated in Ref. [399] by ablation of a metal Zn target in an SDS aqueous solution with the use of a Nd:YAG laser ( $\lambda = 1064$  nm,  $\tau_p = 10$  ns, f = 10 Hz). It was shown that low SDS concentrations are associated with predominant formation of ZnO nanoparticles, whereas Zn particles are only partly oxidized at a high SDS concentration, since they are rapidly encapsulated in the surfactant. The resultant NPs have the spherical core-shell structure of Zn/ZnO.

Thus, the available results of the studies indicate that PLA of solid targets in a vacuum, ambient gas, or liquid comprises a relatively simple and widely used method for NP production especially suitable in manufacturing nanocrystals and nanostructures; it has a diversity of advantages over other techniques. Laser ablation of targets in a liquid is preferred for making nanocrystals in the metastable phase, such as diamonds and related materials, as well as binary NPs, including inmiscible alloy NPs. The initial phase of nanocrystal formation can include both a liquid and a solid, which permits choosing and combining the desired targets and solutions for the creation of nanocrystals and nanostructures of new compounds for basic research and potential applications.

## 9. Optical laser nanolithography

#### 9.1 Physical principles and certain results

Almost all modern electronic devices are built around key semiconductor components known as integrated circuits (ICs) and manufactured by a rather complicated lithographic process. Optical lithography is referred to as a method for replicating patterns used to create IC configuration on a photoresist layer sensitive to radiation exposure and coated over a silicon or other semiconductor wafer. Lithography includes imprinting the circuit pattern (template),



**Figure 13.** Variants of optical lithography: (a) contact or shadow printing, (b) shadow printing with a gap, and (c) projection printing [400].

photoresist technology, and mask making [400–404]. Lithography was introduced to the semiconductor industry in 1958 when integrated circuits were invented.

There are a few variants of realizing optical lithography (Fig. 13): contact or shadow printing (a), shadow printing with a gap (b), and projection printing (c). Shadow printing was employed in optical lithography up to the early 1980s. It was later replaced by projection printing, which proved much more effective in terms of achieving smaller critical dimensions, because the minimal size restricted by the diffraction limit is proportional to the radiation wavelength [see relation (9.1)], rather than to the square root of the wavelength as in the shadow method [400].

Optical projection lithography is characterized by an intrinsic resolution limit (conditioned by light diffraction) or characteristic size, R, and depth of focus (DOF) defined by the following relations [401, 402, 404]:

$$R = \frac{k_1 \lambda}{\mathrm{NA}} ,$$
$$\mathrm{DOF} = \frac{k_2 \lambda}{(\mathrm{NA})^2} , (9.2)$$

where  $\lambda$  is the radiation wavelength, NA is the numerical aperture, and  $k_1$  and  $k_2$  are constants depending on the concrete parameters of the lithographic equipment and technological process. In many cases,  $k_1$  and  $k_2$  values fall into the range of 0.3–1 and 0.5–1, respectively. The numerical aperture (NA) is described by the following expression

$$\mathbf{NA} = n\sin\alpha\,,\tag{9.3}$$

where *n* is the refractive index of the ambient medium, and  $\alpha$  is the half of acceptance angle of the objective lens of the lithographic system (Fig. 13c). It follows from relation (9.1) that the resolving power can be improved by either decreasing the radiation wavelength or increasing the numerical aperture of the objective. New powerful radiation sources are needed to decrease the wavelength, whereas widening the numerical aperture is hampered by technological difficulties and the necessity to take account of optical aberration. Moreover, because the numerical aperture enters quadratically the denominator of formula (9.2), its widening decreases the DOF and thereby the stability of the lithographic process against deviations of the substrate surface from an ideally smooth one.

In the beginning, optical lithography made use of visible ( $\lambda = 436 \text{ nm}$ ) and UV ( $\lambda = 365 \text{ nm}$ ) light emitted by a mercury vapor lamp (g- and i-lines, respectively). The



Figure 14. Moor's law for lithography. The continuous decrease in radiation wavelength and increase in numerical aperture allow the minimal characteristic size of ICs to be systematically reduced. Transition from 193 nm to 13.5 nm is a major jump being experienced in industrial lithography up to now [404]. Symbols along the abscissa designate spectral ranges: V—violet, UV—ultraviolet,  $DUV_1$ —deep ultraviolet-1,  $DUV_2$ —deep ultraviolet-2, and EUV—extreme ultraviolet.

utilization of these wavelengths made possible the fabrication of ICs with the characteristic size  $R \ge 500$  nm [400– 402, 404] (Fig. 14). Characteristic size R is also called the technological standard or critical size. Mercury vapor lamp lines ceased to be employed after technological developments allowed the critical size of ICs to be decreased to 0.5 µm. In due course, this approach was replaced by laser projection nanolithography with the use of a shorter wavelength generated by deep-UV lasers [excimer KrF lasers ( $\lambda = 248$  nm) and ArF lasers ( $\lambda = 193$  nm)] that allow obtaining ICs with  $R \le 100$  nm [400–404]. Many studies have been carried out exploiting an excimer  $F_2$  laser ( $\lambda = 157$  nm) (see papers [405, 406] and references cited therein) to fabricate nanostructures with  $R \leq 80$  nm [405]. However, the introduction of this laser to lithography technologies has been postponed for its showing a little promise in practice, and, in particular, for lack of the desired efficiency and poor optical characteristics at the specified wavelength. A suitable optical material for this wavelength would be crystalline CaF<sub>2</sub>, but it exhibits residual birefringence and is therefore impractical for the purpose.

Optical projection lithography is always at the leading edge of the semiconductor industry as opening up good prospects for IC miniaturization. The density of transistors on a chip doubles every two years, as was predicted by Moore in 1975 (Moore's law) [407] (see Fig. 14). In order to maintain such a rate of transistor miniaturization for lithography, it is necessary to apply progressively shorter wavelength radiation. Technical standards of modern optical projection lithography have gone far beyond the diffraction limit toward smaller sizes and are now beginning to utilize the characteristic size R = 22 nm. The current level of technological developments is determined by 193-nm lithography combined with immersion and double patterning [403, 408]. This approach makes it possible to create ICs with a characteristic size of 22 nm or less (Fig. 15).



**Figure 15.** Network diagram of lithography for semiconductors [International Technology Roadmap for Semiconductors (ITRS), 2007]. It predicts that EUV lithography will find certain applications in pilot plants for 32-nm technology and will be extensively used for full-scale production in 22-nm technology [404]. DRAM — dynamic random access memory; Flash — flash memory, and pitch — the pitch between adjacent conductors on the wafer.

Figure 16 shows a TEM image of an insulated gate field transistor [409] taken with the adoption of two double exposures and phase-shift masks. The channel length measured only 9 nm. The structure was fabricated by lithography using a KrF laser ( $\lambda = 248$  nm). Thus, the structure size was less than 4% of the exposing radiation wavelength, which means that practically any standard starting from 10 nm can be realized by traditional optical lithography. Therefore, the choice of the lithographic technology is now a matter of economic efficiency rather than the possibility of technical realization [400]. Analysis of 45-, 32-, and 22-nm standard microprocessor technologies performed in 2008 by SEmiconductor MAnufacturing TECHnology (SEMATECH, USA) consortium revealed the advantages of optical lithography for the 45- and 32-nm standards and EUV lithography (extreme UV radiation with  $\lambda = 5-50$  nm) for the standards starting from 22 nm [404], taking into account all economic factors (cost and effectiveness of equipment, materials, masks, etc.).



Figure 16. TEM image of the section through an IC field transistor obtained by two double 'patternings' [409]. Channel length measures 9 nm.

A more recent analysis, dated 2010, gave preference to the 22-nm standard over the 32-nm one. This means that technological standards of 16 nm and less are the province of EUV lithography [400].

