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Organized Molecular Assemblies: Creation and Investigation of Their Functional Properties

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SUMMARY: One of the most important problems of modern chemistry, both preparative and theoretical one, is the creation of organized atomic - molecular assemblies i.e., atoms and molecules bound in a definite manner and interacting with each other, as a jointly, they become able to behave like an assembly, a single mechanism, to perform some functions, for example, to recognize separate molecules of environment (receptors), to transform an electromagnetic signal to electric field (photosynthetic), to memorize (memory cell), catalyze function and others.

The chemistry of preceding period had been developing as the science of properties and transformations of individual compounds and substances. At present the progress in the notion of the nature of chemical bonds, a new level of understanding of the chemical reactions mechanism, the knowledge of the regularities of nonstationary states in reactive media and the data on the at processes interfaces have determined the up to day problem of organized molecular assemblies with a required functionality.

Thermal oxidation of silicon crystals which is the key process in the technology of integral circuits production can be represented, in its main features, by the mechanism of semiconductor dissolving in the condensed phase. A characteristic feature of silicon oxidation is that the silicon activation energy of the limiting stage is lower than that of the formation of gas - phase monoxide , difference being the energy of siloxane net reorganization in silicon dioxide. The analysis shows that within the row of possible systems semiconductor - dielectric, it is silicon - silicon dioxide that is distinguished by a maximum self - organizing effect. This is one of the main reasons why only silicon could be chosen among large number of semiconductor substances for use in the technology of integral circuits.

A molecular system of amphiphilic long - chain molecules, obtained according to the Langmuir - Blodgett method is an example of simplest assembly on the basis of

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which the elements of gas sensors can be prepared, as well as the systems of quantum dots, the objects of the low - dimension physics.

We have investigated assemblies constructed from multimolecular compositions using the Langmuir - Blodgett technique and thin - layer systems based on glassy and amorphous silica films with fragments of organic molecules introduced into the matrix.

Molecular engineering is a new level of the modern preparative chemistry; moreover, it is a system of concepts introducing a new culture in technology. In this sense, it is most important to realize the evolution principle in the strategy of science research.

Introduction

The notion of an organized molecular assembly has become current about 20 years ago. This concept is connected with the origination of a new strategy of scientific research which has received the name of molecular engineering. This direction can be characterized by the words of H. Kuhn who is among the pioneers of this field:

Molecular engineering - the design of a complex system of molecules that interlock and interact like the parts of a machine and the search for possibilities to construct it - is a great challenge, particularly in preparative chemistry. In the past and at present chemists main interest is in the isolated molecular species. Investigating pure substances has turned chemistry into a modern science. Today chemist is challenged to construct organized systems of interlocking and cooperating molecules. The synthesis of molecules for the purpose of being components of an assembly designed as an "intelligent" device should be a fascinating and promising new goal in preparative chemistry with potential interest in developing microelectronics, integrated optics, memories with high storage capacity, micro-sensors, new catalysts for complex reactions, and arrangements for solar energy conversion.

Attempts to engineer at molecular level are certainly strongly stimulated by molecular biology showing how molecules interact in biosystem forming highly intricate machineries. But molecular engineering has its own style and attitude to approach problems, quite different from molecular biology, - Andre Barraud would say its own culture - and this particularity should be emphasized.

Two very different features of molecular engineering should be considered. Molecular engineering as a tool to construct organized molecular aggregates - organizates - , and molecular engineering as a style of thinking in terms of molecular machines: the search for principle types of molecular machines, principle pathways to their design. How to design a *molecular machine for a given task and invent ways to construct it? Or in much broader sense, how can complex molecular machines originate and develop under appropriate conditions? In what ways can they develop, what can molecular machines do, what possibilities for their action can we imagine?*[1)].

The goal of the present report is to discuss the concept of an organized molecular assembly. This notion will be shown to bring a new methodology of investigations and technological applications into modern chemistry, both the preparative and theoretical one. This concept which arose under strong influence of molecular biology has deep foundations in physical chemistry. The analysis of the history of this question allows us to generalize the concept of an organized molecular assembly.

General characterization and classification of organic molecular assemblies

A distinctive feature of the organized molecular assembly is the ability to produce a response corresponding to a definite perturbation of the system, or functionality. Speaking of an organized molecular assembly we assume it to be condensed, i.e. solid or liquid. For gases, this notion is identical to that of a chemical compound.

A substantial feature of an organized molecular assembly is the presence of a matrix which is a compound of the known chemical composition and structure. Single atomic or molecular units comprising an assembly are incorporated in a definite manner into a matrix and undergo electron-phonon interaction with it. As far as the quantitative aspect is concerned, these assemblies are often present at a low level. Because of this, many physicochemical and thermodynamic properties of the matrix can insignificantly differ from the properties of an individual compound. The presence of an organized molecular assembly can be revealed only by its response to a specific perturbation of the system (matrix - organized molecular assembly).

Individual characteristics of an assembly are its chemical composition and the short-range grouping order of atoms or molecules comprising it. The simplest assembly consists of a single atom, e.g. as a defect or impurity in the lattice or as a molecule incorporated into the inner cavity of a structured liquid of which water is a classic example. The connection between the matrix and the assembly can be performed via weak intermolecular interaction as in the case of micelles formation. In another limiting case, the interaction can be realized through the formation of strong covalent bonds. An example is the formation of receptor centres in polysiloxane matrix. The position of the assembly in the matrix is governed by the system preparation method and by the structure of the matrix. Cases are possible when the assemblies are distributed over the volume of the matrix at distances comparable with the size of the assemblies themselves. This case represents a three-dimensional topology of their distribution. In case if the assemblies are distributed over a plane this is a two-dimensional system. Examples of a unidimensional system of the assemblies will be presented below. Finally, when the assemblies are distributed in the matrix at distances much longer than the size of a single assembly, we speak of a zero-dimensional system.

The methods of preparation of the organized molecular assemblies are various. For example, the assemblies can be obtained as a result of a thermodynamically equilibrium process or as a product of self-organization of definite chemically interacting media. A convenient method to prepare the assemblies is the Langmuir-Blodgett procedure which involves consequent transfer of monomolecular layers of amphiphilic molecules from the surface of the liquid phase onto the solid substrate. Other methods to prepare molecular assemblies are the processes of sequential adsorption of several components (molecular layering), joint coagulation, e.g. with the participation of polysiloxanes (sol-gel technology), processes involving the participation of intercalates and matrices with large inner surface like silica gels and zeolites2).

