SEMICONDUCTIVE NANOSTRUCTURES – MATERIALS FOR SPINELECTRONICS: NEW DATA BANK REQUIREMENT

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1 INTRODUCTION

Nanoscience, the interdisciplinary science that draws on physics, chemistry, biology, and computational mathematics, is still in its infancy. Control and manipulation on a nanometric scale allow the fabrication of nanostructures, the properties of which are mainly determined by quantum mechanics and differ considerably from that of the common crystalline state. Nanostructures constructed from inorganic solids such as semiconductors have new electronic and optical properties because of their size and quantization effects [1, 2]. The quantization effects reflect the fundamental characteristics of structures as soon as their size falls below a certain limit. An example of the simplest nanostructure is the quantum dot formed from the energy well of certain semiconductor materials with 5-10nm thickness sandwiched between other semiconductors with normal properties. Quantum dots, for example, have led to important novel technology for lasers, optical sensors, and other electronic devices. The application of nanolayers to data storage, switching, lighting, and other devices can lead to substantially new hardware, for example, energy cells, and eventually to the quantum-based internet. Nanoscience and nanotechnology encompass the development of nano-spinelectronics, spinelectronics materials production, and nano-spinelectronic measuring devices and technologies. Nano-spinelectronics, based on usage of magnetic semiconductors, represents a new and emerging area of science and engineering of the 21st century. It is a primary example of the creation and enhancement of new materials and devices for information technologies, operating with charge and spin degrees of freedom of carriers, free from present-day limitations. This new multi-disciplinary direction of science and technology is very much in need of support from new data banks, which will function as a source of new ideas and approaches.

2 SPIN – POLARIZED TRANSPORT IN SEMICONDUCTORS

An essential focus of nanotechnology scientists is concentrated on studying the spin-polarized transport in multilayer structures, which include alternating layers of ferromagnetic metals and non-magnetic semiconductors. The central task of such research is the creation of systems with effective spin injection into a non-magnetic semiconductor. The relevant work in solving this problem involves searching for and investigating new ferromagnetic materials, which are capable of reliability and of being good spin injectors. Among such objects the magnetic discrete alloys are very promising. They are multilayer systems composed of submonolayers of a ferromagnetic material in the matrix of a non-magnetic semiconductor, for example, Mn/GaAs or Mn/GaSb. It is well known that these alloys have high Curie temperatures and sufficiently high spin polarization. Also important is the possibility of controlling and managing the "ferromagnetic metal - semiconductor" boundary surface immediately during the synthesis of these materials. As has been investigated recently, these materials should be prepared only by the methods of MOS hydride epitaxy or laser epitaxy using pulsed annealing of epitaxial layers. These technologies are rather simple and, at the same time, allow the doping of layers under the over-saturated condition.

The study of the possibility of carrying electrons with spatially oriented spins (spin transport) from a magnetoactive (ferromagnetic) material in**to** a paramagnetic material represents one of most exciting areas of solid-state physics. This applied research in microelectronics is called “spin electronics engineering” or simply “spintronics”. The significance of spintronics is stipulated by perspectives of the development and creation of new types of non-volatile memory with random access (MRAM), quantum single-electron logical structures, and ultra dense information storage media. Thus, here the elementary information storage unit will be represented by an electron spin [3, 4]. In this case, probably, the limits of the information magnetic recording will be reached.

The realization of spin-polarized current transfer opens new possibilities for solid-state electronics also. For instance, there are observations of spin-polarized luminescence and creation of high frequency diodes, output characteristics which one can change by an external magnetic field [5, 6]. Another example is the possibility for

creating a new generation of narrow-band devices of solid-state electronics in millimetre- and submillimeter-wave ranges, such as generators, amplifiers, receivers, and filters, modulated and frequency tuned by magnetic fields and fully current controlled.

The discovery of the giant magnetoresistance effect (GMR) by Fert and colleagues in 1988 [7] can be considered undoubtedly as the beginning of the "Spintronics Era". This phenomenon was observed during the study of thin films with alternating layers of ferromagnetic and non-magnetic metals. It was found that, depending on the width of a non-magnetic spacer, there can be a ferromagnetic or antiferromagnetic interaction between magnetic layers, and an antiferromagnetic state of magnetic layer can be transformed into a ferromagnetic state by an external magnetic field. The spin-dependent scattering of conduction electrons is minimal, causing a small resistance of material when magnetic moments are aligned in parallel, whereas for antiparallel orientation of magnetic moments, the situation is reversed. The effect GMR has demonstrated, that spin-polarized electrons can carry magnetic moment through non-magnetic materials with spin saving coherence, is the meaning of the term “spin transport” nowadays.