## 9.2 Methods for overcoming the diffraction limit

A decrease in IC characteristic size was achieved thanks to the development and application of a variety of methods for overcoming the diffraction limit (see, e.g., reviews [400–403] and references cited therein). The most important of them include immersion [411, 412], artificial phase shift [413, 414], and double exposure and double patterning [408, 415]; others are optical proximity correction [416, 417] and off-axis mask illumination [413].

The **application of immersion** gave a powerful impetus to the development of microelectronics and allowed the minimal size of IC elements to be significantly decreased. In this method, the space between the objective lens and photoresist is filled with a liquid. It was shown in paper [411] that water (transparent at 193 nm and having refraction index n = 1.44) can be used for the purpose. The wavelength of an excimer ArF laser in water is 134 nm, not 193 nm. According to formula (9.1), this accounts for the decrease in the IC characteristic size by a factor of 1.44. It is equally possible to adopt liquids with a higher refraction index, but water is more convenient for practical applications.

Introduction of artificial phase shift is an effective tool for making IC elements with a size beyond the diffraction limit. The method was proposed in the early 1980s by Levenson et al. [414]. A higher-contrast mask image can be obtained by introducing additional elements (additional layers deposited or grooves produced) to the proper sites of its structure that shift the phase of light passing through the mask. If, for example, the phase shift  $\varphi = 180^\circ$ , a wave of electromagnetic radiation propagating through the mask (phototemplate) in two complementary parts of the micropattern may produce zero intensity due to interference and enhance image contrast at this site. Up to five variants of the inserts are adopted for different parts of the IC to induce the phase shift [400, 413, 414].

Application of the recently proposed **double exposure and double patterning schemes** [408, 415] permits the most effective reduction of the critical size of IC elements. Double exposure is based on the use of two photomasks showing different (complementary) patterns when one and the same layer of photoresist is exposed. Double patterning is a more radical procedure including the successive creation of two mutually complementary micropatterns with the aid of a pair of matched photomasks (templates). The photoresist is deposited, exposed, and developed twice to obtain two micropatterns built into each other. Such technologies became practicable only after a new class of photoresists (chemically amplified photoresists) was developed and made available [411, 412].

**Optical proximity correction** is applied to eliminate pattern defects resulting from light exposure of structures smaller than the limiting size defined by expression (9.1), such as narrowing or underexposure of a long narrow line, shortening and rounding its ends, and filling up narrow gaps and acute angles. Compensatory elements are created on a photomask to correct such defects [416, 417]. Methods for correction of optical proximity effects are applied when fabricating very large-scale ICs.

**Off-axis mask illumination** is applied for optimal illumination of masks with elements smaller than the diffraction limit and for more adequate replication of the pattern onto a photoresist [413]. The patterns are formed therewith using objectives with a smaller numerical aperture and greater DOF. The employment of immersion and other methods for breaking through the diffraction limit ensured considerable progress in the creation of IC elements with a significantly smaller size than the wavelength of lasers exploited in lithography.

# 9.3 Some problems and prospects of lithography in the extreme UV range

The new generation of lithographic technologies, known as short-wavelength lithography, has been extensively investigated in recent years for the production of ICs with the characteristic size  $R \leq 22$  nm. The next generation of lithographic techniques is supposed to exploit EUV radiation (13.5 nm), X-ray radiation (0.4 nm), and electron and ion beams with a very short de Broglie wavelength [404, 418]. EUV lithography, also termed as soft X-ray lithography [404], was proposed in 1988 [419] and rapidly developed thereafter. Since 1999, it has been considered to be the most promising technology of new-generation lithography (see reviews [400–404, 418, 420]).

Unlike other technologies of the new generation with a single reduction of membrane mask images (proximity X-ray lithography, electron and ion beam projection lithographies), EUV lithography makes use of a four-fold reduction, allowing the design of photomasks based on existing technologies. However, the huge technological jump from the 193- to 13.5-nm wavelength created a host of difficult problems related to the development of both an effective source of EUV radiation [404, 418–422] and the technological process itself. EUV lithography requires totally new approaches to manufacturing photoresists, printers, and masks, as well as new metrological instruments and quality methods of checking and defect control.

Potential radiation sources for EUV lithography are synchrotron radiation, free-electron lasers [423–425], and hot plasma [421, 426]. The last source is preferred for lithographic applications [419, 421, 427–429]. Hot plasma can be generated by electric discharge or heating the target with a powerful laser pulse. The study of both approaches is currently underway [418, 421, 426]. The effective generation of EUV radiation by laser heating of the target requires an energy of 0.5–1.0 J and a pulse length of 5–10 ns. Pump radiation intensity at the target must be around  $3.0 \times 10^{11}$  W cm<sup>-2</sup> [427], and the coefficient of its conversion into EUV radiation at least 2–3% if the mean radiation power needed for EUV lithography is to be realized at an intermediate focus of 180–200 W in the two-percent spectral interval with the center at 13.5 nm [418, 421, 426].

Ly<sub> $\alpha$ </sub> lines of hydrogen-like Li<sup>2+</sup> ions (13.5 nm) and the radiation maximum associated with transitions in the Xe<sup>9+</sup> ion were initially regarded as possible EUV emitters [421, 426, 430]. However, lithium was very early found to be unsuitable as a material for the purpose due to technological difficulties encountered in its production and the threat of pollution of the entire lithographic system with this highly aggressive chemical element. Xenon experiments demonstrated a low coefficient of pump radiation transformation (roughly 0.5– 0.7%) for pulsed discharge plasma [421, 426, 430]. This seemingly insurmountable problem was resolved by the adoption of multiply charged tin ions [421, 426, 430]. Detailed studies of the tin plasma spectrum in a vacuum

A very complicated problem encountered in the development of EUV lithography arises from the fact that all existing materials strongly absorb EUV radiation. Therefore, only reflective optics can be applied in EUV lithography (mirrors instead of lenses) and the process has to proceed in a deep vacuum. EUV light is reflected by multilayer mirrors known as Bragg's reflectors. Unlike optical mirrors, with a reflection coefficient of around 99%, Bragg's reflectors have a reflection coefficient of about 70% at 13.5 nm, which accounts for the markedly reduced efficiency of the lithographic process and imposes a limitation on the number of reflective surfaces to be exposed. Usually, a mirror consists of a few molybdenum and silicon (Mo/Si) or molybdenum and beryllium (Mo/Be) layers [418, 435, 436]. Creating mirrors for this spectral range is a quite serious issue challenging EUV lithography. Manufacturing precision and the smoothness of mirror surfaces must correspond to atomic layer accuracy. Both the mirrors and masks manufactured by the same technology must be reflective.

Another challenge facing EUV lithography is contamination of mirrors, masks, photoresists, and other components of lithographic machines with ablated fragments of target material (charged and neutral atoms, clusters, and microparticles); hence, the necessity of anti-contamination protection, which may, in turn, lower the radiation power and overall effectiveness of the lithographic machine.

In concluding this section, it is worth noting that longterm investigations (over 20 years) of EUV lithography have not yet resolved all the problems encountered in the development of radiation sources, the elucidation of the mechanisms and potential of this process, and the estimation of the effectiveness of its practical application. For all that, EUV lithography is supposed to constitute the next generation of nanolithography and provide a basis for the largescale manufacture of ICs with the characteristic size  $R \le 22$  nm in the near future [400, 418, 421, 422, 426]. In the long run, it is expected that EUV lithography will move into the 6.5-6.7 nm range and manufacture ICs of the characteristic size  $R \leq 10$  nm [437–439]. Plasmas of the rare-earth elements terbium and gadolinium showing intense emission lines in this region will serve as a radiation source, and multilayer  $Mo/B_4C$  coatings with a reflection coefficient of about 40% as reflective mirrors [437–439].