The whole possible variety of organized molecular assemblies is characterized in Table 1 in a compressed form according to the matrix type and the topology of their distribution.

The functionality of the assembly is determined by the ability to produce a response to one or another action upon the system. For example, if the registered characteristic is the change of the chemical composition of a medium, the assembly acts as a catalyst. If chemical interaction is accompanied by the change of the field or by the charge transfer, the assembly acts as an odour receptor or as a chemical sensor. In the case when the chemical composition of a medium is changed under the action of photons, the assembly acts as a photosynthesis cell. These examples help one to understand the character of other assemblies listed in Table 2.

Organized molecular assemblies of three-dimensional topology

In 1940, R.L.Muller, Professor of the Leningrad University, proposed in his Dr. of Sciences Thesis to use the notion of structural units to describe vitreous solids3). This approach was developed in the works of S. V. Nemilov4).

A structural unit is a minimal possible set of atoms in the nearest coordination sphere which depicts the coordination of a given atom and the features of its building into the material matrix. The basic structure of quartz glass corresponds to the formula $SiO_{4/2}$. So, an assemble

Tab.1. Characteristic examples of organized assemblies

Topological type of an assembly	Matrix type			
	Crystal	Glass or amorphous solid	Liquid	Multimolecular systems
Three-dimensional	Defects, impurities	Assemblies of structural units. Supported catalysts. Clathrates. Zeolites.	Structured liquids, H_2O	Liquid crystals. Peptides.
Two-dimensional	Adsorption layers. Superstructures. Graphite compounds.	Supported catalysts.	Liquid surfactants. Langmuir layers.	Langmuir-Blodgett layers.
Uni-dimensional	Molecular beam epitaxy on the GaAs (311) surface	Sulphur. Selenium. Sulphur nitride.		Polyacetylenes.
Zero-dimensional	Quantum points	Nanoclusters distributed over polysiloxanes.	Micelles.	Semiconductor nanoclusters.

Tab.2. Functionality of molecular assemblies differing by the character of response for a type of action

Action Response	Chemical	Photons	Electric field
Chemical	Catalyst	Photosynthesis cells	Ion pump
Configuration changes	Odour receptor, chemical sensor	Memorizing unit	Valve,switch, molecular conductors, Memorizing unit
Charge transfer		Energy converter, Memorizing unit	
Photons		Non-linear optical converter	Light emitter

composed of 5 atoms built in the matrix by covalent bonds allows us to describe many properties of the glass. It became clear that, depending on the methods of glass preparation, it is also necessary to consider other types of structural units. in particular, an assembly of the type $Si_{1/4}$-O-$Si_{1/4}$ with the SiOSi angle varying within the range 90° - 180° describes the formation of inner cavities in siloxane systems and determines the adsorption properties of silicon dioxide (Fig.1).

$SiO_{4/2}$ $Si_{2/4}O$

Fig. 1: Two types of structural units describing short- and middle- range order in silicon dioxide matrix.

Amorphous layers of silicon, silicon nitride, and silicon dioxide obtained by chemical vapour deposition are not individual compounds. Their structure should be described by a set of structural units. As an example, Table 3 shows the set of structural units necessary for the description of silicon nitride layers properties[5)].

Tab.3. Characteristics of structural units

Structural unit	Type of reaction	Reaction enthalpy / kcal/mol
$SiN_{4/3}$	$SiH_4+4/3NH_3 = SiN_{4/3} + 4H_2$	-51
$SiN_{3/3}(NH)_{1/2}$	$SiH_4+3/2NH_3 = SiN_{3/3}(NH)_{1/2}+4H_2$	-42
$SiN_{2/3}(NH)_{2/2}$	$SiH_4+5/2NH_3 = SiN_{2/3}(NH)_{2/2}+4H_2$	-34
$SiN_{1/3}(NH)_{3/2}$	$SiH_4+11/6NH_3 = SiN_{1/3}(NH)_{3/2}+4H_2$	-26
$Si(NH)_{4/2}$	$SiH_4+2NH_3 = Si(NH)_{4/2}+4H_2$	-18
$Si(NH)_4$	$SiH_4+4NH_3 = Si(NH)_4+6H_2$	+62
$SiN_{3/3}Si_{1/4}$	$5/4SiH_4+NH_3 = SiN_{3/3}Si_{1/4}+4H_2$	-44
$SiN_{2/3}Si_{2/4}$	$6/4SiH_4+2/3NH_3 = SiN_{2/3}Si_{2/4}+4H_2$	-35
$SiN_{1/3}Si_{3/4}$	$7/4SiH_4+1/3NH_3 = SiN_{1/3}Si_{3/4}+4H_2$	-27
$SiSi_{4/4}$	$2SiH_4 = SiSi_{4/4}+4H_2$	-19
$HSiN_{3/3}$	$SiH_4+NH_3 = HSiN_{3/3} +3H_2$	-38
$H_2SiN_{2/3}$	$SiH_4+2/3NH_3 = H_2SiN_{2/3}+2H_2$	-26
$H_2Si(NH)_{2/2}$	$SiH_4+NH_3 = H_2Si(NH)_{2/2}+2H_2$	+25

It is the presence of the groups incorporating N-H and Si-H bonds that determine the memorizing effect of silicon nitride layers. This effect is the foundation stone of MNOS memory elements.

The presence of the assemblies of structural units of the type $HSiSi_{3/4}$ and $H_2SiSi_{2/4}$ in the layers of amorphous silicon determines electrical conductivity of these layers used in solar elements.

These assemblies are built into the matrix by means of covalent chemical bonds. An interesting type of the assembly composed of single molecules bound in the matrix by means of weak intermolecular interactions was discovered in our studies into the kinetics of semiconductors dissolving in liquids^6). It is known that a germanium crystal is readily dissolved in polar solutions containing bromine. Not only Br_2 molecules are the reagents but also the molecules of the solvent, for example H_2O and CH_3OH. Fig. 2a shows the changes of germanium dissolution rate in a solution containing a fixed concentration of bromine and varied concentration of CH_3OH in CCl_4. A maximum dissolution rate corresponds to a maximum content of single CH_3OH molecules not associated by hydrogen bonds. This conclusion is confirmed by independent spectra studies.