The GMR effect has been used in a new generation of magnetic field sensors, which first appeared in 1994 as commercial products on the market. However, the present boom in industry that produced the information storage devices started a bit later, in 1997, when IBM presented the first hard drives with GMR reading heads. The implantation of this technology has allowed more than an order of magnitude increase in the density of the information storage on magnetic disks, and the size of the market of these reading heads already exceeds 1 billion US dollars.

Sensors operating with tunnel magnetic junctions (MTJ) fall into the second class of spintronics devices. Here ferromagnetic electrodes are divided by a very thin dielectric layer, and electrons tunnel through a nonconducting barrier under the influence of applied voltage. The tunnel conductivity depends on the relative orientation of electrode magnetizations. Tunnel magnetoresistance (TMR) is small for parallel alignment of magnetizations of electrodes and high in the opposite case. In contrast with the GMR of devices, electrodes are magnetic independent in this case and have different critical fields for changing the magnetic moment orientation. The first laboratory samples of ($NiFe/Al_2O_3/Co$) MTJ structures were demonstrated by Modera and colleagues in 1995 [8], where the TMR effect reached 12 % at room temperature.

Some of the large manufacturers of electronic technology, including IBM, have recently announced the development of new in essence memory devices, so-called MRAM [9]. These include storage units based on MTJ structures and allow users not only to increase essentially the storage density and the access speed to a memory but also to provide complete saving of data at the disconnection of the power supply. The first industrial designs of such memory devices appeared in 2003 in the commercial market. A disadvantage of these devices is the small scale of integration, bound with the necessity of using additional controlling transistors. The possibility of overcoming these limitations is connected nowadays only with the development of semiconducting spintronics and, in particular, with the creation of spin transistors. In this case, spintronic devices can not only switch or detect electrical and optical signals but also can enhance them and be used as multifunction units.

Because of this, the third direction in the development of spintronic devices is based on the development of multilayer nano-structures of ferromagnetic semiconductors, which demonstrate properties not available for their metal analogs. One can see in a number of these properties the possibility to control the magnetic state of a material by an electric field [10] and the giant planar Hall effect, which exceeds on several orders of magnitude the Hall effect in metal ferromagnets. The super-giant TMR effect observed for the first time in epitaxial (Ga,Mn)As/GaAs/(Ga,Mn)As structures [11] is no less promising for applications.

Surprisingly, the development of spintronics in the 20th century was driven practically irrespective of the semiconductor technology. Naturally, the association of these two directions is necessary for the purpose of combining well-controlled electronic properties inherent in semiconductors with additional possibilities for devices in which the spin degree of freedom of current carriers is used. This represents the essence of semiconductor spintronics, and the central problem today is the search for an effective method of spin injection in a semiconductor from the spin-polarized reservoir.

There are no effective ways to inject the spin-polarized current into non-magnetic semiconductors at the present moment, [12, 13]. Spin injection from magnetic semiconductors into non-magnetic ones gives good results in a number of cases [14], but it takes place only at low temperatures, far from room temperature. So-called magnetic discrete alloys [15, 16] today are the most promising materials for solving the spin injection problem.

These alloys involve a periodic system of sub-monolayers of magnetic ions (for example, Mn), placed between semiconductor layers (GaAs, GaSb, InAs) forming a magnetic superlattice. There are incidentally distributed Mn ions and 2D magnetic islands of MnAs (or MnSb) as well in manganese containing layers. These discrete alloys have high Curie temperatures (above 300 K for the GaSb-system), demonstrate extraordinary Hall effect at high temperatures [15, 16], and have a relatively high degree of spin polarization. It is possible in such systems to not only control quality of the border "ferromagnetic metal - non-magnetic semiconductor" but also manage the current carrier's concentration and change the type of magnetic ordering. The discrete alloys should be considered as random magnetic systems owing to inhomogeneous allocation of a magnetic phase in sub-monolayers.

3 NANOSTRUCTURES OF WIDE FORBIDDEN ZONE CONDUCTORS

High-temperature semiconductors with wide forbidden zones are also very promising materials for modern nano-electronics. Materials based on carbon and boron provide complicated substances with unique structural properties. The technology for their film preparation has advanced, and they have desirable electric and physical properties, such as mechanical hardness and chemical resistance. Research conducted during the last decades of the 20th century has shown that carbon and boron crystals form clusters, the essential structural elements of which contain 4, 12, 60, or 84 atoms. These nanoelements, because of their thermodynamic properties, transform to amorphous or crystalline films, layers, and other deposits, which have some advanced properties. Clusters having a stable configuration under equilibration conditions take the forms of different geometrical figures - from triangular to dodecahedral and icosahedrical [17, 18].