## 10. Laser interference lithography

## 10.1 General consideration

Interference lithography (IL) serves as an effective tool for manufacturing nanometer-sized templates having a relatively large area [440, 441]. In this method, template features are replicated into a light-sensitive material known as photoresist, whose response shows nonlinear dependence on incident radiation intensity due to interference between two or more coherent light beams. Photoresist-based templates produced by IL are platforms on which to form nanostructures and grow functional materials and the building blocks for developing nanoscale devices. Relatively simple large-area IL is based on the irradiation of the photoresist layer with two or more laser beams without a mask. This method is sometimes referred to as holographic lithography. Its principal advantages are a rather high resolving power as compared with other optical techniques for the fabrication of nanostructures, low cost, and high efficiency as against the other beam techniques [442]. The employment of short-wavelength lasers and/or the immersion technique makes it possible for IL to obtain periodic structures less than 50 nm in size. Variants and potential applications of IL are reviewed in [440, 441, 443, 444].

In terms of certain characteristics (e.g., the possibility of treating large areas with a desired quality), IL compares with modern optical lithography (capable to manufacture ICs measuring  $\leq 45$  nm [445]; see Section 9.1), nanoimprint lithography (NIL) [446], and other self-assembly modalities, such as nanosphere lithography (NSL) (see Sections 11 and 12 below). However, these methods have some disadvantages hampering their much investigation and widespread application. Suffice it to mention the costly equipment needed for modern optical lithography and very clean premises in which it is operated. NIL requires very expensive and hard-to-get three-dimensional masks commensurate in scale with the structures it produces. NSL utilizes monodispersed colloidal spheres deposited onto a surface in the form of dense structures often lacking long-range order, because the particles tend to aggregate.

Considerable progress in many research areas has been achieved by applying serial nanolithographic technologies, such as electron-beam lithography [447], ion-beam lithography [448], and atomic force microscopy. However, the low throughput of these universal, much enabling techniques hampers their wide application. IL has a diversity of advantages over other nanolithographic techniques.

## 10.2 Physical basis of interference lithography

The physics behind interference lithography is rather simple. A beam of coherent laser radiation with wavelength  $\lambda$  is usually splitted into two halves incident on a photoresistcoated substrate at the angles of  $+\theta$  and  $-\theta$ . The resulting interference pattern has a period of  $\lambda/2\sin\theta$  [443]. Because any proper laser can be utilized for this purpose, most studies have been carried out at wavelengths especially suitable for photoresists employed in the semiconductor industry:  $\lambda = 364$  nm (continuous wave ion argon laser) and  $\lambda = 355$  nm (third harmonic of a pulsed Nd:YAG laser). The two wavelengths match photoresists designed for 365 nm. Both the next 244-nm wavelength (2nd harmonic of an Ar<sup>+</sup> laser) and 248-nm wavelength (KrF laser) are well suited to photoresists designed for KrF lasers ( $\lambda = 248$  nm). Finally,  $\lambda = 213$  nm wavelength (5th harmonic of an Nd:YAG laser) and  $\lambda = 193$  nm wavelength (ArF laser) are very suitable for industry-standard UV photoresists intended for the 193-nm wavelength. The limiting half-width values of interference patterns thus obtained (which would run close to  $\approx \lambda/4$  under irradiation in air) are 91, 89, 61, 54, and 48 nm for the respective lasers.

The size of the structures can be further decreased by involving immersion techniques. Most studies on the use of immersion IL have been conducted at the wavelength of an ArF laser ( $\lambda = 193$  nm); they are of interest for the technology of silicon-based devices. Water (refractive index 1.44 [449]) is a good medium for immersion research at this wavelength,





**Figure 17.** Layout of interferometers for IL. (a) Lloyd's mirror converts a laser beam with  $TEM_{00}$  mode into itself. (b) Prism geometry analogous to scheme (a) that is easy to use in immersion IL [440].

inasmuch as it allows the interference pattern half-width to be decreased to 33 nm. Other liquids with refractive indices higher than that listed above are less convenient than water [450]. X-ray IL based on synchrotron radiation was also investigated in Refs [451, 452]. The results proved comparable to those obtained with ArF lasers. At the same time, the theoretical half-width of nanostructures fabricated by radiation at 13 nm may be as small as 3 nm. The contrast strength of the structures obtained by IL depends on optical beam polarization, especially at large incidence angles and with the application of immersion lithography [440].

Optimization of the geometry of an interferometer used in IL depends on the degree of coherence and other properties of the laser. In the case of lasers operated in a single transverse mode TEM<sub>00</sub>, a convenient geometry is achieved by Lloyd's mirror arrangement (Fig. 17a). In this scheme, the upper half of the laser beam is reflected by a mirror and reaches a photoresist deposited onto the substrate. The lower half of the beam is incident directly on the photoresist. Maximum fields are realized at normal incidence (Fig. 17a), when the intensities of the upper and lower parts of the beam impinging on the photoresist are identical. In this case,  $\theta = 45^{\circ}$ , and the period of the interference pattern is  $\lambda/\sqrt{2}$ . Incident beam intensities in space must be roughly equal if maximum contrast is to be obtained. Therefore, the beam center of a TEM<sub>00</sub> laser must coincide with the center of the mirror system and the beam should be expanded in order to achieve the required homogeneity of radiation intensity in the beam cross section. It was estimated that homogeneous radiation intensity at the level of 5% across the sample for a Gaussian laser beam can be reached if the beam is expanded so that 95% of the laser power remains unutilized at all. Lloyd's system has the advantage of stability against external vibrations that have practically no influence on the interference pattern.

A similar geometry with the adoption of a prism instead of a mirror is depicted in Fig. 17b. The peculiarities of prism geometry arise from the presence of many optical surfaces in the immediate proximity to the photoresist layer. Therefore, the surfaces need to be coated with an antireflective material to prevent multiple reflections responsible for distortion of interference patterns. This geometry is convenient to apply in immersion lithography. A thin film of an immersion medium can be inserted between the output face of the prism and the photoresist-coated substrate. There are many other IL schemes built around cw and pulsed lasers, including those utilizing three and more laser beams and polygonal prisms [440, 441, 453–455]. Other options include the scanned laser beams or scanned photoresist-coated substrates [440, 456]. IL makes it possible to fabricate N-dimensional periodic structures  $(N \leq 3)$  due to interference (N+1) of laser

beams focused on different planes at the photoresist. The shape and symmetry of the resulting structures can be modulated by altering the radiation geometry, laser beam intensity, polarization, and phases [440, 441].

### 10.3 Certain results obtained by interference lithography

IL allows fabricating periodic structures, one-dimensional lattices, two-dimensional peaks or holes, and three-dimensional periodic structures [440, 441, 453-455]. More intricate structures can be obtained by alternating IL and traditional microlithographic methods, such as metal deposition, including electrochemical, and etching, comprising ion etching. The treatable surfaces may be large enough, the typical results being comparable to those obtained by optical lithography. Thus, certain authors processed photoresist on whole silicon wafers 7.5 cm [457] and 15 cm [458] in diameter. Irradiation of substrate areas as large as 1 m<sup>2</sup> has also been reported [458]. Phase shift between interference patterns and repeated irradiation of a photoresist were involved to place new structural inserts on finished structures; also, structures with doubled line density were obtained (thereby, the diffraction limit was surpassed two-fold) [459]. As a consequence, IL made it possible to synthesize nanostructures-templates, including large-area ones used to obtain various one-, two-, and three-dimensional nanostructures and quantum dots, metamaterials, and materials with a negative refractive index; moreover, nanoparticle ensembles have been formed by means of self-assembly [440, 441, 454, 455].