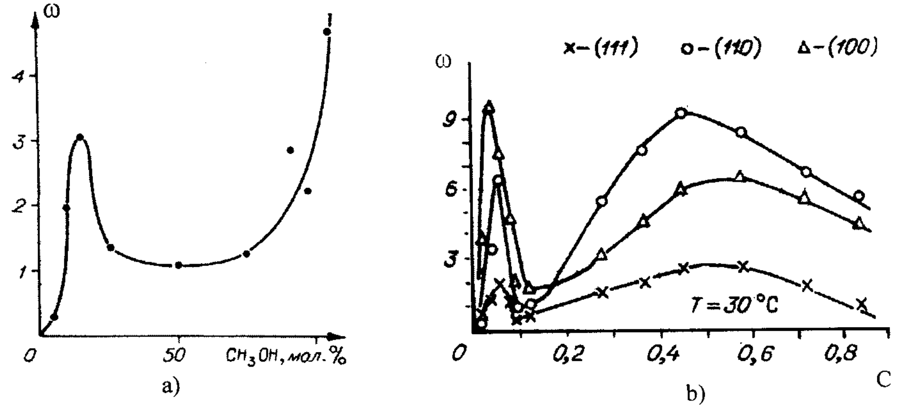

Fig. 2: The effect of assemblies of single solvent molecules on the dissolution rate of Ge and Si crystals. **a)** dissolution of Ge in the solution of Br_2 in CH_3 + CCl_4, **b)** dissolution of Si in aqueous ethylendiamine solutions. **C** mol parts ethylendiamine, ω - g.atoms/ cm^2 s, c- mol %.

Similar single-molecule assemblies can also be observed in aqueous solutions of ethylenediamine during the dissolution of silicon crystals (Fig. 2b)^7).

An example of organized molecular assemblies with an ordered three-dimensional distribution over a multimolecular matrix was shown in our work[8)]. The use of diacetylene derivatives of pyridine and amides according to the Langmuir-Blodgett procedure allows to obtain a system containing receptor centres adsorbing H_2S or SO_2 reversibly. It is essential that the amount of the gas adsorbed is proportional to the relative amount of receptor centres in the layer and to the total number of layers.

Organized molecular assemblies of two-dimensional topology

The idea of two-dimensional distribution of active assemblies was put foward by N.I.Kobozev in 1939[9)]. The theory describing the formation of catalytically active assemblies was based on the experiment which demonstrated that the catalytic action of iron in the reaction of ammonia synthesis was independent of the type of carrier (carbon, asbestos). It was found that the active assembly participating in this reaction is organized of three iron atoms[10)]. Further studies involving supported catalysts confirmed the conclusion that the assemblies composed of single metal atoms are catalytically active[11)].

Explicit description of two-dimensional assemblies makes us come across the phenomenon of self-organization of the interphase boundaries. Perhaps we were the first to pay attention to this fact in our work[12)].

When studying self-organization it is natural to use the ideas developed in the works of I.Prigozhin[13)] and the further works[14,15)]. The major idea is as follows. The evolution of an open system exchanging energy and substance with the environment can proceed with the occurrence of states with lower entropy compared to the initial one. This state, though of extremely low probability from the point of view of the equilibrium thermodynamics, can exist indeterminately long if the situation is stationary.

Any system under investigation possesses a spatial and time structure which is determined by the processes that occur in this system. One can usually determine the threshold states the transition through which leads to a qualitative change of system's organization. The evolution of a system as a sequence of transitions from one quasi-stable state to another, each of them being characterized by definite organization parameters, is called self-organization.

To provide a more precise definition for the notion of interphase boundary, only two terms should be considered as pithy, namely, the surfaces dividing and of the reaction zone. According to Gibbs, dividing surface is a non-uniform region (of a finite thickness) between the contacting phases. The properties of this region are the parameters of the state (temperature, pressure, chemical potential, etc.)[16,17)]. The properties of dividing surface can be investigated experimentally in the case if the thermodynamic equilibrium is established in the system gas - solid (e.g., many adsorption processes) or in the system vacuum--solid when the equilibrium can be established between the bulk of a solid and the dividing surface.

The notion of the reaction zone was defined as a result of the studies into the catalytic processes and topochemical reactions. The reaction zone is a layer of a solid (of finite thickness), its chemical composition and structure are the characteristics governed by the action of the reacting mixture. These characteristics describe the system's organization for a definite stationary state.

Self-organization of the reaction zone was discovered rather long ago in the studies into heterogeneous catalysis. In 1980, G. K. Boreskov analyzed the experiments accumulated in the field of studying the structure of metal and oxide catalyst surfaces under the conditions of interaction with reactants and concluded that the surfaces of solid catalysts under these conditions could not be characterized by the constant properties assigned, so the surface of a catalyst should be considered as a labile component of the reaction mixture depicting the changes in composition and other process parameters. Expressive examples of this statement are: reconstruction effects observed during oxygen chemisorption on the (110) and (100) faces of nickel and auto-oscillations of the rate of heterogeneous oxidation reactions18,19).

Reaction zone in the systems semiconductor-gas and semiconductor-liquid

Dissolution and oxidation of semiconductors are based on their interaction with halogens, oxygen and other oxidizing agents. Wide experimental material accumulated by present was depicted in a series of reviews20-24). On this basis we shall discuss the results in terms of the problem outlined.

Table 4 summarizes kinetic characteristics of the major types of chemical reactions occurring on the surface of silicon and germanium surfaces, i.e., adsorption, dissolution of crystals in liquids and dissolution of crystals in gases (chemical evaporation).

The reactions that occur on the surface of semiconductors with the participation of molecules or atoms are mostly related to adiabatic processes, their rates being not so high to make it necessary to take account of the deviations from Maxwell-Boltzmann distribution. Because of this, the approaches developed in agreement with the theory of absolute reaction rates are correct, and the reaction rate constant k is determined according to the equation:

$$k = \nu \exp(\Delta S/R) \times \exp(-\Delta H/RT)$$

Here T is temperature, K; R is the gas constant, ΔS is the entropy of reaction activation, ΔH is the enthalpy of activation.

