CRYSTAL INTERFACE ENGINEERING & HIGH FUNCTIONAL METAL NANOSYSTEMS

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Abstract

Central to nanoscience is the assembly and manipulation of fundamental building blocks on a nanoscale level to create high-functional nanosystems (NS). Interfaces play a central role in NS, therefore information on the behavior of matter at interfaces is becoming increasingly important. The original crystal interface engineering methods and thermodynamic and synergy considerations are applied for the creation of high-functional metal NS. To optimize NS structural design and achieve desirable characteristics, the processes of internal structural self-organization of NS should be in resonance with processes of managing external influences.

From this standpoint, discussed are

1. processes of preferential formation of low-energy special boundaries to obtain high coercive sintered permanent magnets on the basis of SmCo$_5$ powder,
2. processes of structural self-organization and special boundary design upon the formation of bismuth thin films with a big length of electron mean free path. The films were deposited by the methods of different degrees of nonequilibrium (thermal evaporation and self-ion assisted deposition),
3. processes of managing external influences for raising the level of self-organization of the interface reaction zone in the CVD-method in order to obtain high conductive, with good adhesion, structure-stable thin tungsten films on a silicon substrate.

1. INTRODUCTION

Interfaces play a central role in nanoscience and nanotechnology and manipulation of interface structure on nanoscale allow the creation of high functional nanosystems (NS), including structures, materials, devices. NS are thermodynamically open and metastable, highly complex and heterogeneous in shape and substance, and dominated by interfaces. It is obvious that information on the organization of matter at interfaces, that is the atomic structure, composition, conformation and orientation of matter at interfaces becomes increasingly important. To optimize structural design, forecasting and achievement of high performance characteristics, the processes of internal structural self-organization of a system should be in resonance with processes of external influence of different fields (composition, temperature, deformation, electrical, magnetic fields, etc.) [1].

This approach, together with earlier developed crystallochemical methods of searching for symmetry-preferred interfaces of heteroepitaxy [2,3] allow the modeling generation and experimental selection of nanosystems with desirable functional properties. The paper is mainly devoted to the application of the original crystal interface engineering methods and synergy considerations for the creation of high functional metal NS.

2. THERMODYNAMICS CONSIDERATIONS OF NANOSYSTEMS (NS)

In NS with highly extended interfaces practically all thermodynamic characteristics should undergo essential changes. The surface and interface phenomena are convenient to classify according to the generalized equation of the $1^{st}$ and $2^{nd}$ laws of thermodynamics:

$$dG = -SdT + VdP + \sum_j \sigma_j dA_j + \sum_j \mu_j dN_j + \sum_k Y_k dX_k$$

(1)
$G$ is the Gibbs energy; $T$ - the temperature; $V$ - the volume; $P$ - the pressure; $\sigma, A$ are the surface tension and the area of a surface (interface); $\mu, N$ are the chemical potential and the number of moles of $j$-st component; $S$ is the entropy of the system; $(Y, X)$ are other thermodynamic conjugated variables, acting in the system (for example, the electric potential and electrical charge; the magnetic moment and magnetic field, etc.).

According to [4] the entropy of an open thermodynamic system consists of two items:

$$dS = dS_e + dS_i$$

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 the system, i.e. $|dS_i / dt| > |dS_e / dt|$, 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 nonequilibrium 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 to entropy maximum near an equilibrium state or to minimum entropy production near a stationary state. According to [5] the evolution of nonequilibrium open systems at self-organization occurs under the conditions of minimum entropy production.

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

In general, interfaces are nonequilibrium defects, but we can speak about local metastable equilibrium of a definite stationary interface under external conditions. Interface structures, both stationary and moving are very diverse, from amorphous to crystalline state with high periodicity, and they can undergo phase transformations under external fields. The substance evolution in the interface layer tends to the stationary-state. Low energy interfaces responding to an extremum of energy, determined by symmetry [2], can be chosen as states-attractors in NSs.

The available experimental data allow some conclusions concerning the macro- to nanostate transition: (1) NS formation is accompanied by the appearance of coherent interfaces; (2) polysynthetic twinning is a typical mechanism of NS formation during polymorphic phase transitions; (3) nanophases are stabilized by the host crystal due to the elastic strain energy of coherent interfaces and are metastably conserved under variable $P$, $T$, $P_{CO}$, $P_{H2O}$.

