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Interface design and processes of self-organization in nanosystems

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Abstract: The role of structural design of nanosystems, i. e. systems with high density of surfaces, boundaries and interfaces greatly increases as material science rapidly develops in the direction of molecular and atomic assembly technology of materials and constructions. The processes occurring in interface layers determine the unique properties of nanosystems. The evolution of a substance in a boundary layer tends to a stationary state corresponding to external conditions. For micro(nano)-systems interfaces corresponding to a symmetry dictated energy extremum can be selected as states -attractors. To optimize structural design, forecasting and achievement of desirable characteristics, the processes of internal structural self-organization of a system should be in resonance with processes of controlling external influences (synergy resonance principle). This approach, together with earlier developed crystallochemical methods of searching for symmetry preferred interfaces of heteroepitaxy, allows one to carry out modeling generation and experimental selection of nanosystems with desirable properties and purposeful nanodesigning to create new materials, structures and devices. In view these tasks the discussion concentrates on: (1) Processes of special boundary texture formation in order to obtain high stable magnetic properties of permanent magnets on the basis of Sm-Co powders; (2) Processes of structural self-organization and boundary design upon Bi, Bi-Sb nanofilm formation with a big length of electron mean free path; (3) Creation of coherent solid-state heterojunctions of superionic conductor- an electronic conductor in order to conserve fast ionic transport and low activation energy of ion-movement in the crystal layer interface. Formation of such heterojunctions is of the key role in the creation of new types of devices with high frequency - capacitance characteristics and a necessary element for the future information technologies, namely, wireless networks of autonomous microsensors and microrobots.

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Interfaces play a central role in nanoscience and nanotechnology and the progression: "possible-achievable-desirable" [1] in this area can be realized by modern methods of interface engineering. The general level of understanding of interface physics is noticeably lacking in many cases of technological interest. This is the reason of large actuality of investigating the influence of the interface atomic structure on functional possibilities of low-dimensional solid state structures and devices. The aim is to gain a control over materials and devices at the atomic level, so that materials with properties meeting the needs of Hi-Tech. could be designed. Nature's achievements are therefore benchmarks for our increasing control over nanosystems (NS) and their properties.

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1 Some thermodynamic considerations of nanosystems (NSs) with interfaces

In NSs with highly extended interfaces, almost all thermodynamic characteristics should undergo essential changes. The surface and interface phenomena are convenient to classify according to the generalized equation of the 1st and 2nd lows of thermodynamics:

$$dG = -SdT + VdP + \sum_i \sigma_i dA_i + \sum_j \mu_j dN_j + \sum_k Y_a dX_a \tag{1}$$

G is the Gibbs energy ; T is temperature;.V is volume; P is pressure; σ_i and A_i are the surface tension and the area of the surface (interface); μ_j and Ni are the chemical potential and the number of moles of i-th component; S is the entropy of the system; (Y,X) are other thermodynamic conjugated variables, acting in the system (for example, (φq)- electric potential and electrical charge; magnetic moment and magnetic field, etc.).

The entropy of an open thermodynamic system consists of two items:

$$dS = dS_i + dS_e \tag{2}$$

where dS_e is the external entropy contribution, i. e., energy transfer through external borders of the system, and dS_i characterizes the contribution of internal entropy, produced inside the system ($dS_i > 0$).

If the entropy delivery in a unit of time exceeds the internal entropy production ($P = dS_i/dt$) inside a system, i. e., $|dS_e/dt| > |dS_i/dt|$, then $dS/dt < 0$. This situation is possible in non-equilibrium systems because in an equilibrium state the item $dS_i > 0$ always prevails. For irreversible non-equilibrium processes, the entropy production (P) plays the same role as the entropy in equilibrium situations. All processes of structure ordering are caused by thermodynamic driving forces and directed to extreme values of thermodynamic parameters such as the entropy maximum near an equilibrium state or the minimum entropy production near a stationary state. According to[2] the evolution of non-equilibrium open systems during self-organization occurs under the conditions of minimum entropy production.