Tab.4. General characterization of the reactions that occur on the surface of silicon and germanium crystals *

Reaction type	Temperature range, °C	ΔH, kcal/mol	ΔS, e.u.
Evaporation of Si, Ge; $Si+O_2$, $Ge+O_2$ (thermal oxidation)	600 - 1000	60 - 80	0 - 20
Reactions of Ge and Si with Cl_2, Br_2, I_2, tetrahaloids	200 - 500	30 - 40	0 - 10
Dissolution of Si, Ge in a liquid	25 - 100	15 - 20	$-5 \div -20$
Adsorption of O_2, S_2, Br_2	200 - 600	0 ± 1.5	−20

* rate constant $k = \nu \exp(\Delta S/R) \times \exp(-\Delta H/RT)$

Table 4 shows that all the reactions involving the interaction of an active gas phase with the semiconductor crystal and leading to the formation of gas-phase products are characterized by a small increase in the entropy while adsorption and crystal dissolution in liquids are accompanied by the decrease in the activation entropy by 5 - 20 entropy units. In the latter two cases, the effect os self-organization of the reaction zone is clearly expressed.

As a rule, the structure of the reaction zone is not identical to the structure of monomolecular adsorption layer. The formation of chemisorbed layer is usually accompanied by the formation of reconstructed layer of subsurface atoms. For separate types of reactions, the formation of supermonolayer coatings was discovered. This coating can be referred to as a layer of physically adsorbed molecules (Fig.3)[21)].

The formation of di- and tetra-halides is characteristic of silicon (germanium)-halogen system:

$$Ge+Br_2 \rightarrow GeBr_2$$

$$Ge+2Br_2 \rightarrow GeBr_4$$

When halogens are adsorbed on atomically-pure surface, the pre-adsorption state is formed without any activation barrier, the translation degrees of freedom being lost but the rotational ones being partially conserved. Due to the complexity of the technique, the formation of

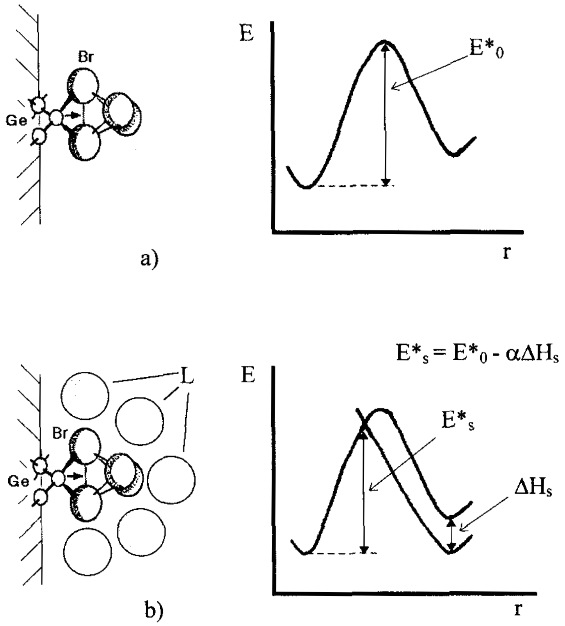

Fig. 3: Two -dimensional distribution of the assemblies in the reaction zone in the interaction of Ge with Br_2. **a)** The reaction in gas phase, **b)** The reaction in non-polar solution. **L** - molecules of solvent. On the right, the change of the system energy E with the reaction coordinate is shown schematically. $\mathbf{E^*_0}$ - the activation energy of gas phase reaction. $\mathbf{E^*_s}$ - the activation energy of the reaction in non-polar solvent. $\mathbf{\Delta H_s}$ - the heat of solvatation of reaction product.

dihalides was not studied. Estimates show that the activation energy of this reaction is 80 - 90 kcal/mol which is close to the heat of thermal evaporation of the crystal.

The formation of tetrahalides occurs via the structure of supermonolayer adsorption. This structure is stable and is conserved on the surface during the transition from the gas phase to non-specific solvent, for example in the system Ge - $(Br_2{+}GeBr_4)^{24)}$.

A different structure is formed when the reaction between silicon and and oxygen is performed in an open system, oxygen flow being passed above the surface of silicon crystal (Fig.4.).

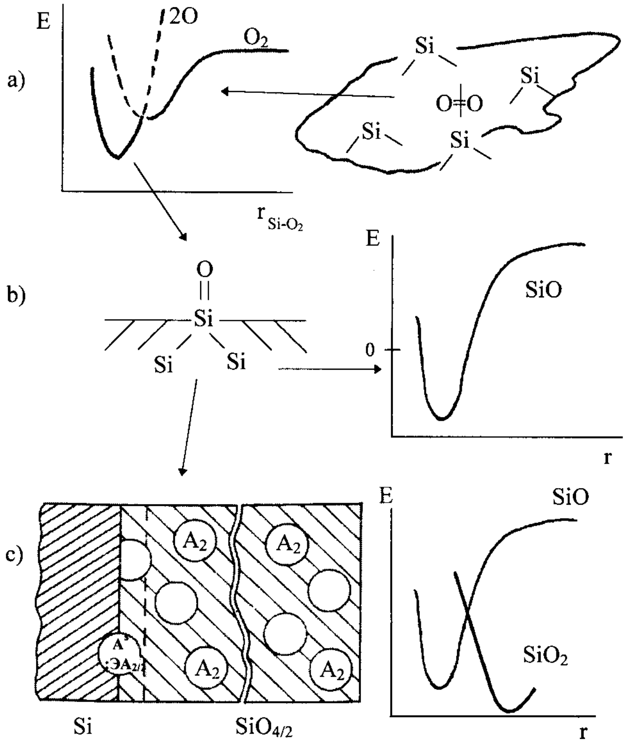

Fig. 4: The scheme of evolution of the reaction zone structure and potential profiles for the silicon - oxygen system depending on the reaction conditions. **a)** pre-adsorption state and dissociative adsorption of O_2, **b)** SiO desorption stage, **c)** reaction of thermal silicon oxidation. **A** - the atom O, **Э** - the atom Si.