It should be emphasized that the application of templates fabricated by IL makes possible the targeted self-assembly of NPs, e.g., colloidal particles, to be used for producing the desired structures [460, 461] (Fig. 18). The periodic nature of interference patterns facilitates the creation of differently shaped periodic nanostructures by IL. A combination of IL and ion etching has yielded silicon nanopost structures with needle-like sharp tips and nanograting structures with bladelike sharp tips [462] (Fig. 19). In Refs [463-465], IL was applied to produce periodic arrays of nanostructured lines and dots [463] (half-height size of 50-60 nm) in polymethilmethacrylate (PMMA) photoresist overlaid on a silicon wafer with the help of compact desk-top EUV lasers (Ar + capillary discharge lasers:  $\lambda = 49.6$  nm,  $\tau_p = 1.2$  ns [463], and 1.5 ns [464, 465]). EUV IL with the use of lasers and other sources was studied in Ref. [466], where line structures were generated



**Figure 18.** SEM images of targeted self-assemblies of colloidal NPs at hard templates prepared by IL. (a) Silicon nanoparticles 80 nm in diameter in a 200-nm wide groove. (b) Silicon NPs 50 nm in diameter in a 120-nm wide groove. (c) Silicon NPs 80 nm in diameter in nanoholes 200 nm in diameter [460]. (d) Polystyrene NPs 250 nm in diameter in an array of square nanoholes. Each neighboring nanohole is vacant. (e) Side view of 250-nm polystyrene particles in an array of square holes. (f) Colloidal polystyrene crystals on a square nanohole template [461].



**Figure 19.** SEM images of sharp-tip silicon nanostructures. Tips of nanostructures with positively tapered smooth sidewall profiles were sharpened by thermal oxidation followed by oxide etching; they measure less than 5 nm in tip apex radius of curvature. (a, b) Nanopost structures with needle-like sharp tips: (a)  $114 \pm 11$  nm in height and  $11^{\circ} \pm 1^{\circ}$  in cone angle, and (b)  $460 \pm 17$  nm in height and  $5^{\circ} \pm 1^{\circ}$  in cone angle. (c, d) Nanograting structures with blade-like sharp tips: (c)  $180 \pm 10$  nm in height and  $12^{\circ} \pm 1^{\circ}$  in cone angle, and (d)  $600 \pm 18$  nm in height and  $4^{\circ} \pm 1^{\circ}$  in cone angle [462].

by synchrotron radiation in a photoresist (PMMA) with the then record for photon-based lithography resolution (11-nm wide half-pitch in line and spacing patterns).

Other IL applications have also been reported [440, 467]. For example, nanowire assemblies from organic polymers are of interest for designing organic light-emitting diodes, field transistors, sensors, and organic solar cells. IL combined with plasma etching or other methods makes it possible to fabricate dense arrays of such structures over large areas [467, 468]. Therefore, laser IL serves currently as a powerful nanofabrication technique [440, 441, 443–445, 453–455] expected to find increasingly wide novel applications in nanotechnology for the creation of structured surfaces, including large-area ones.

## 11. Laser nanosphere lithography

### 11.1 General considerations

Nanosphere lithography (NSL) is a simple, effective, and relatively inexpensive parallel nanofabrication technique yielding various nanostructures and well-ordered two-dimensional nanoparticle assemblies [469]. A variety of materials are suitable for NSL. Moreover, it is a universal method for producing nanoparticles and nanostructures involved in the investigation of their size-dependent optical, magnetic, electrochemical, thermodynamic, catalytic, and other properties [469, 470] (see Section 11.5). It should be noted that lasers are used in this method largely for the fabrication of nanoparticles and nanostructures from refractory materials (see Section 11.3).

The invention of NSL dates to 1981, when Fischer and Zingsheim published their paper [471] describing the use of polystyrene latex beads as a mask for contact imaging with visible light. In 1982, Deckman and Dunsmuir [472] considerably extended this approach by demonstrating that a self-assembled monolayer of nanospheres can be used as a mask for both material deposition and in etching. Deckman coined the term 'natural lithography' to explain this process. He and his co-workers studied many parameters of the NSL process, but always used a single nanosphere layer as a mask [472–476]. The third period in the development of natural lithography, renamed NSL, was described more fully in the work of Van Duyne and his colleagues [469, 470, 477]. These authors extended the NSL method to the use of both singleand two-layer nanosphere masks together with an atomic force microscope and obtained defect-free periodic silver NP structures over an area of 10–100  $\mu$ m<sup>2</sup> on a mica surface, which enabled them to study their optical properties [470].

The fabrication of nanostructures by NSL on a substrate surface includes the simultaneous self-assembled deposition of a colloidal crystalline structure (mask) of monodispersed particles. There are several methods for satisfying the condition of free NP diffusion over such a surface structure in search for the minimal energy position. As the solvent (usually water) evaporates, capillary forces bring NPs together, which leads to their crystallization into a hexagonal single-layer close-packed structure (mask) located on the surface. Similar to any naturally formed crystal, the nanosphere mask thus obtained has numerous defects resulting from the polydispersity of nanospheres, their random distribution, point and line defects, and the presence of domains.

Defect-free zones are usually ranged from 10 to 100  $\mu$ m in size. The nanosphere mask having been formed, atoms and small clusters of metals or other materials are deposited through it normally onto the surface. Particles of the target material are obtained either by thermal heating of the target or by its irradiation with an electron beam or laser pulse. Once deposition is completed, the nanosphere mask is removed by ultrasonic treatment in an aqueous alcohol solution, while the deposited structures remain on the substrate surface.

### 11.2 Single- and double-layer periodic nanoparticle arrays

In the simplest NSL technique, a single close-packed nanosphere layer with a hexagonal structure serves as the mask. When the material from a collimated source is deposited through such a mask normally onto the surface, the threesided interstices between spheres allow its atoms and clusters to reach the substrate and create an array of triangularly shaped nanoparticles (Fig. 20). This array is referred to as a single-layer periodic particle array (SL PPA). Nanoparticle thickness  $d_m$  depends on the duration and other conditions of the deposition process and on the nanosphere diameter. Simple geometric calculations [469, 478] define the relation-



**Figure 20.** (a) Schematic illustration and (b) AFM image of a single-layer periodic Ag nanoparticle array (thickness  $d_m = 48$  nm). NPs were fabricated with the use of a mask from nanospheres (diameter D = 542 nm) by thermal evaporation of metallic silver and subsequent ultrasonic treatment in methylene chloride for 3 min [469].

ship between the perpendicular bisector  $a_{SL}$  of the triangular nanoparticles and the interparticle spacing  $d_{ip}$  with nanosphere diameter *D*:

$$a_{\rm SL} = \frac{3}{2} \left( \sqrt{3} - 1 - \frac{1}{\sqrt{3}} \right) D \simeq 0.233 D,$$
 (11.1)

$$d_{\rm ip} = \frac{1}{\sqrt{3}} D \simeq 0.577 D \,. \tag{11.2}$$

In experimental studies with the most commonly used singlelayer masks, the deposited nanoparticle ensemble covers roughly 7.2% of the surface area.

Nanospheres present in a colloidal solution at high concentrations may give rise to a colloidal crystal composed of two layers of close-packed nanospheres. When a second nanosphere layer assembles onto the first one, every other three-sided hole is blocked in the first layer and smaller-density hexagon interstices result. After depositing material through the two-layer nanosphere mask, the mask is removed and a regular pattern of hexagonal NPs remains at the surface [469]. Such a structure is called a double-layer periodic particle array (DL PPA). As in the SL PPA, the size of the DL PPA nanoparticles can be tuned by the deposited nanosphere size, duration, and other parameters of the deposition process. The following geometric calculations define the relationship of the nanosphere diameter:

$$a_{\rm DL} = \left(\sqrt{3} - 1 - \frac{1}{\sqrt{3}}\right) D \simeq 0.155 D,$$
 (11.3)

$$d_{\rm ip} = D \,. \tag{11.4}$$

In the DL PPA scenario, the nanoparticles cover approximately 2.2% of the substrate area.

An extremely promising application of the DL PPA architecture lies in the area of magnetic nanomaterials for data storage [479], which makes magnetic nanoparticles a good prospect. Like all physical properties, magnetic properties are size-dependent. As magnetic nanomaterials reach sizes of 100–500 nm, the physical size of the nanoparticle dictates that the lowest energy structure is one in which all magnetic moments point in the same direction, thus creating a single-domain magnet. Magnetic force microscopy investigations of DL PPAs [480, 481] show that single-domain magnetic nanoparticles can be fabricated with the NSL technique.

