Nanostructures, magnetic semiconductors and spintronics

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Abstract

The aim of this paper is to give a brief overview of recent advances in the area of semiconductor nanomaterials, which represent extremely promising applications for materials with the spin-polarized transport of the charge carriers. It is shown on the basis of the last theoretical and experimental achievements that the development of diluted semiconductors with the controlled disorder and the wide energy gaps as well as the study of their molecular structures are very prospective routes for producing of novel magnetic semiconductors.

Keywords: Semiconductor; Spintronics; Nanostructure; Magnetic properties; Spin-polarized transport

1. Introduction

Modern nanoscience is the interdisciplinary branch of investigations, which covers physics, chemistry, biology and computational mathematics researchers to gain the well-controlled manipulation of objects (atoms, molecules and clusters) on the nanometre scale. The final goal is the “Bottom-Up” (atom-by-atom) or the “Top-Down” (layer-by-layer) fabrication of nanostructures with properties determined by the quantum mechanics mainly.

A permanent interest in this class of artificial materials is caused by the fact that physical properties of such solids can be well controlled and varied in very wide limits by changing matrix and filling materials, as well as the granular concentration and shape. In particular, it is possible to get a material with any preset conductivity in the range from a good metal to a good dielectric\[1–3\].

For instance, quantum dots have opened the brilliant perspectives for novel laser and optical sensor technologies. Application of the nanolayered materials is extremely perspective to produce the media storage devices, switching, lighting and other electronic elements. The essential part of nanoscience and nanotechnology encompass the development of the spin-electronics (spintronics and nanospintronics) materials production, nanoscale measuring devices and both “Bottom-Up” and “Top-Down” technologies. Nanospintronics, based on the usage of magnetic semiconductors, represents new area of science and engineering due to the perspective of the development and creation of principally new materials and devices for information technologies. These devices will use both the charge and the spin degree of freedom of carriers and will be free from the limitations inherent for the metal spintronic devices.

The significance of spintronics is stipulated by the prospects for development of new types of non-volatile memory with random access (MRAM), quantum single-electron logical structures, and ultra-dense information storage media. Thus, the elementary information storage unit will be represented by an electron spin\[4,5\]. In this case, probably, the limits of the information magnetic recording will be reached.

The realization of the spin-polarized current transfer opens up new possibilities for solid-state electronics as well. For instance, there are observations of spin-polarized luminescence and creation of high-frequency diodes, the output characteristics of which one can change with an external magnetic field\[6,7\]. Another example is the
possibility for creation of a new generation of narrow-band devices of the solid-state electronics of millimetre and submillimetre wave ranges like generators, amplifiers, receivers and filters, modulated and frequency tuned with the magnetic field and fully current controlled.

The discovery of giant magnetoresistance effect (GMR) by Pert and co-workers in 1988 [8] can be considered as a new important step for development of spintronics. This phenomenon is observed during the study of thin films with alternating layers of ferromagnetic and non-magnetic metals. It is found that, depending on the width of a non-magnetic spacer, there can be a ferromagnetic or antiferromagnetic interaction between magnetic layers, and antiferromagnetic state of the magnetic layer can be transformed into the ferromagnetic state with an external magnetic field. The spin-dependent scattering of conduction electrons is minimal, causing the small resistance of material when magnetic moments are aligned in parallel, whereas, for antiparallel orientation of magnetic moments, the situation is inversed. The GMR effect has clearly demonstrated that spin-polarized electrons can carry a magnetic moment through non-magnetic materials with saving spin coherence. This is the meaning of the term “spin transport” nowadays.

The sensors operating with the tunnel magnetic junctions (MTJ) fall into the second class of spintronic devices. Their ferromagnetic electrodes are divided by a very thin dielectric layer, and electrons are tunnelling through a non-conducting barrier under the effect of applied voltage. The tunnel conductivity depends on the relative orientation of the electrode magnetizations, and tunnel magnetoresistance (TMR); it is small for parallel alignment of magnetizations of electrodes and is high in the opposite case. In contrast (TMR); it is small for parallel alignment of magnetizations of electrodes, whereas, for antiparallel orientation of magnetic moments, the situation is inversed. The TMR effect has clearly demonstrated that spin-polarized electrons can carry a magnetic moment through non-magnetic materials with saving spin coherence. This is the meaning of the term “spin transport” nowadays.