There are two stationary states corresponding to different routes:

$$1)\ Si + \tfrac{1}{2} O_2 \rightarrow SiO$$

$$2)\ Si + O_2 \rightarrow SiO_2$$

A definite set of oxygen pressure values and temperature corresponds to the reaction following each of these routes.

Two stages are involved in the first reaction route (Fig.4 a, b):

$$O_2(\text{gas}) + \text{silicon} \rightarrow O_2\,(\text{ads})$$

$$O_2\,(\text{ads}) \rightarrow 2\ \ {>}\text{SiO}$$

$$>\text{SiO} \rightarrow \text{SiO}\,(\text{gas})$$

The first stage runs rapidly through the intermediate pre-adsorption state with the formation of >SiO complex. A large amount of experimental data and the results of molecular calculations show that the pre-adsorption state corresponds to a one-centre form of adsorption when oxygen molecule looses its translation degrees of freedom and conserves one rotational degree of freedom. This corresponds to the decrease in the entropy of gas molecules by 20 - 40 e.u. Independent of what face of silicon crystal the reaction takes place on, the final state corresponds to the >Si=O structure. This means that the surface reconstruction occurs in the subsurface layer, this process being most substantial at the (111) face. SiO desorption into the gas phase occurs as a synchronous rupture of the bonds of twice-coordinated silanone group. Thus we arrive at the conclusion that two structures exist during the stationary etching of silicon by oxygen. They are: non-dissociated O_2 molecules in the pre-adsorption state, and twice-coordinated silanone group.

This conclusion is rather general since a similar character is exhibited by the processes that occur in the systems Ge+O_2 and Ge+$S_2$$^{24)}$. By varying oxygen pressure or the temperature of the system, it is possible to transfer to another stationary state which corresponds to the reaction occurring via the route 2. These critical conditions correspond to a nearly monolayer filling of the surface in the form of >Si and to the formation of supermonolayer filling of oxygen. This is a third form of organized structures at the surface. It is characterized by the reversible supermonolayer adsorption of oxygen molecules possessing a definite degree of two-dimensional mobility. A decrease in the entropy is ~10 e.u.

Extensive experimental data have been accumulated in the studies into the thermal oxidation of silicon. The jointy of regularities thus discovered can be outlined using the sequence of stages (Fig. 4 c)

$$O_2^{\text{oxide}} \leftrightarrow O_2^{\text{reaction zone}}$$

$$>\text{Si} + \tfrac{1}{2}\,O_2^{\text{reaction zone}} \rightarrow\ >\text{SiO}\cdot O_{\text{ads}}\ (\text{an instantaneous stage})$$

$$>\text{SiO}\ O_{\text{ads}} \rightarrow\ >\text{SiO}_{2/2}\ O_{\text{ads}}$$

$$>\text{SiO}_{2/2}\ O_{\text{ads}} \rightarrow \text{SiO}_{4/2}$$

The first stage corresponds to the transition of oxygen dissolved in silicon dioxide into the reaction zone. Then an instantaneous stage occurs that involves the dissociative chemisorption of oxygen molecule. The second stage corresponds to the transition of silicon atom from the crystal to the SiO_2 matrix. The third stage is a final one. The structural unit formed ($SiO_{2/2}O_{ads}$) gets built into the $SiO_{4/2}$ matrix.

When analyzed in terms of the reaction occurring at the interphase boundary between the covalent crystal and the dioxide, the major regularities of thermal oxidation of semiconductors can be reduced to the dissolution of semiconductors in the condensed phase[22,23)]. The essence of this approach can be illustrated using the interaction of silicon with oxygen as an example. The limiting stages of the formation of either the gas-phase silicon monoxide or the structural unit of silicon dioxide are similar in nature and correspond to a barrier-free rupture or transformation of chemical bonds in twice-coordinated silanone group >SiO with the atoms of the lattice. A characteristic feature of oxidation process is that the activation energy for this stage is lower than that for the reaction of gas-phase product formation by the SiO_2 silicon-oxygen net reorganization energy. These values can be easily estimated using the data on the strength of chemical bonds. They are shown in Table 5 for the three systems.

The absolute value of the reorganization energy is maximal for the silicon-oxygen system which means that this system is characterized by a maximum efficiency of semiconductor atoms building up into the net of the vitreous dielectric layer. Using ΔH and temperature corresponding to a mean of the range in which oxidation occurs in the systems mentioned, the entropy changes ΔS corresponding to the self-organization of the reaction zone under the conditions of stationary oxidation processes were determined.

We considered the self-organization effects for interphase boundaries (the surfaces of phase discontinuity and of the reaction zones) using the examples of typical semiconductors for the systems which are the foundation stone of the basic technological processes in microelectronics. The analysis shows that it is the silicon-oxygen system that provides a maximum self-organization effect of the reaction zone or, as this is usually calles, the silicon-to-silicon dioxide interface.

It is important to note that the former expectations of many physicists to obtain a semiconductor surface, which would be perfect with respect to its electrophysical properties, were connected with the use of high-vacuum technique. Until recently, the results of the studies aimed at the preparation of the semiconductor-electrolyte interphase boundary practically devoid of the surface electronic states (P.P.Konorov, Yu.V.Pleskov[25)]) remained not interpreted. At present, it is clear that the effects of self-organization at the semiconductor-

Tab.5. Enthalpies and entropies of the reaction zone self-organization in the processes of thermal oxidation of silicon and germanium

System	$-\Delta H$, kcal/mol	T, K	$-\Delta S$, e.u.
Si / O_2	32	1200	30
Ge / O_2	14	900	15
Ge / S_2	7	700	10

electrolyte and semiconductor-dielectric interphase boundaries are the foundation of the technology aimed at the preparation of electrophysically perfect semiconductor surface. The absence of surface electronic states, including the recombination ones, in the silicon-silicon dioxide system is a fundamental phenomenon that has determined the modern level of integrated microcircuits. This analysis suggests that for the silicon-silicon dioxide system the self-organization degree is maximum among many possible systems. Because of this, only silicon, among large number of chemical compounds and elements exhibiting semiconductor properties, has been successfully used in industry.