#### 11.3 Nanorings

In the process of creating and studying SL and DL PPAs for magnetic and catalytic applications using transition metals (nickel, cobalt, platinum, and palladium), a third NSL periodic structural motif, the nanoring, was discovered [469]. The high melting points of the transition metals require that they be deposited onto the substrate surface by electron beam or laser pulse evaporation rather than thermal evaporation to avoid melting the polystyrene nanosphere mask [469]. Nanorings are usually fabricated with the employment of single-layer masks.

The detailed mechanism of nanoring formation remains to be clarified. Its probability is believed to strongly depend on the kinetic energy of the atoms being deposited that emerge from metal evaporation by an electron beam or laser



**Figure 21.** Schematics of the fabrication of NP assemblies by angularresolved NSL. (a) Samples positioned at  $0^{\circ}$ . Spacings between mask nanospheres are equally sized and equidistant. (b) Samples positioned at  $30^{\circ}$ . Spacings between mask nanospheres have two different sizes that became smaller. (c) Samples positioned at  $45^{\circ}$ . Spacings between nanospheres on the side of deposited particles resemble lines [469, 478].

pulse [469]. At a low kinetic energy of these atoms ( $\sim 0.1 \text{ eV}$ ), they propagate along the straight lines towards the substrate surface, stick where they strike the surface, and form trihedral nanoparticles. In contrast, high kinetic energy atoms ( $\sim 1-10 \text{ eV}$ ) that travel along off-normal trajectories can be reflected (because of excess kinetic energy) from the surface and having been reflected from lower parts of nanospheres they then continue to travel in the direction of the nanosphere bases, adhering to the substrate surface and ultimately forming the nanorings [469]. Such structures may find future applications as optical traps, components of nanocylinders [469].

Generally speaking, the above periodic NP arrays are two-dimensional structures. However, the NSL methods considered in this section can be applied equally well to fabricate three-dimensional periodic nanostructures [469, 478].

### 11.4 Angle-resolved nanosphere lithography

Angle-resolved nanosphere lithography (AR NSL) constitutes one more variant of nanosphere lithography [469, 478, 482] providing a simple and convenient tool to fabricate nanostructures of various shapes and sizes. The principle of the method is illustrated by Fig. 21. The material is deposited through a mask at a certain angle  $\theta_{dep}$  to the surface. Also, the azimuthal angle  $\varphi_{dep}$  lying in the perpendicular plane can be altered. Changing these angles and the size of the nanospheres forming the mask, it is possible to obtain NP arrays of various sizes, shapes, and interparticle distances and to easily regulate these parameters. This makes the method universally applicable [469, 478, 482]. An important characteristic of AR NSL is that it allows obtaining small-sized NPs [469, 478]; for example, 5–100-nm nanosphere masks are needed to fabricate nanoparticles measuring 1–20 nm. However, the creation of well-ordered two-dimensional structures by self-assembly of such small nanospheres is difficult because the polidispersity of nanospheres increases as their size decreases. At the same time, AR NSL makes possible a four-fold reduction in NP size (in the plane of incidence) by changing angle  $\theta_{dep}$  from 0° to 25° [478].

AR NSL is used first and foremost to produce NPs of different shapes and sizes by depositing materials once through a one- or two-layer mask, but it can be just as well applied for multiple deposition of one and the same or different materials through a single mask. Varying the angle of incidence  $\theta_{dep}$  between two or more successive deposition processes allows obtaining such structures as nanooverlaps, nanogaps, and nanochains with the help of AR NSL [469].

## 11.5 Fabrication of nanostructures

## by laser nanosphere lithography

Laser-assisted NSL is utilized to fabricate nanostructures of different sizes and shapes for the study of their optical, magnetic, electric, and catalytic properties and for their application as optical sensors in biology and medicine. For instance, Ref. [483] reports the fabrication by the laser NSL of nanostructures of ferroelectric BaTiO<sub>3</sub> with the perovskite structure and the investigation of their properties. The authors used latex nanospheres 1 µm in diameter. The target material (BaTiO<sub>3</sub> ceramic) was ablated by an excimer KrF laser ( $\lambda = 248$  nm) with a pulse energy of 400 mJ and repetition rate of 1 Hz. It yielded assemblies of well-separated nanopyramids and hexagonal nanocrowns. It was shown that structures shaped like a hexagonal crown with an internal diameter of less than 1 µm and a height of around 9 nm retain as yet ferroelectric properties.

In Ref. [484], laser NSL was employed to obtain arrays of gold prismatic NPs with different heights on a quartz substrate with the aim to study their optical properties. The authors observed intense absorption peaks related to surface plasmon resonances in the spectral range from visible to UV regions. It was shown that the peaks shifted to the high-frequency region with increasing NP height. Periodically structured Au(Fe) NP arrays around 80 nm in size were prepared on the quartz substrate using masks from polystyrene nanospheres 200 nm in diameter. Investigation of their optical properties revealed strong nonlinearity ( $\chi^{(3)}/\alpha = 6.15 \times 10^{-12}$  CGSE cm, where  $\chi^{(3)}$  is cubic susceptibility, and  $\alpha$  is the absorption coefficient) and fast optical response.

An effective laser NSL-based method for fabricating assemblies of hierarchical micro- and nanoparticles was developed in Ref. [486]. It yields structures that cannot be obtained by traditional lithographic techniques. This method was applied to produce hierarchical micro- and nanostructures of  $F_2O_3$ , ZnO, and CuO on a silicon substrate. Laser NSL was employed in Ref. [487] to fabricate ZnO NP assemblies using Pt, Au, and Ag catalytic templates overlaid on silicon wafers. The crystallinity and photoluminescent properties of ZnO NPs were studied. Pt templates were revealed to be the best catalyzer of this process. The PL spectrum of the ZnO NP assembly differed from that of a thin ZnO film due to the morphological difference between these materials and, possibly, different surface defects.

Periodic gold NP arrays on a quartz substrate were obtained by laser NSL in Refs [488-490] with the aim of studying their nonlinear optical properties using femtosecond laser pulses ( $\lambda = 800$  nm,  $\tau_p = 50$  fs). The mask was formed from polystyrene nanospheres  $820 \pm 5$  nm [488] and  $160 \pm 5$  nm [489] in diameter. The target material was ablated using an excimer KrF laser ( $\lambda = 248$  nm) with a radiation energy density of around 2 J cm<sup>-2</sup>. Assemblies of triangular gold NPs 190 nm [488] and 37 nm [489] in size were obtained along with gold NP assemblies measuring 37, 70, 140, and 190 nm [490]. It was shown [488] that gold NP arrays exhibit rather strong optical nonlinearity ( $\chi^{(3)} \simeq$  $(8.8 \pm 1.0) \times 10^{-10}$  CGSE). Such assemblies may find application in fast-operating nonlinear photonic devices and computer engineering. More data obtained by laser NSL can be found in review [491].

## 12. Laser nanoimprint lithography

### 12.1 Principles of the method

Traditional lithographic techniques make use of focused electron, ion, and photon beams to create functional nanostructures by means of physical or chemical modification of the resist overlaid on the surface treated. Nanoimprint lithography (NIL) is a high-throughput, scalable, and relatively inexpensive unconventional lithographic method for precision imprinting of nanostructures on polymer templates [446]. Unlike conventional lithographic techniques, NIL is based on direct mechanical deformation of resist material with the help of templates. Therefore, it allows overcoming constraints imposed on ultimate resolution by light diffraction and the electron or ion beam scattering. The main principles of mechanical nanoprinting, requirements for print templates, properties of the resist surface, and material essential for the successful replication of nanostructures are thoroughly considered in review article [446].