By nature, NS are open thermodynamic systems and their treatment occurs in non-equilibrium conditions, therefore the evolution of a system during the synthesis proceeds in conditions far from equilibrium and the driving force of the process can be the tendency of the system to a minimum of entropy production [5]. From this point of view the formation of coherent low energy interfaces in NSs is providential. Seemingly, the synergy processes of structural self-organization which lead to the formation of low-energy interfaces responsible for "unique" properties of a final material will have the pivotal value in NSs.
3. THE SPECIFIC PROPERTIES OF PHASE AND GRAIN BOUNDARIES CONTROLLING THE HIGH COERCIVITY OF SINTERED PERMANENT MAGNETS (SPM) ON THE BASIS OF Sm-Co ULTRADISPERSED POWDERS

High coercivity and/or high magnetization of SPMs require special structures and chemical compositions. The effect, a microstructure exerts on the coercivity of SmCo₅-type SPM, 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 formed intercrystalline boundaries. Secondary phases Sm₄Co₇ and Sm₂Co₁₇ are usually formed during the preparation of SmCo₅-type SPM. They appear as thin layers along the grain boundaries of the major SmCo₅ phase. The major coercivity decrease is found to be due to the appearance of a magnetically softer Sm₂Co₁₇ phase. The SmCo₅ powder based magnets with high coercivity had either a single-phase SmCo₅ structure or a structure containing the SmCo₅+ Sm₂Co₇ phases. The crystallographic parameters suggest that a multiple volume (topotaxic) correlation exists between the SmCo₅ (P6/mmm space group) and Sm₂Co₇ (P6₃/mmc space group) phases [6,7]. Therefore, interphase boundaries between these structures should have a rather good lattice matching. This is particularly characteristic of the boundaries in the basis plane of the (0001) hexagonal lattice, because elementary cells in this plane are virtually equal by their area in both planes and have the same point and translation symmetry and interface (0001 SmCo₅)/(0001) Sm₂Co₇ responding to an extremum of energy, determined by symmetry.

The distribution of spontaneous magnetization in magnetic materials has the form of a domain structure. The interaction of this structure with the grain and phase boundaries (major defects in ultradispersion systems) determine the magnetic properties of SmCo₅-type SPM. Intercrystalline boundaries are of crucial importance for the properties of solids prepared from ultradispersion powders. Among large angle boundaries, there are low-energy special coincidence boundaries whose structure is of high coherence. These boundaries arise at certain misorientation angles (θ) and are characterized by a reciprocal density of coincidence sites (Σ). As compared to an “ideal” lattice plane, any intercrystalline boundary has an excess free volume, which makes it more porous, facilitates impurity atom alignment in the boundary regions and boundary phase precipitations. These processes are typical for non-coincident structure disordered arbitrary boundaries.

The appearance of coincidence lattices (CL) and special boundaries with reciprocal density of coincidence sites Σ=7;13;19 at certain rotations θ around the [0001] axis in the SmCo₅ lattice is shown in Fig.1.

![Figure 1 Coincidence lattices and special grain boundaries with Σ =7; 13; 19 at certain misorientations (θ) of neighbouring grains around the [0001] axis.](image)

Fig.2 shows common cells and coincidence boundaries for interphase boundaries in SmCo₅–Sm₂Co₁₇, which were observed in experiment [6]. Note that interphase tilt coincidence boundaries (mutual rotation axis is in the boundary plane) appear in prismatic planes of the hexagonal Sm₂Co₁₇ phase (P6₃/mmc space group) and the angle of mutual rotations for the interphase boundary are close to that of a special grain boundary with Σ=13 in SmCo₅.
The predominance of special boundaries in the polycrystalline structure of SPM (certain textures and boundary design) increases its density, because special boundaries are highly coherent and have a smaller free volume than general (arbitrary) ones and decreases the number of defect sites for the nucleation of magnetization reversal domains because such nuclei are usually formed on the disordered intercrystalline boundaries in single magnetization axis SmCo$_5$-type magnets.

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 SmCo$_5$ SPM with the highest coercivity (~20kOe) had either a single-phase SmCo$_5$ structure or a structure containing the SmCo$_5$+ Sm$_2$Co$_7$ phases. The predominance of special boundaries in the 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 because such nuclei are usually formed on the intercrystalline boundaries in single magnetic axis SmCo$_5$-type magnets.

The preferential formation of the (111)$_R$=(0001)$_H$ texture has been observed [6,7] 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 misorientation 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.