Organized molecular assemblies of unidimensional topology

Classic examples of this type of assemblies are elementary sulphur and selenium which form vitreous substances composed of linear chains $SS_{2/2}SeSe_{2/2}$. Much attention in the physics of low-dimensional systems is attracted to unidimensional systems obtained by means of molecular-beam epitaxy on GaAs (311) matrix crystals[26)].

During the recent decade, great interest is attracted tolinear polymers based on polyacetylene. Starting with the works of Shirakawa[27,28)] it is known that trans-polyacetylene doped with J_2 exhibits metallic conductivity. Theoretical estimates show that when the structure of the layers is perfect, their conductivity can even exceed the conductivity of copper[29)]. The use of Ziegler-Natta catalytic polymerization process for these purposes hinders technological application of polyacetylene layers. In this respect, the use of Langmuir-Blodgett procedure is attractive.

We were the first to perform the studies, by means of the in situ automatic ellipsometry and IR - ATR, of the topochemical UV-initiated polymerization of long-chain alkyl-substituted acetylenes as Y-type layers obtained from $C_{21}H_{43}C{\equiv}CCH_2OH$ monomers according to the Langmuir-Blodgett procedure[30)]. The orientation of monomer molecules governed by the preparation procedure helps to obtain trans-configuration of polyacetylene layers.

Polymerization is completed within 15-20 min as mean in both cases. Polymerization occurs via triple bonds which is confirmed by spectroscopic studies. Absorption bands in the IR spectrum of the initial sample are observed at 2286 cm^{-1} and 2220 cm^{-1}. These bands correspond to the stretching vibrations of the -C≡C- group. The intensity of these bands is decreased during polymerization, and they disappear after the polymerization is completed.

It is convenient to create unidimensional assemblies of polydiacetylenes in a multimolecular Langmuir-Blodgett matrix which is of interest for use in the physics of non-linear optics[31)].

Zero-dimensional organized assemblies

The materials representing a system of semiconductor clusters distributed over an organic or silicate matrix attract an increased interest of the researchers working in the field of nano-electronics and non-linear optics. Examples of these systems are cadmium and lead sulphides in silicate glass or in the matrix of Langmuir-Blodgett layers based on fatty acids[32-34)].

Multimolecular layers of the salts of fatty acids, obtained according to the Langmuir-Blodgett technique, when subjected to gas-phase hydrogen sulphide, exhibit the behaviour of a topochemical reaction and form a composite system of multimolecular layers of fatty acids in which nanoclusters of metal sulphides are distributed.

Sulphidation of multimolecular behenate layers is based on a heterogeneous chemical reaction which can be written for cadmium behenate as follows (Fig.5):

$$Cd[OOC(CH_2)_{20}CH_3]_{2\,(solid)}+H_2S_{(gas)}=CdS_{(solid)}+2\ HOOC(CH_2)_{20}CH_{3(solid)}$$

Sulphidation is accompanied by the change of volume which can be estimates as the difference between the molecular volumes of cadmium behenate and the reaction products, i.e., cadmium sulphide and twice the molecular volume of behenic acid. Using the densityvalues and X-ray diffraction data we obtain the change of molecular volume equal to 8.1×10^{23} cm^3. Let us assume that the area occupied by a single behenate molecule in the film corresponds to a doubled area occupied by the molecule of behenic acid on the surface of the liquid subphase which is 8.1×10^{-23} cm^{-3}. This means that one can expect an increase in the monolayer thickness by 2.0 A as a mean during sulphidation. Because of this, it is convenient to follow the process using ellipsometic technique.

The system of Langmuir-Blodgett multimolecular layers is characterized by an important feature which simplifies the macro-kinetics of sulphidation, i.e., the reaction proceeds within the film volume. In other words, the rate of hydrogen sulphide diffusion into the layer is fast, and there is no reagent concentration gradient over the layer thickness.

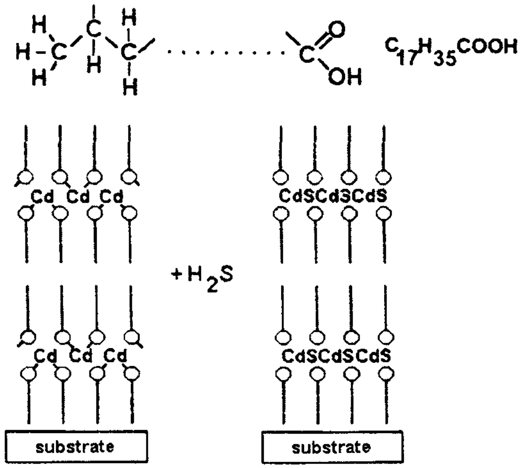

Fig. 5: The scheme of creation of the zero- dimensional assemblies in multimolecular matrix of Langmuir - Blodgett layers for sulphidation of cadmium behenate as an example.

The following stages can be selected as the major ones in the sequence of elementary reaction steps: the stage of chemisorptive interaction of H_2S with the behenate cation (Cd^{2+} or Pb^{2+}), chemical interaction leading to the formation of a single sulphide molecule (CdS or PbS) and two molecules of behenic acid; finally, the stage involving association or condensation of single sulphide molecules into clusters accompanied by structural relaxation of the molecular matrix of behenic acid.

One can assume that the chemisorption complex H_2S-$Pb(Bh)_2$ is formed without any activation barrier due to hydrogen bonds involving carboxyl groups. Chemical interaction proceeds with the participation of electronically excited states of the chemisorption complex and involved the transformation of H-S bonds into H-O, and Pb-O into Pb-S. Estimates made on the basis of the strength of chemical bonds show that the overall process is exothermic, 19.0 kcal/mol for lead and 33.2 kcal/mol for cadmium.

As a first approximation, the association stage of single sulphide molecules can be considered as phase transition accompanied by the condensation heat evolution subtracting the energy consumed for the formation of a void in the matrix of behenic acid. This is equal to the difference between the evaporation heat of the sulphide and that of behenic acid, or -41 kcal/mol and -45 kcal/mol for cadmium and lead, respectively. This analysis allows to come to the conclusion that the limiting stage of the process is most likely the transformation of the chemisorption complex.