According to the classical idea of particle formation and growth and in correspondence with the so-called atomistic process of conception, atoms, the germ of the solid phase, unite in aggregates (clusters) where their quantity is dependent on their atomic potentials. Statistical calculations of the thermodynamic properties of small clusters carried out by means of computer modelling have shown that the potential energy of the atomic cluster components is the main factor in determining the chemical potential of the cluster. The elemental atoms in small aggregates can be packed according to the laws of crystallography together with that of non-crystallographic pentagonal symmetry. However, the pentagonal symmetry of clusters, despite its small deviation from crystallographic packing, is energetically less advantageous. This becomes particularly apparent when the crystal growth in the complex is accompanied by a corresponding increase in inter-atomic space.

The growth in the quantity N of atoms in the cluster results in the increase of the thermodynamic potential P (N), caused by the increase in atoms at the 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 [19]. Further growth in the aggregate [20, 21] leads to an increase in the volume by means of a gradual addition of atoms on 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, 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. Such volume clusters consisting of separate clusters of lesser dimensions have much lower density than the matrix substance. Often they are the simplest structural elements (tetrahedrons, cubes, bi-piramides, etc.), with one or several surfaces stuck together.

The formation of small particles (clusters) is actually carried out by various methods, among which are supersonic outflow of vapors 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 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 [22]. The greatest interest is in modes of small particle production providing high dispersion and purity as well as the study of the processes of cluster conception and growth. Established theory and experiment have shown that elementary boron atoms group into an aggregate of icosahedrical form consisting of 12 boron atoms (B_{12}) [23, 24]. Usually the boron small particles consist of one or more icosahedrons united in a cluster or various configurations depending on the thermodynamic conditions at formation.

Designating the chemical potential of the structural element (in boron this is a 12-atom icosahedron, in carbon it is a 4-atoms tetrahedron) as E and the chemical potential of the flat particles (cluster) as P, it is apparent that equilibrium between the longitudinal dimensions and flat cluster thickness will be achieved when:

$$\mu \text{ E} - \mu \text{ P} = 2\alpha v/r$$

where α is the surface specific 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), and r is the radius vector. Given that the equilibrium form is subordinated to the second order non-linear differential equation [25, 26] and the difference μ E - μ P is constant over the whole surface of a particle; the solution of this equation represents the envelope of the cluster:

$$\vec{n}\ \vec{r} = 2\alpha\ (\vec{n}\ )\ \nu\ /\ (\mu \text{ E} \quad - \mu \text{ P})$$

where $\vec{n}$ is the vector of the normal to the envelope (the surface) of the small particle as determined by the radius vector $\vec{r}$ = r (the expression is analogous to the Curie-Wulf formula [27]). 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.1) under given thermodynamic conditions.

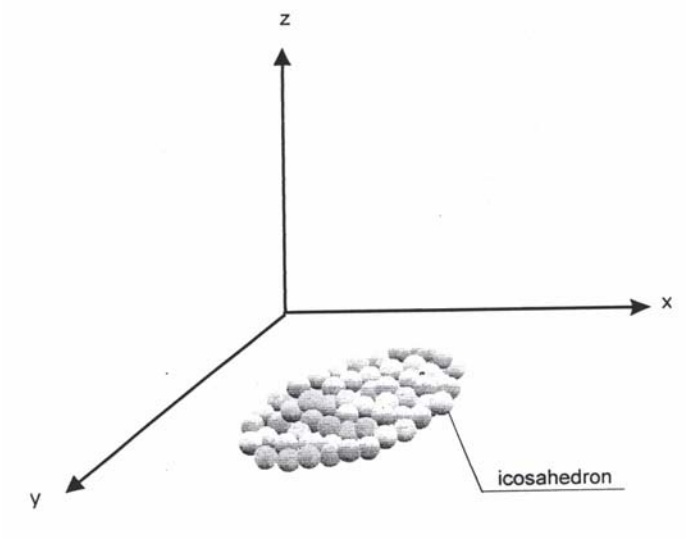

Figure 1. Schematic picture of a cluster of 12 - atom icosahedrons in plane form

During electron microscope studies and testing of the structure of elementary boron produced by means of BCL_3 reduction with hydrogen and laser-chemical, multi-photon dissociation of the dichlorboran molecule, the observed structural elements - boron icosahedrons - are statistically created in an amorphous condition and in a crystalline condition with rhombohedric symmetry. Investigation and testing were conducted with light-permissible electron microscopy (HEM) EM-100/OR "OPTON." The study used free-poured ultra-dispersed amorphous boron powder [27] produced by plasma-chemical reduction of BCL_3 with hydrogen.