**4. BOUNDARY DESIGN AND PROCESSES OF STRUCTURAL SELF-ORGANIZATION UPON Bi NANOFILM FORMATION WITH A BIG LENGTH OF ELECTRON MEAN FREE PATH**

Bismuth is a promising material for metallic nanoelectronics. One of its limitations is caused by the short electron mean free path (less than 100 nm) in submicron Bi (R$^{3}_3$m space group) films, thus impeding 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 [8] Bi films 50 to 60nm thick with conducting electron mean free paths of 1.5 µm were obtained by thermal evaporation (TE) in vacuum at $10^{-6}$ Pa [8]. Such long mean free paths were explained by a 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 transport properties of the Bi films depend on the grain size, boundary structure, impurity content, etc., which may considerably change the film conductivity at low temperatures particularly (for instance, to decrease the conductivity by 3-4 times at helium temperature). The tendency of Bi grains to decrease the surface and interface energy leads to the formation of the large-grained film with the preferential grain texture axis <00.1> oriented along the substrate normal. This axis of mutual grain misorientation (corresponding to the trigonal axis <111> in the rhombohedral presentation is a characteristic feature of low energy coincidence boundaries in bismuth (Table 1, Fig.3).
Table 1 Crystallographic parameters (rotation axis [HKL]R – in rhombohedral presentation and angle θ) of coincidence grain boundaries in Bi. (letters a,b indicate the coincidence lattices of the same reciprocal density of coincidence sites (Σ) but of different symmetry)

<table>
<thead>
<tr>
<th>Σ</th>
<th>[HKL]R</th>
<th>θ°</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>[111]</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td>[111]</td>
<td>38.21</td>
</tr>
<tr>
<td>11</td>
<td>[111]</td>
<td>87.39</td>
</tr>
<tr>
<td>13</td>
<td>[111]</td>
<td>27.79</td>
</tr>
<tr>
<td>17</td>
<td>[100]</td>
<td>69.33</td>
</tr>
<tr>
<td>19</td>
<td>[111]</td>
<td>46.82</td>
</tr>
<tr>
<td>21a</td>
<td>[111]</td>
<td>21.79</td>
</tr>
<tr>
<td>21b</td>
<td>[111]</td>
<td>21.79</td>
</tr>
</tbody>
</table>

In [9] the initial stages of growth of Bi films deposited by the methods of different degrees of nonequilibrium, such as thermal evaporation (TE, the deposition rate is 1.5-3.0 nm/min) and self-ion assisted deposition (SIAD, the deposition rate is 2-3 nm/sec) were investigated.

The Bi films deposited by TE on an amorphous substrate are formed by the Volmer-Weber mechanism and characteristically contain faceted islands of different orientations. Among the small isolated islands of different shapes, islands of triangular and honeycomb shapes can be discerned (Fig 4a). This island morphology corresponds to (111)R≡(0001)H orientation parallel to the substrate surface. The (0001)H plane is the lowest energy surface in Bi. The number of islands with such orientation increases with increasing substrate temperature. In comparison with the spectrum of islands observed in the high vacuum TE-method, no variability of island shapes was observed in the films deposited by the SIAD-method. Among the faceted islands, islands with triangular and honeycomb shapes were the most frequently observed. There were twins in some islands. This points out that during the film growth by the SIAD-method, islands of predominantly (0001) orientations are formed even at earlier stages.

In the TE–method the island interaction during crystallization on cold substrates occurs without coalescence. An abnormal growth of grains with (111)R≡(0001)H planes that are parallel to the substrate surface occurs during condensation on a warm substrate (100°C, Fig. 4). Annealing leads to a more perfect crystallographic texture and an increase in the number of grains with the (111)R orientation. The formation of ordered special grain boundaries, “transparent” for moving electrons leads to an increase of the film electron mean free path.

In contrast to the TE-method, the condensation of atoms via vapour-crystal mechanism by the SIAD-method occurs via a liquid phase because of the effect of a “thermal spike” [10] which is a result of ion bombardment. As a result, in the more nonequilibrium SIAD-method
(compared with TE-method) we can obtain films with a more perfect film structure and a high electron mean free path.