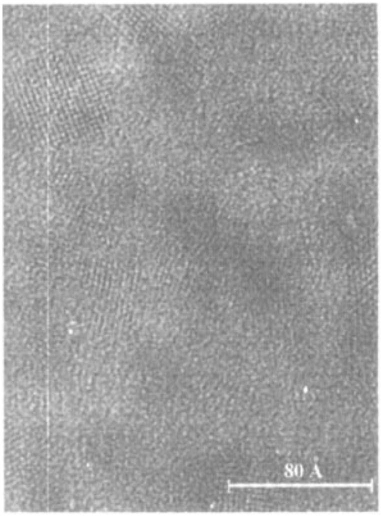

Fig. 6: The HREM photograph of PbS nanoclusters in the multimolecular matrix of behenic acid.

The calculation of the enthalpy of sulphidation for PbS gives the value -21.0 kcal/mol. However, the experiment shows that the final degree of behenate transformation during sulphidation is independent of temperature because sulphide appears as a finely dispersed phase. Using the estimates of the surface energy[35)] we obtain the particle size at the level of about 10 A. Direct electron microscopic studies give the cluster size about 30 A. (Fig.6.).

Organized molecular assemblies in terms of the problems of microelectronics

In 1989, Mr. Ken Bean, a distinguished Fellow of Texas Instruments, has said that *the electronics and semiconductor industries have had a greater effect on the world than even the invention of the wheel or fire. These is practically nothing electrical that you have today that does not have electronic devices.*

A consequent decrease in the dimensions of the integrated circuits allowed the technologists to approach submicrometer values neighbouring to the physically determined limit of miniaturizing. It is sufficient to say that the field-effect transistor channel of the dimensions 0.25x0.25 μm contains only 600 atoms of doping impurity and about 1000 electrons. At this level, fluctuations of non-uniformity in the distribution of doping impurities over the crystal and non-uniformity of charge carrier concentration, including their generation by cosmic rays, become essential.

In fact, by present, microelectronics has approached the limit of complexity for the integrated microcircuits within the frames of modern technology. Within the last decade, the processes involved in the preparation of artificial crystals have entered the field of microelectronics. These crystals are usually called semiconductor heterostructures or modulated lattices of the GaAs/AlAs or GaAs/InAs type with a prescribed sequence and thickness of alternating layers. These structures are obtained in high vacuum using the directed molecular beam technique. This method allows to prepare the systems of decreased dimensionality (two-, uni- and zero-dimensional systems)26). Using up-to-date investigation methods, a physicist has won the possibility to investigate the behaviour of a single electrone in the electric and magnetic fields. This direction is called nanoelectronics. At present, it is not clear yet whether these studies will lead to the creation of a new technological basis for the information means or remain the subject of investigation in the physics of low-dimensionality systems.

The discussion of a possible way to overcome the limitations in solid-state electronics began several years ago. F.L.Carter proposed an approach to the creation of electronic devices at the molecular level36). The most probable physical phenomena to be used for the creation of switch-over elements are electron tunneling in unidimensional periodic structures and the transport of solitons in the systems with conjugated double bonds.

In 1962, when considering the problem of tunneling through a system of identical potential barriers separated by identical potential wells, E.A.Pshenichnov37) demonstrated that, in the case if quasi-stationary states occur, resonance effects are observed which lead to anomalously high transmission coefficient. Any local deviation of the potential diminishes the transmission coefficient exponentially with respect to the number of barriers.

Soliton characterizes the way of transferring the excitation in the condensed medium as a solitary wave. Unlike common waves which are periodic spatial repetitions of the deviations from the mean value of the physical characteristic (density), solitons represent a solitary thickening propagating as a whole at a definite velocity38). Though the movement of a soliton is relatively low compared to purely electron switch-over, fast-operation of this assembly does not fall out of the subnanosecond range. The memorizing effect of molecular structures can be realized using conformational transformations of the structures under the action of a field or light. This direction of investigations is referred to as molecular electronics.

At present, a series of molecular assemblies have been proposed and studied experimentally which are able to perform switching-over, memorizing, emitting light. Molecular devices operating on the basis of the single electron transition effect are extensively studied[2)].

Organized molecular assemblies as receptor centres of chemical sensors

The problem can be re-formulated in general as the problem of creating an "artificial nose". The mechanism of odour perception by living organisms has been guessed in its general features. This question has been worked out in most detail[39,40)] on the basis of stereochemical approach. The basic idea is that the receptors of olfactory organs possess centres characterized by definite stereochemical dimensions, and their interaction with gas-phase molecules is possible only if the demand for their complementarity is met, i.e., they correspond to the clue-lock principle. This mechanism can explain exclusive ability of living creatures to discover odours at dilutions $1{:}10^8$.

Two types of organized molecular assemblies can be considered in the aspect of interest. They are: the assemblies based on multimolecular compositions prepared according to the Langmuir-Blodgett procedure, and thin-layer systems based on vitreous and amorphous silicon dioxide layers in the matrix of which the fragments of organic molecules or metal clusters of atomic dispersity have been introduced[41)].

Molecular system of amphiphilic long-chain molecules prepared according to the Langmuir-Blodgett procedure is an example of the simplest assembly. In these systems, the ratio of active surface of molecular layers to the volume of the system is rather large. As a consequence, the interaction of gas-phase molecules with amphiphilic molecules causes a substantial and rapid change in the properties of the assembly as a whole. This change can be registered relatively easily by measuring the electrical conductivity of the layer. The use of phthalocyanides is characteristic of these applications. An assembly of eight layers of asymmetrically substituted copper phthalocyanide in the Z-type configuration allows, under the action of gas medium containing NO_2, to register NO_2 content at a dilution of about $1{:}10^6$ by registering the changes in the layer conductivity at the relaxation constant of about 1 min. It is generally accepted that this effect is determined by the shift of π-electrons of the phthalocyanide ring to NO_2 molecules[41)].