In NSs with a great density of interfaces, the contribution of item $\sum_i \sigma_i d A_i$ in the total system energy is big and its reduction can proceed by the shrinkage of interface area (A_i) via coalescence and coagulation of NS component parts, i. e. by interface movement, or due to surface tension (σ_i) reduction, i. e. the formation of low-energy interfaces. Thus, the interface energy can transform into other kinds of energy which cause to certain surface phenomena (change of reactivity, adhesion, interface diffusion, various electric effects, etc.).

In general, interfaces are non-equilibrium defects, but we can speak about local metastable equilibrium of a certain stationary interface under certain external conditions. Interface structures, both stationary and moving, are very diverse, from amorphous to crystalline, with high periodicity and they can undergo phase transformations under external fields. The evolution of a substance in an interface layer tends to a stationary state. Low energy interfaces corresponding to an extremum of energy, determined by symmetry[3-5], can be chosen as states-attractors in NSs.

By nature, NSs are open thermodynamic systems and their treatment is carried out under non-equilibrium conditions, therefore the evolution of a system during synthesis occurs in conditions far from equilibrium and the driving force of the process can be the system tendency to a minimum of entropy production.[2]. From this point of view, the formation of coherent low energy interfaces in NSs seems predetermined. Obviously, the synergy processes of structural self-organization which lead to the formation of a certain type of low-energy interfaces responsible for "unique" properties of a final material will have a pivotal value in NSs. An efficient control over complex NSs can be carried out only under the condition of adequacy ("resonance") of external influence of different fields (composition, temperature, deformation, electrical, magnetic fields, etc.) to the internal collective properties of NSs arising as result of self-organization [5].

2 High stable magnetic properties of permanent magnets (PM) on the basis of Sm-Co powders and processes of special boundary texture formation

High coercivity and/or high magnetization of PMs require special structures and chemical compositions. Magnetic properties of sintered permanent magnets (SPM) on the basis of $SmCo_5$-powders are strongly influenced by the appearance of secondary phases of Sm_2Co_{17}, Sm_2Co_7, Sm_2O_3, oxides and pores. The effect of microstructure exerts on the SPM magnetic properties is due to (1) the distribution of magnetic phase precipitates, oxides and pores in the structure; (2) misorientation and type of bonding among grains and (3) imperfection of the particle surface, i. e. the state of intercrystalline boundaries formed [6].

The appearance of coincidence lattices (CL) and special boundaries with reciprocal density of coincidence sites $\Sigma=7,13,19$ at certain rotations θ around the[0001] axis in the $SmCo_5$ lattice is shown in Fig. 1