5. THE STRUCTURE ATOMIC MODELS OF W/Si INTERFACES AND PROCESSES OF SELF-ORGANIZATION OF INTERFACE REACTION ZONE IN CVD GROWTH OF THIN TUNGSTEN FILMS ON SILICON SUBSTRATE

Tungsten thin films are perspective materials for multilayered contact metallization of integrated circuits. Among desirable properties are a high melting point, low electrical resistivity, low activity of oxidation, high resistance to electromigration, high radiation hardness, etc. The main difficulties in fabricating W thin film microstructures are their sufficiently low adhesion to silicon and spalling of metal layers.

In [11] high–conducting, structurally stable thin tungsten films on silicon were obtained with specific resistance 8 ×10⁻⁶ ohm cm close to the value of a compacted metal. These films were produced via hydrogen reduction of tungsten hexafluoride by chemical vapour deposition (CVD) and gas-phase deposition with the plasmochemical stimulation of hydrogen. The characteristic feature of high-functional thin film heterostructures is formation of a W₅Si₃ self–limited nanometric sublayer at the W/Si interface. The experimental data on a CVD of tungsten onto silicon substrates are given in Table 2.

Table 2 Experimental data of the tungsten silicides formation during CVD and magnetron sputtering of the W thin film on silicon substrate

<table>
<thead>
<tr>
<th>№</th>
<th>The process</th>
<th>Temperature of the W₅Si₃ formation</th>
<th>Thickness of the W₅Si₃ sublayer</th>
<th>Temperature of the WSi₂ formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LP LT CVD W (WF₆/H₂)</td>
<td>W₅Si₃ formed at 100°C</td>
<td>~20 nm</td>
<td>WSi₂ formed at 600-700°C</td>
</tr>
<tr>
<td>2</td>
<td>LP LT HFP CVD W (WF₆/H₂)</td>
<td>W₅Si₃ formed at T&gt; 200°C</td>
<td>&lt;10nm</td>
<td>WSi₂ formed at 700-800°C</td>
</tr>
<tr>
<td>3</td>
<td>LP LT PE CVD W (WF₆/H₂)</td>
<td>W₅Si₃ formed at T&gt; 200°C</td>
<td>&lt;10nm</td>
<td>WSi₂ formed at 700-800°C</td>
</tr>
<tr>
<td>4</td>
<td>Magnetron sputtering</td>
<td>W₅Si₃ is absent</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The presence of the W₅Si₃ sublayer during CVD growth leads to high adhesion, the W/Si system stabilization, and formation of high quality functional structures. So the goal now is to understand these phenomena and find possible ways to enhance the control over and optimize the CVD-growth of high functional thin film tungsten nanostructures by applying the crystal interface engineering and synergy methods.

The low pressure (LP), low temperature (LT)-CVD of tungsten films is a nonequilibrium process with many variable growth parameters. The nucleation of a new phase occurs at the interface and is determined either by the composition of the intermediate interfacial layer (reaction zone) and by the energy required to form the compound. Therefore, both thermodynamic and kinetic arguments are necessary for the understanding of observed regularities.

The selective phase growth is determined by the composition of a reaction zone, which is possibly regulated by reagent flows in CVD. The resulting chemical reaction of the CVD-process can generally be defined as:

\[ I(g) + I(s) \rightarrow F(s) + F(g) \]  \hspace{1cm} (3)

where \( I(g) \), \( I(s) \) are the initial gaseous \( g \) and solid-state \( s \) reagents, \( F(s) \), \( F(g) \) – the solid-state and gaseous products of the reaction. That is, for initial gaseous reagents \( I(g) \), the reaction leads to formation of structural units of a precipitate layer \( F(s) \) and final secondary gaseous products \( F(g) \). For analyzed CVD of tungsten \( I(g) \) are WF₆, H₂; \( I(s) \) is Si; \( F(s) \) are WSiₓ (W, W₅Si₃, WSi₂, etc.); \( F(g) \) are HF, SiF₄, SiH₄, etc.

Figure 5 presents a schematic picture to illustrate the kinetic model of the CVD tungsten film formation on the (001)Si substrate from the gas phase WF₆/H₂. The two interfacial layers are indicated as 1 and 2. The free energy of hypothetical compounds is schematically drawn.
in Fig. 5 as a function of composition. Therefore, if interface 2 has the composition (a), the compound formed should be WSi$_2$, if the reaction zone composition is changed from (a) to (b), a new phase will form as W$_5$Si$_3$.