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Due to this reason, the third trend in the development of spintronic devices is based on the development of multi-layer nanostructures of ferromagnetic semiconductors, which demonstrate the properties not available for their metal analogs. One can refer to a number of these properties such as the possibility of controlling the magnetic state of material with an electric field [10] and the giant planar Hall effect, which exceeds the Hall effect in metal ferromagnets by several orders of magnitude. The super-giant TMR effect observed for the first time in epitaxial (Ga,Mn)As/GaAs/(Ga,Mn)As structures [11] is not less promising for applications. There are no effective ways of injection of the spin-polarized current in non-magnetic semiconductors at the present moment [12,13]. The spin injection from magnetic semiconductors in non-magnetic ones gives good results in a number of cases [14], but while it takes place only at low temperatures, far from room temperature.

2. Spin-polarized transport in semiconductors

Recently, the anomalous Hall effect was observed above the room temperature in GaSb highly doped with Mn and containing MnAs nanograins [35]. Such material could be a good candidate for spin injectors.

The essential efforts of scientists are concentrated now on the preparation and studying of the spin-polarized transport in the nanosized multilayered structures including the alternating layers of ferromagnetic metals and non-magnetic semiconductors. The studies of metal-dielectric nanocomposites and methods of their manufacture also have a long history. Recently, the technological progress has ensured the development of a wide collection of new methods and techniques suitable for production of nanoparticles and nanomaterials, including nanocomposites. It is possible to classify these methods as the following:

- crunching in various mills with subsequent pressing and/or sintering [3];
- chemical methods, which consist of coating of granules by ligands or inorganic molecules and forming the materials from granules covered by insulating material [15,16];
- implantation of granules into monomers with subsequent polymerization, oxidation by the tip of atomic force microscope [17–19];
- filling pores of various porous materials, such as zeolites, opals, porous silicon and aluminum, with metals or semiconductors or use of these materials as a mask for nanostructure preparation [20,21];
- radiative methods, such as implantation and selective removal of atoms [22,23];
- imprinting (printing by nanostructured die) [24];
- various lithographic methods: laser interference photolithography;
- ultraviolet photolithography and electronic lithography [25].

The ion-beam sputtering (IBS), the electron-beam sputtering (EBS) and the magnetron sputtering (MS) are the most popular methods for granular material production, but one of the most universal method is IBS [26].

Production of composite films by the IBS and EBS methods is based on knocking out atoms, molecules and ions from the target surface, made from depositing material or its components with the subsequent precipitation of material ions on the substrate surface. Control of ion beam is performed by means of voltage applied to elements of the IBS (EBS) facility. Typical scheme of the IBS facility is shown in Fig. 1. Often an additional ion-beam source, not shown in this figure, is placed in the sputtering chamber with the aim to clean the substrate surface.

For the granular nanocomposite processing, the non-testability and insolubility of all its components is required,
in order to avoid mixing of separate materials that compose the nanocomposite. In particular, one should avoid the mixing and solubility of granules and matrix materials. Just by fulfilling these conditions, metal atoms will collect themselves into granules during the deposition process.

Obligatory condition for operation of almost any spintronic device is the existence of the efficient spin injection from a magnetoactive (ferromagnetic) material in a paramagnetic material alongside with the spin detection, control and manipulation. The main part in solution of this problem is devoted to searching of new semiconducting ferromagnetic materials, which are capable to be reliable and good spin injectors.

There are no effective ways of injecting the spin-polarized current in non-magnetic semiconductors at the present moment. The spin injection from magnetic semiconductors in non-magnetic gives good results in a number of cases, but while it has a place only at low temperatures, far from room temperature.

Recent observation of the anomalous Hall effect at room temperature in GaSb with embedded MnAs grains gives a good perspective for spin injection in normal semiconductors because in that case no Shottki barriers arises [35].

So-called magnetic discrete alloys are today the most prospective materials for solution of the spin injection problem. These alloys involve a periodic system of sub-monolayers of magnetic ions (for example, Mn), placed between semiconducting layers of (GaAs, GaSb, InAs) forming a magnetic superlattice. There are as incidentally distributed Mn ions and 2D magnetic islands of MnAs (or MnSb) as well in manganese containing layers (Fig. 2). The discrete alloys have high Curie temperatures (above 300 K for the GaSb-system), demonstrate extraordinary Hall effect at high temperatures and have a relatively high degree of the spin polarization.

It is possible in such systems to control not only quality of the border “ferromagnetic metal–non-magnetic semiconductor”, but also manage of the current carrier’s concentration and change the type of magnetic ordering.

The discrete alloys should be considered as random magnet systems owing to hardly inhomogeneous allocation of a magnetic phase in sub-monolayers.

The interest in so-called diluted magnetic semiconductors is given an impetus by the recent demonstration of the ferromagnetic critical temperature $T_c = 110\, K$ in GaMnAs. To date, most theoretical models proposed assume that the holes occupy a Fermi sea in the valence band [27].