This section deals with other approaches to NIL for obtaining nanostructures and nanopatterns, which rely on applying lasers. The utilization of laser radiation in a nearfield conditions permits overcoming the diffraction limit and making nanostructures and nanopatterns measuring up to tens of nanometers [492, 493], while the employment of optically transparent nanospheres allows significantly enhancing laser irradiation by virtue of the lens effect [494–496]. It is these two factors—the use of the lens effect for transparent nanospheres and operation in the near-field mode-that constitute the basis of laser NIL. According to the Mie theory, irradiation of a sample surface with intense laser pulses passing through transparent nanospheres with a diameter exceeding the laser wavelength focuses and enhances laser radiation at contact points between the nanospheres and the sample surface. This leads to strong heating and melting of the sample at these points. Spreading of the molten material under the action of surface tension forces promotes the formation of nanoparticle-based assemblies [497]. Concrete examples of this process are considered in the next section.

#### 12.2 Fabrication of nanostructures

## by nanoimprint lithography

Reference [498] describes a method for making nanohole assemblies in thin (100 nm) Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST) films with the aid of a pulsed laser and transparent monodispersed nanospheres. Such films are characterized by a relatively low melting temperature (616 °C) compared with other materials. The method is as follows. A  $2 \times 2 \text{ mm}^2$  mask formed from transparent monodispersed nanospheres of SiO<sub>2</sub> or polystyrene (with diameters ranging 140-1000 nm) is applied to the film surface. At first, mask nanoparticles dissolve in a liquid and the resultant suspension is disposed onto the film surface. As the particles dry up, they self-assemble into an ordered close-packed monolayer hexagonal structure. Then, the nanosphere-coated film surface is irradiated by discrete pulses from a KrF laser ( $\lambda = 248$  nm,  $\tau_p = 23$  ns) with controlled energy densities in a range from 5 to  $11 \text{ mJ cm}^{-2}$ . The size of the laser spot having a uniform cross section  $(25 \times 5 \text{ mm}^2)$  exceeds the mask size.

It was shown experimentally that the diameter of the nanoholes thus obtained and the profile of the surrounding surface strongly depend on laser radiation energy density. Thus, nanohole arrays have similar diameters of 120 nm at a laser fluence of 5.8 mJ cm<sup>-2</sup> (Fig. 22a). Also, their shape remains identical up to 7.2 mJ cm<sup>-2</sup>. However, sombreroshaped bumps appear on the film surface at 8.5 mJ  $\rm cm^{-2}$ , and halo-shaped dents form at 10.5 mJ cm<sup>-2</sup>. The nanostructures of different shapes result from strong heating and surface melting of the film just under the nanospheres, giving rise to convective flows inside the liquid layer [497]. Thermocapillary and chemicapillary forces therewith change the surface tension [499]. Since the transverse distribution of nanosphere-enhanced laser radiation takes the Gaussian form, the temperature decreases from the center of the molten zone to its edge. Therefore, for a uniformly distributed film material concentration, the temperature gradient causes an outward flow of the molten material from the center to the edge, which causes the formation of holes, bowl-shaped rims around them, and nanodents. Calculations made in Ref. [498] showed that laser radiation passing through 1-µm polystyrene particles is locally enhanced up to 60-fold compared with incident radiation intensity. The laser beam is concentrated at a time into a spot of less than 100 nm in size in the lower part of the nanosphere (Fig. 22b). The distance between mask particles and the substrate surface is another important parameter, besides fluence, allowing control of the nanohole diameter. Its growth leads to an increase in the laser spot and, consequently, in the size of the resulting nanostructures (Fig. 22b). Both nanohole position and characteristics can be regulated by beam inclining to the surface [498, 500]. Thus, this method permits one to rather easily obtain periodic nanohole arrays in thin films and to control their parameters.

A limitation of laser nanoimprint lithography is that many materials whereout nanospheres are made turn out to be opaque to laser radiation with a small wavelength. For example, radiation of an excimer F<sub>2</sub> laser ( $\lambda = 157$  nm) is readily absorbed by many materials. Therefore, smaller nanospheres have to be used when forming small-sized structures. However, the smaller the monodispersed nanospheres, the more difficult it is to fabricate them. Smaller nanostructures may be formed using the 2nd, 3rd or 4th harmonics of a femtosecond laser ( $\lambda \approx 800$  nm). In this case,



**Figure 22.** (a) SEM image of nanohole arrays formed on the surface of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> thin film after one pulse of KrF laser irradiation ( $\lambda = 248$  nm) at a laser fluence of 5.8 mJ cm<sup>-2</sup> and an angle of incidence 0° [498]. (b) Radiation intensity distribution inside and outside a polystyrene particle 1 µm in diameter illuminated by a laser pulse at  $\lambda = 266$  nm. (c) Schematic of laser nanoimprinting [498].

the combination of nanosphere-enhanced light and the multiphoton absorption effect (see Section 13) makes it possible to obtain nanoholes and other small-sized nanos-tructures [498].

Other drawbacks of the laser NIL technique include: (1) difficulties in obtaining large masks (up to a few centimeters) by self-assembly of nanoparticles; (2) the necessity of removing nanospheres from the sample surface after each pulse, since they tend to re-deposit at nearby sites as contaminants; (3) the impossibility of reusing the nano-spheres, and (4) difficulties in preparing a complete nanopar-

ticle mask for imprinting the full-scale structure of a concrete nanodevice. Taken together, these drawbacks confine the scope of use of the method in nanoengineering.

A transparent mask applied to a quartz substrate as shown in Fig. 22c could be a feasible way to solve the above problems. The underside of the substrate surface is fabricated into half-sphere shapes by photolithography and chemical etching. As the laser beam propagates through the mask, the half-sphere transparent structures induce light enhancement and replicate the mask pattern onto the substrate surface. One of the key advantages of this method is that there is a fixed transparent mask available, and it can be utilized repeatedly, including sample irradiation with many laser pulses, to fabricate deeper nanoholes or other nanostructures.

Practical applications of the method being considered imply the possibility of structuring not only plane but also curved surfaces. A relatively simple method for preparing transparent nanosphere masks for the fabrication of nanostructures by laser NIL on curved surfaces was proposed in Ref. [501]. In this technique, a close-packed monolayer hexagonal structure of spherical SiO<sub>2</sub> particles is first formed by self-assembling on the glass surface. Then, it is trapped with transparent adhesive tape pressed to the glass and transferred to the sample surface to be structured by laser radiation. The authors of work [501] employed this method to treat with laser radiation the surface of a tube from a refractory material [Ti, which has a much higher melting temperature ( $\sim 1870$  °C) than many other metals]; the diameter of the tube measured 1 cm. By this means they demonstrated that the method can be applied to deposit micro- and nanostructures on the surface of many metals with a lower melting temperature than titanium. The diameter of the nanospheres forming the mask was 4.74 µm. Radiation was generated by an Nd:YVO<sub>4</sub>-laser ( $\lambda = 532$  nm,  $\tau_{\rm p} = 7$  ns, f = 1 - 30 kHz) at energy densities of 0.223-0.97 J cm<sup>-2</sup>. High energy density ( $\ge 0.5$  J cm<sup>-2</sup>) was associated with degradation of the adhesive tape (although it permitted 93% of the light to pass through) and deposition of its fragments onto the tube surface. At moderate energy density  $(0.379 \text{ J cm}^{-2})$ , the structure composed from isolated holes 200–250 nm in depth with a diameter from 1.0 to 1.2 µm formed on the tube surface. The interhole spacing equaled the nanosphere diameter. Hole diameter decreased to 437 nm at energy densities of up to 0.223 J cm<sup>-2</sup> (Fig. 23). No structures formed on the tube surface at lower energy densities due to the lack of Ti ablation.