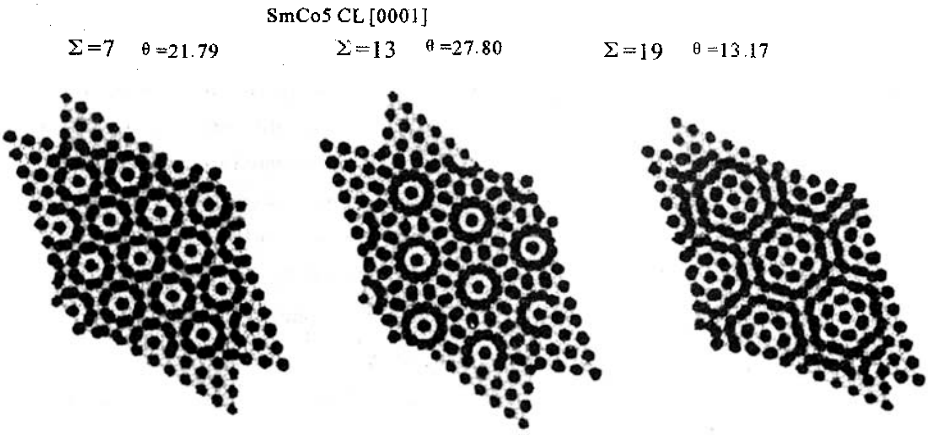

Fig. 1

Fig. 2 shows common cells and coincidence boundaries for interphase boundaries in $SmCo_5$- Sm_2Co_{17}, which observed in experiment[6]. The coercivity of $SmCo_5$- powder based SPM is strongly influenced by the perfection of intercrystalline boundary structures and secondary phase and pore distribution in the microstructure. The major coercivity decrease is found to be due to the appearance of a magnetically softer Sm_2Co_{17} phase. It is shown that powder $SmCo_5$-based magnets with the highest coercivity either had a single-phase $SmCo_5$ structure or a structure containing the $SmCo_5 + Sm_2Co_7$ phases. The predominance of special boundaries in polycrystalline structure of SPM (certain textures and boundary design) increases its density and decreases the number of defect sites for the nucleation of magnetization reversal domains. The preferential formation of the {111}R({0001}H texture has been observed for high coercivity SPMs. This texture facilitates the formation of the spectrum of low-energy special twist and tilt boundaries with the[0001] mutual grain rotation axis, coinciding with the main magnetic axis of $SmCo_5$. The formation of reverse domains at this type of boundaries is impeded in comparison with other types of boundaries.

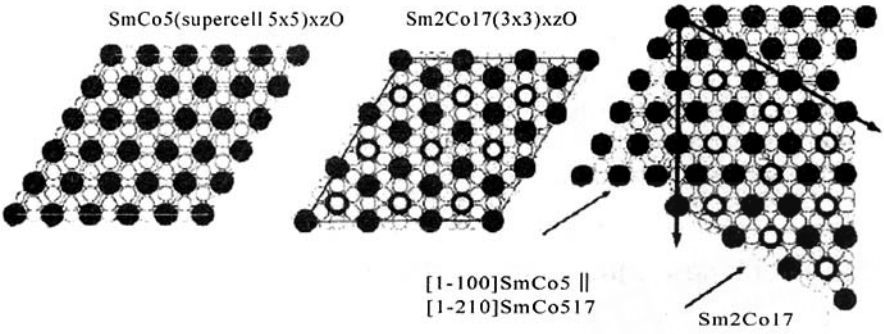

Fig. 2 Common cells and coincidence boundaries for interphase boundaries in $SmCo_5$ - Sm_2Co_{17}

3 Processes of structural self-organization and boundary design upon Bi, Bi-Sb nanofilm formation with a big length of electron mean free path

Bismuth is a promising material for metallic nanoelectronics. One of the limitations is caused by the short electron mean free path (less than 100 nm) in submicron Bi films, thus ensuring fast device operation. Such a short mean free path is believed to be due to the small grain size in Bi films which is usually 100-300nm. In [7-8] Bi films of 50-60nm in thickness with conducting electron mean free paths of 1.5 μm were obtained by thermal evaporation (TE) in a vacuum at 10^{-6} Pa. Such long mean free paths were explained by the strong influence of the grain boundary structure on the electrical resistivity of the submicron Bi films, which was improved during evaporation and/or recrystallization. The electron diffraction patterns of the large grains show that crystalline (111) R planes are parallel to the substrate surface. The mutual rotation axis and the angle between large grains often corresponds to low energy CL- type boundaries[8], transparent for moving electrons. Microstructure evolution of bismuth thin films in TE-method is represented in Fig. .3.

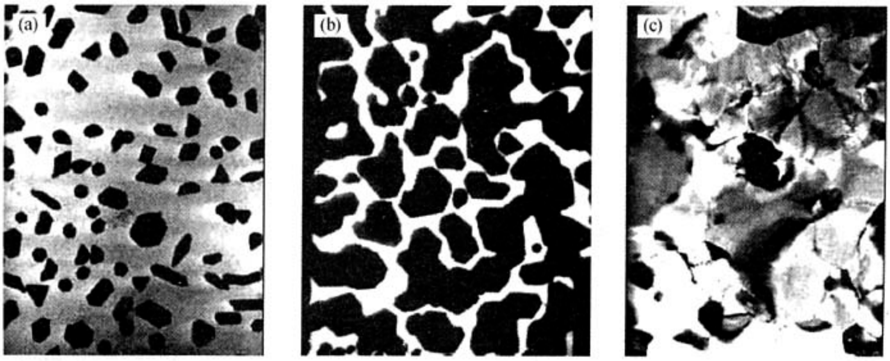

Fig. 3 Microstructure evolution of bismuth thin films deposited by TE on an amorphous (SiO_2) substrate at a temperature of 100 ℃