Theoretical models of the virtual crystal approximation have been used to study the influence of disorder on transport and magnetic properties of magnetic semiconductors. The Boltzmann equation with the Born approximation scattering rates has provided estimates of the anisotropic magnetoresistance effect of order up to 12%. The key of understanding the kinetic and magnetic anisotropy effects is a strong spin–orbit coupling in the basic semiconductor valence band.

The most striking feature in the off-diagonal conductivity coefficients for example in (GaMn)As and other arsenide and antimonide of diluted magnetic semiconductors is the large anomalous Hall effect, which occurs because of the spin–orbit interactions. In the metals standard assumption is that the anomalous Hall arises because of spin–orbit coupling component in the interaction between band quasi-particles and crystal defects, which can lead to the skew scattering with Hall resistivity contribution proportional to diagonal resistivity. For diluted magnetic semiconductors, the anomalous Hall effect is based on the spin–orbit coupling in the Hamiltonian of an ideal crystal and implies the final Hall conductivity even without disorder.

Usually, two possible theoretical mechanisms for anomalous Hall effect are under discussion, they are the skew scattering and the side jump mechanisms. Recently, it was
suggested the new one which was called the intrinsic mechanism and which was pointed out to be the most important for DMS, especially in the case of 2D structures [36,37]. Studies of anomalous Hall effect in quantum well structures GaAs/InGaAs/GaAs delta doped with Mn show even qualitative agreement with above theory [38]. It should be mentioned that high mobility of such structures makes them perspective for spin-transistor structures.

The effects of the \( \text{As}_\text{Ga}–\text{As}_\text{Ga} \) transition to the ferromagnetism of (GaMn)As can be explained by the Mulliken orbital populations of the d-shell for both majority and minority spins and the corresponding spin polarization for the ferromagnetic configuration. In this case, the ferromagnetic coupling is strengthening considerably by the distortion, and that all together the energy splitting and Mulliken orbital population of \( \text{As}_\text{i}–\text{V}_\text{Ga} \) are the very similar to those of defect free (GaMn)As. These suggest that the ferromagnetic order in (GaMn)As is unaffected by the presence of \( \text{As}_\text{i}–\text{V}_\text{Ga} \) pairs. This result is in agreement with the hole-mediated picture of ferromagnetism, and can understood by noting that \( \text{As}_\text{i}–\text{V}_\text{Ga} \) defects energy levels show minimal splitting in (GaMn)As [28].

Experimental studies of disorder in DMS is not very popular yet, but it is started and it is shown that disorder in DMS causes a set of new effects (see Ref. [39]).

More detailed studies of disorders will combine Kondo description of the spin interactions as well as relevant Monte Carlo techniques applied to both metallic and insulating conditions.

3. Semiconductor nanostructures with wide energy gap

High-temperature semiconductors with wide forbidden zones are also the very promising materials for modern nanoelectronics. Materials based on carbon and boron provides complicated substances with unique structural properties. The technology for their film preparation is promising with their desirable electric and physical properties such as mechanical hardness and chemical resistance. Research conducted during the last decades of the 20th century have shown that carbon and boron crystals form clusters, the essential structural elements of which contain 4, 12, 60, or 84 atoms. These nanoelements, due to their thermodynamic properties, transform to amorphous or crystalline films, layers and their deposits, which have some advanced properties.

The clusters having a stable configuration under equilibration conditions take the forms of different geometrical figures—from triangular to dodecahedral and icosahedral.

Statistical calculations of the thermodynamic properties of small clusters carried out by means of computer modelling have shown that the potential energy of the atomic cluster components is the main factor determining the chemical potential of the cluster.

The growth of a cluster with \( N \) atoms leads to increase of the thermodynamic potential \( P(N) \) due to increase of atoms at the cluster surface. At the same time, the increase of surface energy accompanying the additional atoms is not continuous, but discrete because of the differences between the energetic contributions of the atoms completing the formation of the co-ordinating sphere [29].

Further growth in the aggregate leads an increase in the volume by means of a gradual addition of atoms from the sides to the growing cluster—volume growth. Using the established and recent approach to the mechanism of cluster formation, it is easy to show that the appearance of small particles analogous to the so-called fractal clusters very often takes place. Following this, the particle growth occurs not by the joining of separate atoms to their existing aggregate, but by a conglomeration of aggregates with stable configuration, which preserves their individual properties. The formation of small particles (clusters) is actually carried out by various methods, among which are supersonic outflow of vapours into the vacuum, thermo-, laser- and plasma-chemical modes of substance reduction from their gas-phase compounds, vapour precipitation upon cold substrates, reaction of molecular effusion from a cell, etc. These techniques are being used to study the process of the small particle formation, volume growth and growth on specially prepared surfaces.