Reference [502] describes the application of laser NIL for sample irradiation with only a few laser pulses using an assembly of monodispersed SiO<sub>2</sub> nanospheres 1 µm in diameter as the mask, and a KrF laser ( $\lambda = 248$  nm,  $\tau_{\rm p} = 15$  ns, f = 1 Hz). This approach allowed simultaneously obtaining over  $6 \times 10^6$  nanolines 360 nm in width, nanoholes, and homogeneous semicircular nanostructures over an area of  $5 \times 5 \text{ mm}^2$  of a thin (20-nm) eutectic Sb<sub>70</sub>Te<sub>30</sub> film overlaid on a polycarbonate substrate. Laser fluence ranged  $1-10 \text{ mJ cm}^{-2}$ . The shape of the structures was controlled by varying the angle of incidence of the laser beam on the surface. The minimal hole diameter was roughly 80 nm, i.e., much smaller than the diffraction limit for the laser wavelength; hole depth reached 20 nm. Thus, Ref. [502] demonstrated the possibility of fabricating differently shaped nanostructures by the laser NIL over a relatively large area by irradiating the sample with only a few laser pulses.



**Figure 23.** (a) Debris on a Ti surface at a laser fluence of 0.45 J cm<sup>-2</sup>. (b, c) SEM images of patterns generated on the Ti surface at 0.379 J cm<sup>-2</sup>. Inset shows the pattern generated at 0.223 J cm<sup>-2</sup> [501].

Periodic arrays of 42-nm high nanopeaks having a halfheight diameter of 260 nm were obtained in work [503] on a silicon wafer with the use of polystyrene nanospheres 1 µm in diameter and an excimer KrF laser ( $\lambda = 248$  nm,  $\tau_p = 23$  ns) at a radiation energy density of 150 mJ cm<sup>-2</sup>. Nanopeaks ~ 92 nm in height were fabricated in Ref. [496] under similar experimental conditions on the silicon surface by an excimer XeCl laser ( $\lambda = 308$  nm,  $\tau_p = 15$  ns) at a radiation energy density of around 200 mJ cm<sup>-2</sup>. The peaks alternated with 50nm deep cylindrical depressions ~ 570 nm in diameter, so that the overall peak height amounted to 142 nm. Irradiation by a



**Figure 24.** Results of sample irradiation by an XeCl laser ( $\lambda = 308$  nm,  $\tau_p = 15$  ns) at radiation energy density of about 200 mJ cm<sup>-2</sup> (a), and by a KrF laser ( $\lambda = 248$  nm,  $\tau_p = 30$  ns) at radiation energy density 166 mJ cm<sup>-2</sup> (b). In the former case, the peaks seem higher due to substrate deepening at their bases. Sample surfaces were not treated with a solution [496].

KrF laser ( $\lambda = 248$  nm,  $\tau_p = 30$  ns) at a radiation energy density of 166 mJ cm<sup>-2</sup> yielded 71-nm high and 340-nm wide peaks having no depressions at their bases (Fig. 24).

Importantly, submerging an array of nanosphere lenses used as a mask into a liquid together with the treated surface allows significantly extending the near-field region toward the incident laser radiation, thereby creating deep micro- and nanochannels by laser NIL both on the surface and in the bulk of the specimen [504]. In this study, a femtosecond laser  $(\lambda = 800 \text{ nm}, \tau_p = 110 \text{ fs}, E = 1 \text{ mJ}, f = 1 - 1000 \text{ Hz})$  and an assembly of SiO<sub>2</sub> nanospheres 5  $\mu$ m in diameter submerged into water on a quartz substrate were utilized to obtain arrays of regular peaks (cones) and depressions. Their characteristic size was  $\sim 60$  nm in the case of irradiation with isolated laser pulses at energy densities of 1 and 4.5 mJ cm<sup>-2</sup>, respectively. To sum up, the above studies showed that laser NIL allows one to obtain nanoholes in films and nanostructures and nanolines on their surfaces, to nanostructure metal surfaces, and to create micro- and nanostructures on the surface and in the bulk of transparent glasses. In other words, laser NIL may serve as a relatively simple and effective method of laser nanotechnology.

## 13. Laser near-field scanning nanolithography

It was shown in Section 5.5 that a scanning probe microscope provides a powerful tool for investigations into the morphological features of various surfaces with a resolving power of up to 1 nm. Once a special tip is attached to a flexible cantilever of this device, it can be operated both as a magnetic force microscope (MFM) and as an electric force microscope (EFM) [491]. An SPM was employed for the fabrication of nanostructures taking advantage of a sharp metal tip (needle) for direct writing on the substrate, and for the dip-pen nanolithography (DPN) regime with a pen-like tip scanned over the surface [505-509]. Molecules deposited on the pen were transferred to the substrate (target) surface. Such experiments are usually conducted in high air humidity when a water meniscus forms around the pen tip. Water makes up a medium through which molecules are transported from the pen surface onto the substrate. The DPN technique can be employed both to transfer molecules to a surface and to remove them from it. In other words, it permits realizing two nanotechnological strategies: 'bottom-up', and 'topdown'.

# **13.1** Combination of a laser and a scanning probe microscope for nanolithography

SPM in combination with a laser comprises a unique instrument for nanolithography [491, 510, 511], operating under usual conditions (in the air) with a high enough resolution ( $\leq 10$  nm), comparable to that of electron–beam nanolithography. The high resolution is due to the small distance d between the needle and the surface ( $\leq 5-10$  nm) that is much shorter than both the radius of curvature R of the needle tip and the light wavelength  $\lambda$  ( $d \ll R \ll \lambda$ ). The radius of plasmon localization in the needle-surface system is on the order of  $\sqrt{dR}$  [511] and decreases with decreasing d. Needle irradiation with a laser pulse excites plasmon resonance oscillations in this system that significantly enhance the local electric near-field in close proximity to the needle tip. Field intensity drops exponentially as d increases. High field intensity and localization enable the fabrication of nanostructures either directly by evaporation of the target material or directly by virtue of structuring the photoresist coating the substrate. Subsequent etching of the resist is performed by standard methods.

In Ref. [512], for instance, a femtosecond laser pulse  $(\lambda = 800 \text{ nm}, \tau_p = 83 \text{ fs})$  irradiated a sharp silicon needle of an SPM during controllable pattern printing on a thin gold film overlaid on the substrate (see Fig. 25 [491]). In this way, nanodot arrays on the film surface were obtained. The spatial resolution reached roughly 10 nm (Fig. 25b). During lithography, the needle worked as an antenna and ultrafast illumination of its tip with the laser pulse significantly increased the electric field (by a factor of 150 [512]). As a result, the foil was evaporated and removed from under the microscope needle tip. An advantage of the application of the femtosecond laser in this experiment lay in simultaneous realization of high spatial, spectral, and temporal resolutions.

In Ref. [513], the tip of a silicon needle of an SPM was illuminated with focused radiation pulses from an Nd:YAG laser ( $\lambda = 532$  nm,  $\tau_p = 7$  ns) second harmonic. The system was operated as an AFM to study the kinetics of nanostructure formation on the gold film surface. Nanoscale craters were produced. Spatial resolution run as high as 10 nm. The size of the craters was found to increase upon



Figure 25. (a) Experimental setup combining laser and SPM for surface nanostructuring. (b) Nanodot assemblies on the surface of a thin gold film [491]. Numbers indicate distances between the probe tip and film surface. Crater sizes increase as these distances decrease.

increasing the number of laser pulses, their energy, and the force acting between the needle and the film surface. Nanosecond pulses-unlike femtosecond ones-may heat the needle and increase its size. Therefore, the mechanism of nanostructure formation in this case appears to be either enhancement of the local field strength or thermally induced mechanical contact of the needle with the surface. Detailed calculations of the temperature dynamics in Refs [514–516] suggest that a rise in silicon needle temperature caused by laser radiation varies from 350 to 800 K, which is insufficient to remove the gold foil material. It is the authors' opinion that the main cause behind the formation of highly localized nanostructures is the enhanced intensity of the local electric field between the needle and the target surface. This method may find application in nanolithography and designing highdensity data recording and storage devices.