Another typical example of organized molecular assemblies prepared according to the Langmuir-Blodgett procedure is a double-layer lipid membrane. The initial reagents for this membrane are phospholipids or glycerols containing long alcyl chains incorporating receptor groups functioning as a clue-lock. This property determines high selectivity of the chemical sensor42). An assembly contains phospholipid molecules as a matrix and the receptor molecules built into it. The interaction of the receptor molecules with an active particle of the medium leads to the formation of complexes, their lifetime being determined by the equilibrium constant. The basic physical effect that accompanies this interaction is connected with the changes in the ionic conductivity of the membrane. These changes can be conditioned by the fact that the selective interaction of a receptor with the particle to be detected is usually accompanied by the perturbation of the built-in dipole potential of the membrane leading to the change of molecular conformations in the assembly and, in its turn, to the change in ion mobility in the membrane.

An example of using Langmuir layers to manufacture a sensor to determine glucose concentration in the solution is as follows. Gold electrodes are placed onto a plate made of glass or oxidized silicon, and the layers of octadecyltrichlorosilane, arachidinic acid, glucose oxidase enzyme and finally arachidinic acid are placed in consequence above them. The structure involves the reaction of glucose oxidation catalyzed by oxidase which leads to the formation of H_2O_2 molecules. At a 0.7 V drop of potential between the gold electrodes the current is proportional to H_2O_2 content43).

Silicon dioxide in the form of silica gels had entered analytical chemistry long ago as a basis fro the preparation of carriers for gas and liquid chromatography. The possibility to use this material in the chemistry of solid-phase sensors is based, firstly, on the fact that vitreous and amorphous silicon dioxide forms microscopic cavities, and second, on the possibility to chemically modify and build receptor groups into the inner voids. The experiments show44) that a characteristic size of microscopic pores in SiO_2 is 25 A, and for the mean porosity of 25 %, the acting surface at the layer thickness of several hundred Angstroms is 10 to 100 times larger than the geometric surface area of the layer. This feature determines the possibility to synthesize organized molecular assemblies distributed over SiO_2 matrix. This is achieved in practice on the basis of the possibilities provided by sol-gel technology or chemical vapour deposition.

An example of sol-gel technology application is described in45). In order to make a solid-phase capacitance gas sensor for SO_2, the property of tertiary amines to form an adduct with SO_2 was used. This adduct is characterized by large dipole moment of about 5D. A sensitive layer was prepared by depositing the colloid onto the plate surface followed by its drying and fusion. The colloid solution was prepared by mixing N, N - dimethyl - 3 -

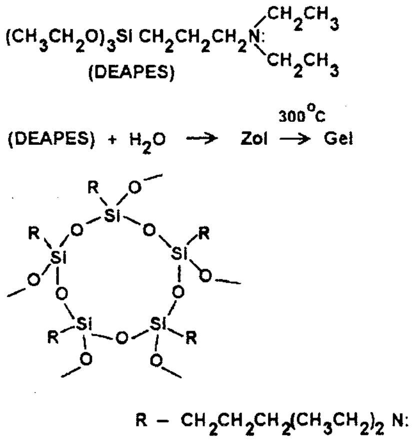

Fig. 7: The formation of three-dimensional receptor centres for SO_2 in polysiloxane matrix provided by sol - gel technology. The characteristic pore size is ~ 2.5 nm, the specific surface is ~ 500 m^2/g.

aminopropyltrimethoxysilane and propyltrimethoxysilane. As a result of hydrolysis and polycondensation, the matrix of -Si-O-Si- bonds arises in which $-N(CH_3)_2$ receptor centres are built. A structure in which the sensitive layer is deposited onto the system of interdigital metal electrodes allows to measure the capacitance changes caused by the action of the atmosphere containing SO_2 (Fig. 7).

Evolutionism in technology

Molecular engineering is surely a new level of preparative chemistry, but extremely important fact is that molecular engineering is also the system of notions bringing new culture to the technology.

From this point of view, the major problem of the approach under consideration is the creation of a scenario of real reasonable conditions starting from the selection of possible microstructures and determination of system evolution through a sequence of experimentally controlled stages. It is essential that the products of the transformation contained information admitting its reproduction at the next cycles of the scenario.

One can see that this problem has been only formulated by present. However, they say sometimes that to formulate problem is a half of solving it. Rather wide range of the compounds which can be the candidates for the role of fragments of molecular assemblies able to act as conductors, keys, switches, memorizing units, etc. has been determined by the present moment.

In the works of Carter[36)], this problem has been investigated as molecular electronics. The forecast for the creation of devices with the element density of 10^{16} per cm^3 has been outlined. If this could be done, the device implanted in human brain could supply a person with the entire bulk of knowledge accumulated by the humanity by present.

One can leave the comments to this forecast for science fiction writers but it is important to stress that the problems of the electronics of future come in connection with the problem of reconstructing life as a phenomenon that occurred as a link in the chain of the events comprising chemical and biological evolution. Famous soviet citolog D.K.Belyaev wrote: *"By the beginning of the XXI century life will be synthesized artificially. I (D.K.) mean not the reproduction of a cell at the level of the gene engineering but a kind of reproduction of the unique process that began long ago in nature: this is not life yet but this is life already".*

This means that the evolution principle is necessarily included into the solution of the problems in electronics as a field of information accumulation and processing. This does not imply the duplication of processes which had lead to the rise of consciousness, especially as we can imagine them only in general. But this means the selection of a small number of molecular assemblies and determination of the conditions and parameters which can provide that the system containing the set of these assemblies becomes able to evolve towards more complicated functionality.

Optimism for the activities in this direction can easily be drawn if we only remember the fact that a living creature in nature has overwhelmed the gravity force during its natural evolution within several million years, and man leaning upon his consciousness succeeded in rising up into the air within several thousand years.

Conclusions

An organized molecular assembly, as a group of atoms or molecules built in a solid matrix due to chemical or intermolecular interactions and possessing, in total, the ability to produce a definite response to the given perturbation, is an attribute of not only organic chemistry alone. The notions of structural units, active assemblies and surface compounds which, in fact, correspond to the definition of a organized assembly, have been employed for a long time with a success in the investigations into the chemistry of glass, catalysis, surface phenomena and heterogeneous reaction kinetics.

For the development of the technological foundations of integrated microcirciuts as an example, we have demonstrated the search for systems that evolve to the formation of two dimensional organized assemblies at the boundary between a semiconductor crystal and a dielectric.

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