(a) — island structure; (b) — "labyrinth" structure; (c) — continuous film

Along with Bi films up to 60 nm thick grown by TE (deposition rate was 1. 5-3. 0 nm/min) the Bi and Bi-Sb (20 at. %) films up to 500 nm thick were grown by more non-equilibrium the self-ion assisted deposition (SIAD) with rate of 150-300 nm/min[9,10]. Both methods are characterized by processes of structural self-organization. The comparative analysis of processes of film formation in TE and SIAD methods shows, that increase of a part of the low ionized atoms in the condensed flux and application of external magnetic fields of the definite symmetry promotes display of the centers of epitaxial crystallization, decrease in temperature of epitaxial growth and give an opportunity to obtain perfect monocrystal submicron Bi films for nanoelectronics.

4 Crystal interface engineering in NSs of advanced superionic conductors (ASIC)

In papers[11,12] the interface approach "from advanced materials to advanced devices" is applied to nanosystems of ASICs which have exceptionally large unipolar ionic conductivity and are optimal for fast ion transport (FIT) crystal structures. Interface engineering at the nanoscale allows one to find the conditions and materials for synthesis of structure-ordered (coherent) ASIC/ electrochemical indifferent electrode (IE) interfaces with conservation of FIT in double electric layers (DEL) at the interface. Such functional coherent heterointerfaces are the basis for creation of solid-state nanoionic supercapacitors (NSC).

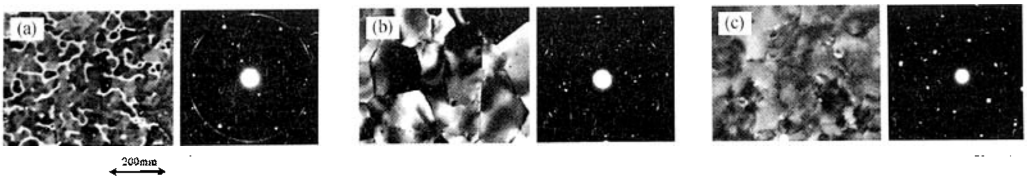

Fig. 4 Sequential stages of bismuth film growth on amorphous (si_3n_4) substrate at a temperature of about 80℃ (a) —"labyrinth"structure; (b) —continuous film; (c) —film annealed in a vacuum for one hour at the temperature 200℃. The film deposited by SIAD

A crystallochemical method for searching for symmetry perfect ASIC/IE interfaces [13,14] includes: (1) determination and selection of lattice matched materials of ASIC/IE heterojunctions; (2) selection of epitaxial interface orientations respondent to symmetry dictated energy extremum; (3) searching for non-Faraday ASIC/IE heterosystems based on thermodynamic considerations; (4) the analysis of the FIT channel arrangement in ASIC/IE heterostructures for a choice of high functional coherent interfaces. The first experimental attempt to create thin film IE/$CsAg_4Br_{3-x}I_{2+x}$/Ag heterostructure (prototype of NSC) with lattice- matched IE- metal alloy of cubic symmetry (space group Fd3m) with a spinel-type structure, ideally polarizable and with lattice parameters close to ASIC (elementary cell parameter 1. 124 nm) was realized [11,12]. The purposeful IE selection enables an increase of specific capacitance (ρ_C) of the $CsAg_4Br_{3-x}I_{2+x}$/IE heterostructure by several times even for a polycrystalline electrode structure and under insufficient vacuum conditions of synthesis. For dry air the heterostructure had $\rho_C \approx 3\ \mu F/cm^2$, and at the relative humidity 50% $\rho_C \approx 10\text{-}15 \mu F/cm^2$[12]. Now in high vacuum conditions, using interface design methods and self-organization processes under application of definite external fields the heterostructures with giant ρ_C are obtained[15]. These results can find applications for creation of NSCs, which may be used in the nodes of countless local wireless microsensors and microrobot networks[16], which will be built into the exponentially growing global data-processing world infrastructure.

5 Conclusion

These examples of interface design in nanosystems of various materials distinctly show that interface engineering methods are urgently needed for R&D of NSs , for the future development of new high-performance nanomaterials and devices.

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