The disadvantage of above-considered technology lies in its relatively low throughput (the scanning rate is only a few micrometers per second), the necessity of precisely controling the nanoscale distance between the needle tip and the target surface, and the risk of contaminating the probe tips or damaging them. Another limitation consists in the small depth (up to 3–5 nm) of the resultant nanostructures and the difficulty associated with their treatment by etching [491]. Furthermore, the method is applicable only to very smooth surfaces but appears impracticable for homogeneous pattern printing when target roughness exceeds 50 nm [510]. At the same time, some publications demonstrate the possibility of its application in other situations. By way of example, it was successfully applied by the authors of Ref. [517] to produce nanostructures on the surface of a thin film so as to spell the letters 'DSI' (Data Storage Institute) in an area of only  $400 \times 400$  nm<sup>2</sup>. Importantly, the throughput of the method can be increased by using several simultaneously illuminated needles instead of a single one.

#### 13.2 Laser nanostructuring

#### with the use of a near-field scanning optical microscope

Near-field scanning optical microscopy (NFSOM) utilizes optical fibers to study the optical properties (reflection, transmission) of thin films [518]. The fibers are pulled by

heating, e.g., with a CO<sub>2</sub> laser, so as to conically shape their ends with a cone angle of  $\sim 20^{\circ}$  and an outlet aperture diameter of about 50 nm. The transmittance of such a system is roughly  $10^{-4} - 10^{-5}$  [519]. The cone surface is usually coated with an Al film to reduce light transmission losses. A conically shaped fiber tip is attached in the NFSOM operation regime to a tuning fork, the movements of which during the scan process are precisely controlled to keep the tip approximately 20 nm over the surface. In this configuration, the optical fiber operates in the near-field regime. The tip opening size of the optical fiber probe and its distance from the surface are much smaller than the light wavelength  $(\lambda = 200 - 800 \text{ nm})$ . The spatial resolution of such a microscope is less than 50 nm [520]. It can also be applied to fabricate nanostructures by passing reaction gases through the aperture and inducing local nanoscale chemical reactions on the surface, e.g., selective oxidation of the photoresist [521].

Figure 26a represents the layout of a typical experimental setup combining a laser with a near-field scanning optical microscope for nanotechnological applications such as the



**Figure 26.** (a) Schematic of a combination of a laser and a near-field scanning optical microscope intended for surface nanostructuring. (b) AFM image of the cross section of an ablated groove on a thin Cr film [491].

fabrication of surface nanostructures (Fig. 26b). Such a combination was employed in Ref. [522] to make 200-nm wide and 100-nm deep grooves on a thin chromium film by means of ablation using the femtosecond laser ( $\lambda \sim 260$  nm) third harmonic and an optical fiber with an aperture diameter of ~ 100 nm. The distance from the aperture to the surface measured 50 nm. The same method was applied in Ref. [523] to eliminate manufacturing defects in chromium film (i.e., to repair the film).

In the method being considered, the distance between the probe and the film surface is controlled by applying the feedback between the shear force and the controling device. This distance is a critical characteristic [524] determining both the size and the shape of the resultant structure because the laser-induced local electric field exponentially decays as the distance increases. At the same time, it greatly contributes to the nanofabrication process [525]. Reference [526] reports the fabrication of two-dimensional periodic structures with photonic crystals on the surface of a polymer (PPV) film using an He–Cd laser ( $\lambda = 325$  nm); the 32-nm high crystals had a lattice constant of 333 nm. Both the size and the shape of the lithographic structures were shown to strongly depend on exposure time. The use of the femtosecond laser ( $\lambda = 400$  nm,  $\tau_p = 100$  fs) 2nd harmonic and an optical fiber with an aperture diameter of 50 nm in Ref. [527] allowed comprehensively studying the influence of the irradiation dose on the size and shape of nanostructures on polymer films. It was demonstrated that the depth and the width of the structures increased with increasing radiation power in the case of a fixed writing speed ( $\sim 8 \ \mu m \ s^{-1}$ ). This method taking advantage of a nanosecond laser and optical fibers with the tip opening diameter of 200 nm has recently been applied in Ref. [528] to form structures on a silicon surface in an atmosphere of air and argon without subsequent etching.

Reference [529] shows that thorough control over laser radiation power and exposure time permits one to obtain nanostructures with a characteristic size of ~ 20 nm equaling ~ $\lambda/20$  ( $\lambda = 400$  nm is the laser wavelength) and ~ D/2 (D is the diameter of the microscope probe aperture). Such a high spatial resolution—comparable to the resolving power of electron-beam nanolithography—may be of use for manufacturing ultradense data recording and storage devices and developing new functional devices. The limitations of the method are the same as those described in Section 13.1, barring the fact that it can be used to fabricate deeper nanostructures in a shorter time. Detailed discussions of the issues considered in the present section can be found in reviews [491, 510].

## 14. Conclusions

The results of the studies reviewed in this publication indicate that considerable progress in the science of nanoparticles and nanomaterials and in nanotechnologies was made due to the application of lasers, which make it possible to fabricate nanoparticles; modify their size and size distribution, shape, and structure; clean surfaces; create core-shell and mixed nanostructures, as well as regular assemblies of NPs and nanostructures; study their dynamics and electronic, magnetic, and optical properties, and produce micro- and nanostructured substances and combine nanoparticles. Laser-assisted production of clusters and nanoparticles in molecular beams permits obtaining free clusters and nanoparticles of metals, liquids, and gaseous substances, and investigating the mechanisms of their formation and their properties [81–85]. Laser-generated cluster and particle beams are used to sputter thin films, synthesize new materials, and create micro- and nanostructures on various surfaces [81–85, 186].

Pulsed laser ablation of solid targets in a vacuum, the surrounding gas, or a liquid is a relatively simple and widely accepted method for the fabrication of nanocrystals and nanostructures having a variety of important advantages over other techniques. Laser ablation of targets in a liquid is especially suitable for obtaining metastable-phase nanocrystals, such as diamonds and related materials, and binary nanoparticles, including particles of inmiscible alloys. Both liquid and solid substances may be utilized at the initial stage of nanocrystal formation, which allows one to choose and combine the desired targets and solutions when obtaining nanocrystals and nanostructures of new compounds for basic research and potential applications [327, 328].

Considerable progress has been achieved in optical laser nanolithography, even though a number of complicated problems remain to be solved. This technique is employed to produce integrated circuits with the element's characteristic size R = 45, 32, and 22 nm. The new generation of nanolithographic technologies is represented by EUV lithography, which is expected to soon provide a basis for the large-scale industrially relevant production of ICs with the characteristic size  $R \leq 22$  nm [400–404, 418, 421, 422, 426]. In the near future, it is planned to move to EUV lithography in the 13.6nm range; thereafter, EUV lithography in the 6.5–6.7-nm range will be possible, and finally ICs with the characteristic size  $R \leq 10$  nm will be available [437–439].

Other laser nanolithographic techniques (interference, nanosphere, nanoimprint, near-field scanning laser nanolithography) are being successfully developed. IL turned into a powerful nanotechnology [440-445, 453, 454] for manufacturing large-area template nanostructures to be used in configurating nanoparticles and nanostructures, e.g., into compact assemblies of nanowires made from organic polymers for the production of light-emitting diodes, field transistors, chip-based sensors, and solar cells manufactured from organic materials [440, 467]. NSL technique is widely applied to produce periodic nanoparticle arrays finding application in fast-operating nonlinear devices for photonics, optics, and computer engineering [469, 491]. Laser NIL permits making nanoholes in films, creating nanostructures and nanolines on film surfaces, nanostructuring metallic surfaces, and creating micro- and nanostructures on the surface and in the bulk of transparent glasses; in other words, laser-assisted NIL constitutes a rather simple and effective laser nanotechnology [498, 501, 504]. Scanning nanolithography in a near field makes it possible to fabricate surface nanostructures, including two-dimensional ones and periodic structures of photonic crystals [491, 510, 529].

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