During the electron microscope study with electron acceleration voltage of 100 kV, light-permissible pictures were produced with microscopic magnification 2×10^{-5}. The additional phase displacement caused by spherical aberration between non-dispersed and diffracted beams defocused the pictures, but this was compensated by the defocusing of the lens. Under the Schercer focus, the particularities of the initial structure of the specimen and its alteration under thermal absorption of the electron beam as well as under the thermal treatment of the particles in deep vacuum were observed. The electron microscopy picture shows that the particle has an amorphous structure; boron icosahedrons are placed non-regularly in the plane.

The analysis of the micro-diffractional pictures, consisting of three diffusion halos and supported by calculations of the interplane spaces, has given values consistent with those for the planes of the icosahedron B_{12}. A number of boron particles partly overlapping each other is shown in Figure 2. 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.

Figure 2. Electron microphotograph of boron particles which are overlapping each other

Thermal treatment of the boron powder in a vacuum $1 \cdot 10^{-6}$ Pa at a temperature of 800° C and for a period of 30 min. leads to the partial crystallization of the internal particle spheres (stripe contrast, typical of crystalline condition), while around these spheres, an amorphous structure is preserved. The analysis of the analogous electron microphotographs shows that the increase of the longitudinal dimensions of the particles under the thermal treatment occurs because of the joining of lammelar clusters formed from boron icosahedrons with an initial dimension 2-5 nm and icosahedron thickness as well as because of their stratification. The space between the normal stripes is 0.8 nm, which is very near to the interplanar space of planes (111) of β - rhombohedrical boron (d111 =0.7962 nm) in the 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 planar structure then advances to the stage of 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-shaped cluster [28, 29]. In other words, the ultra-dispersive amorphous boron powder clusters consisting of statistically (nonregular) distributed icosahedrons have been found. These clusters have an elliptic or ellipsoidal configuration with longitudinal dimensions some tens time the diameter of the structural element B_{12}.

The thermal treatment of the elementary boron powder, which consists of planar 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 rhombohedrical configuration of crystalline boron of β -type. At the first stage there was observed a regulation of the icosahedrons in the flat form (fig.3). Then at the second stage a unification of these forms accompanied the crystalline phase formation. The revealing of elementary boron structural elements in flat clusters characterized only by the near order is direct experimental corroboration of the energetic advantage of the existence of small particles with a flat geometry, of the existence of spaces during the growth of solids from atoms to a cluster, and further to a massive specimen in which the solid substance appears as a flat micro-formation consisting of statistically distributed structural elements (in the case of boron these elements are icosahedrons).

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

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 form of tetrahedral disks. On receipt of a very small portion of energy, they organized into 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 [30].

The Laser Spraying Method for film and layer preparation and its most attractive and an advanced development, Laser Plasma Deposition, were used for boron and carbon thin film and layer production (fig.4). The laser beam was focused on the target placed in the vacuum chamber. The films were deposited on the heated substrates with the temperature varying in the range of 300 – 1300 K. Plates of crystalline boron and carbon (graphite) were used as a target. The energy source may be repetitively pulsed or continuous as well as the other types of laser. These technologies are rather simple but allow the doping of layers under the over-saturated condition.

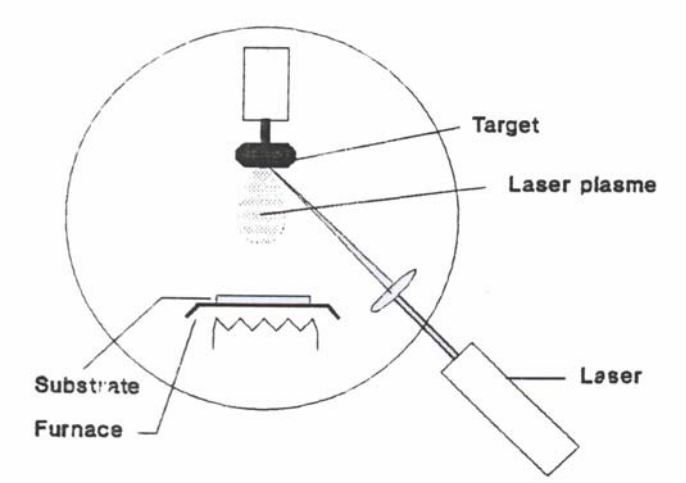

Figure 4. Schematic diagram of the Laser Plasma deposition method

Investigations have shown that the prepared crystalline layers have a diamond-like structure with the lattice parameters close to that of crystalline diamond [31]. Further study of small particles, and their initiation and growth will explain a number of natural phenomena of the formation of small solid structures.

The practical importance of this investigation consists of the possibility to create new technologies for the production of ultra-dispersive materials with given crystalline or amorphous structure and the requisite properties [32, 33]. Recent experimental studies of small solids - particles, and structural elements of some non-organic (carbon, cobalt, etc.) and biological systems (biomolecules, bio-solids) have brought new data regarding the nature of the kinetics of their formation.

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