An effective heat of compound formation ($\Delta H^*$) as function of reacting components concentration in the reaction zone, can generally be defined as [12],

$$\Delta H^* = \Delta H \frac{C_{\text{lim}}}{N_{\text{lim}}}$$

(4)

where $\Delta H$ is the heat of the phase formation from pure components expressed in kJ/gm mol, the units for $\Delta H^*$, therefore, being kJ/gm atom. $C_{\text{lim}}$ is a relative concentration of a limiting component in the reaction zone, and $N_{\text{lim}}$ is the number of atoms of the limiting component in the formed phase.

According to the Walser and Bene postulate [13] the interface between two components under equilibrium conditions has an initial concentration which is near the composition of the lowest eutectic temperature in the silicide binary system. Table 3 shows the heats of formation for silicide phases in the W-Si binary system and the effective heat $\Delta H^*$ for the lowest –melting eutectic concentration.

![Figure 5 Schematic model to explain the compound formation in the CVD tungsten films on a silicon substrate, including thermodynamic and kinetic arguments.](image)

**Table 3** The heats of silicide formation for W-Si system in equilibrium conditions

<table>
<thead>
<tr>
<th>Phase, structure, crystal parameters</th>
<th>Composition</th>
<th>$\Delta H$ kJ/gm. mol.</th>
<th>$\Delta H$ kJ/gm. atom</th>
<th>$\Delta H^*$ kJ/gm. Atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition of the lowest eutectic of the W-Si system (accessible component concentration in reaction zone) W$<em>{0.01}$Si$</em>{0.99}$</td>
<td>W$<em>{0.63}$Si$</em>{0.37}$</td>
<td>-137.6</td>
<td>-17.2</td>
<td>-0.275</td>
</tr>
<tr>
<td>W$_5$Si$_3$ D8$_m$ 14/mcm z=4 Tetragonal a= 9.605 c = 4.964</td>
<td>W$<em>{0.31}$Si$</em>{0.67}$</td>
<td>-78.6</td>
<td>-26.2</td>
<td>-0.786</td>
</tr>
<tr>
<td>WSi$_2$ C11 14/mmm z=2 Tetragonal a=3.211 c = 7.868</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

On the basis of the above thermodynamic analysis and kinetic scheme the composition of the reaction zone (layer 2 in Fig.5) for a preferential formation of the W$_5$Si$_3$ silicide as compared to disilicide WSi$_2$ was determined. It is equivalent to the condition

$$\left|\Delta H^*_{w_5s_i_3}\right| \geq \left|\Delta H^*_{w_s_i_2}\right|$$

(5),

which can be fulfilled if the limiting atoms for W$_5$Si$_3$ and WSi$_2$ silicides (equation 4) are of different types, i.e. they are W for W$_5$Si$_3$ and Si for WSi$_2$. The calculations, that tungsten should be 2.8 times larger than silicon in the reaction zone for a W$_5$Si$_3$ sublayer to form. Such compositions of the reaction zone may be spontaneously achieved by internal processes of the system self-organization or by purposeful manipulations by reagent flows during the CVD of tungsten film growth.

Alongside with thermodynamic and kinetic factors the structure and energy of interfaces formed during CVD are very important. According to calculations of elastic strains
and interface structural models (fig. 6,7), sublayer $W_5Si_3$ has structural conformity (lattice matching) both to $W$, and to $Si$. Up to a certain thickness (~20nm) a more dense structure of $W_5Si_3$ (density is 14.523 g cm$^{-3}$ compared with $WSi_2$ g cm$^{-3}$) serves as an efficient diffusion barrier for the formation of other silicides with a higher silicon content, which leads to an abrupt decrease in conductivity.

The energy of nanosystem stabilization and formation of low--energy coherent interfaces are driving forces of the CVD of thin tungsten films. The matching of the CVD technique with the processes of internal structural self--organization allows obtaining high--conducting, structurally stable nanostructures of W on Si substrates.

**Figure 6** Lattice matching and model of the interface $W_5Si_3$(001)/Si(001)

**Figure 7** Lattice matching and model of the interface $WSi_2$ (001)/Si(001), lattice mismatch $\delta = 1.5\%$.

**6. CONCLUSIONS**

The processes of structure self-organization and formation of low energy interfaces are characteristic properties of nanosystems. The application of crystal interface design methods, comprehensive analysis of processes of structural self-organization and purposeful application of the external influence of different fields (composition, temperature, substrate orientation, deformation, electrical, magnetic fields, etc.) in nanosystems allow one to increase their controllability and to develop new high functional materials, technologies and devices.

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