The production of elementary boron is presently being developed by various powder and film technologies. The greatest interest is with modes of small particle production to provide high dispersion and purity as well as the study of the processes of cluster conception and growth.

Established theory and experiment have shown that the elementary boron atoms group into an aggregate of icosahedral form consisting of 12 boron atoms (B12). Designating the chemical potential of the structural element (in boron this is a 12-atom icosahedron, in carbon it is a four-atoms tetrahedron) as \( E \), and the chemical potential of the flat particles (cluster) as \( P \), it is apparent that an equilibrium between the longitudinal dimensions and flat cluster thickness will be achieved when \( \mu E - \mu P = 2\pi v/r \), where \( v \) is the specific surface free energy per one structural element, \( v \) is the specific volume of cluster per one structural element (this is analogous to the Gibbs–Thomson expression), \( r \) is the radius vector. Given that the equilibrium form is subordinated to the second order non-linear differential equation [30] and the difference \( \mu E - \mu P \) is constant over the whole surface of a particle, the solution of this equation represents the envelope of the cluster

\[
\overline{n} \overline{r} = \frac{2\pi v n}{2 \mu E - \mu P},
\]

where \( \overline{n} \) is the vector of the normal to the envelope (the surface) of the small particle as determined by the radius vector \( \overline{r} = r \) (the expression is analogous to the Curie–Wolf formula). From this equation, it is possible to evaluate the geometric form and longitudinal dimension of the equilibrium state of the cluster of elementary boron in flat form (Fig. 3) under given thermodynamic conditions.
During electron-microscopic studies and testing of the structure of elementary boron produced by means of boron three-chloride reduction with hydrogen and laser-chemical multi-photon dissociation of the dichloroboran molecule, the observed structural elements-boron icosahedrons, are statistically disseminated in an amorphous condition and in a crystalline condition with rhombohedral symmetry.

The electron microscopy pictures show that the particle has an amorphous structure, boron icosahedrons are placed non-regularly in the plane [31].

Boron particles partly overlapping each other are shown in Fig. 3. The particles form plane structures with longitudinal dimension 20–40 times as large as their thickness. The thickness is approximately equal to the linear size of 12-atoms of boron.

The space between the normal stripes is 0.8 nm, which is very near to the interplane space of planes (1 1 1) of \( \beta \)-rhombohedral boron \( (d_{111} = 0.7962 \text{ nm}) \) in crystalline structure and coincides with values calculated from interreflex space data. Thus, the direct observation of small particles of elementary boron using high-permissible electron microscopy shows that the boron clusters (2–5 nm) are the amorphous plane compounds where the ratio of the thickness to the longitudinal dimension varies from 1:10 to 1:40. These clusters which consist of non-regularly thermally treated small particles of boron proceed to crystallization, which at first occurs in the centre of a particle without its plane structure, then advances to the stage of a partly crystallized clusters, stratification and finally volume crystallization.

The elementary particles of boron produced by the plasma-chemical method in the free-poured state have shown an unknown effect—the appearance of a plant-shape cluster. In other words, the ultra-dispersive amorphous boron powder clusters consisting of statistically (non-regular) distributed icosahedrons have been found. The thermal treatment of the elementary boron powder, which consists of plane clusters, in a vacuum furnace as well as in the electron microscope’s beam resulted at first in a transition of icosahedrons from a statistical into a modulated condition and then their grouping into a volume rhombohedral configuration of crystalline boron of \( \beta \)-type. At the first stage, there has been observed a regulation of the icosahedrons in the flat form (Fig. 4), and then at the second stage a unification of these forms accompanied by the crystalline phase formation.

Similar results were observed in the case of ultra-dispersive carbon powders. The electron microscope studies show that the carbon powder consists of small structural elements in the forms of tetrahedral disks. On receipt of a very small portion of energy, they organized into the bigger clusters, sometimes the so-called fullerenes. In the electron microscope beam after treatment they become crystalline structures and in suitable thermodynamic conditions, become diamond.

The same situation occurs with carbon layers prepared by the laser spraying—laser plasma technologies [32].

The laser plasma deposition was used for boron and carbon thin film and layer production. Investigations have shown that the prepared crystalline layers have a diamond like structure with the lattice parameters close to crystalline diamond [33].

Recent experimental studies of small solids: particles, structural elements of some non-organic (carbon, cobalt, etc.) and biological systems (bio-molecules, bio-solids) have brought new data regarding the nature of the kinetics of their formation.

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Fig. 3. Electron microphotograph of boron particles, which are overlapping each other. The insert shows schematic picture of the cluster of 12-atom icosahedrons in the plane form.
References