

LANGMUIR - BLODGETT FILMS: A TREND IN THE DEVELOPMENT OF MOLECULAR MATERIALS SCIENCE

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The Langmuir-Blodgett technique enables to produce ultrathin organic layers on solid substrates. The layers exhibit a high degree of molecular ordering. This article presents new approaches in the LB technology: subsequent treatment of the film (UV polymerization in diacetylenes), formation and deposition of supramolecular layers (fullerene molecules embedded in the amphiphilic matrix). The ordered structure of the LB layers is documented by X-ray diffraction measurements. The analysis of electrical properties in insulating LB films is shown with the emphasis on M-LB-S systems.

1. Introduction

About 80 years ago I. Langmuir published his first work on the study of two-dimensional systems of molecular films at the gas - liquid interface [1]. Some years later, K. B. Blodgett devised a method for transferring the floating monolayers onto solid substrates [2]. The resulting films now bear the name of these two researchers - the Langmuir-Blodgett films.

The origin of the present interest in LB films can be traced back to the early 1960s, to the pioneer work of H. Kuhn who recognized the utility of LB technique as tools to assemble molecules in a systematic and well-organized manner [3]. The concept proposed by him is now known as "molecular engineering". This strategy at least partly results from the fact that optoelectronics and molecular electronics have become areas at the frontiers of materials science. In both cases, there are limitations to what inorganic materials can provide, and therefore ordered molecular organic materials are likely to become increasingly important. It is believed that LB monolayers may provide the desired control on the order at the molecular level and thus should be considered a potential technique for the construction of future molecular organic materials.

In comparison with conventional materials the physical properties of organics can be easier modified by minor changes in the molecular composition and their different properties may be associated at the molecular level for the elaboration of supramolecular

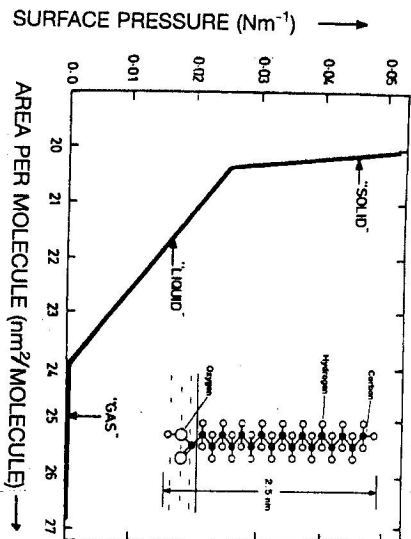


Fig. 1 Typical surface pressure versus area isotherm for stearic acid spread on the air-water interface. Inset: Molecular structure of stearic acid.

ordered materials. The functionality of molecular materials may be envisaged at any scale from the molecular size to bulk through thin films and clusters. One of their prior advantages is environmental biocompatibility. The devices such as resistors, chemical pressure, and magnetic sensors, submicron electronic or ionic devices are very attractive from the point of view of practical use.

In this short review we are presenting a survey of the results obtained in the research field of LB films. The communication itself is not intended as a comprehensive review of the present status but it concerns selected current research activities at the Department of Physics, Faculty of Electrical Engineering and Information Technology, STU in Bratislava, which as the only place in Slovakia has been systematically working in this perspective branch of materials science during the last years.

2. Deposition of Langmuir-Blodgett films

Materials that produce monomolecular layers on the surface of water invariably consist of molecules which possess both hydrophilic and hydrophobic chemical groups. Such molecules are amphiphilic. Inset of Fig. 1 shows the structure of stearic acid, one of the simplest materials suitable for preparing such a monomolecular layer. By adding this material dissolved in a volatile solvent onto the surface of water it spreads over the surface. During the lateral compression the monolayer undergoes a number of phase transformations (Fig. 1). The different phases can be identified by measuring the surface pressure. When the film is in the condensed "solid" form (the steep part of the isotherm) the closest-packed arrangement is achieved by the effective chain-chain interactions. The limiting "area per molecule" estimated from the isotherm is about 0.2 nm^2 being a typical value for saturated single-chain hydrocarbons.

In this condensed state the monolayer can be conveniently transferred from the water surface onto the solid substrate by its dipping and raising through the monolayer. A

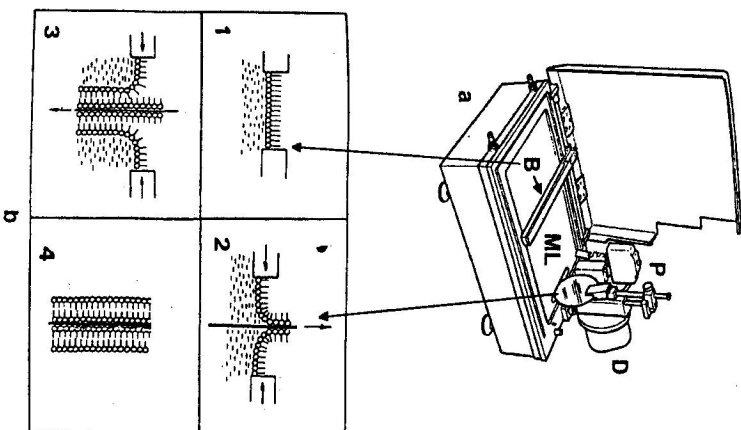


Fig. 2 a Langmuir - Blodgett trough equipped with a dipper D, a surface pressure sensor P and a moving barrier B (model 611D NIMA Technology, England). b The steps of the Langmuir - Blodgett deposition indicating the successive transfer of monomolecular layers ML.

schematic diagram of the experimental device (NIMA Technology, England) for the deposition is sketched in Fig. 2 [4]. On each traversal a successive monomolecular layer is deposited on the substrate surface.

The method although simple has severe requirements on conditions and materials used. The subphase was bidistilled, deionized water ($12 \text{ M}\Omega\text{cm}$), the solvents were spectrophotometric grade chemicals, and stearic acid (Fluka, Switzerland) puriss. standard GC. The whole deposition system is situated in a dust free cabinet (standard micro-electronic laminar flow box).

The Langmuir-Blodgett films have an inherent structural feature, i.e. long periodicity normal to the substrate surface, ranging from a few nanometers, which gives rise to 00L diffraction peaks in the region of small and intermediate angles of X-ray diffraction. The films were analyzed using monochromated $\text{Co-K}\alpha$ radiation and the Bragg-Brentano arrangement. In the case of the LB films prepared from cadmium stearate on a glass substrate the 00L reflections are observed clearly up to the thirteenth within the measurable diffraction angle proving an almost ideal layered system (Fig. 3). The length of the repeat unit was determined 5.05 nm , which indicates that the multilayer is of the Y-type structure, i.e. two adjacent layers have the orientation turned around

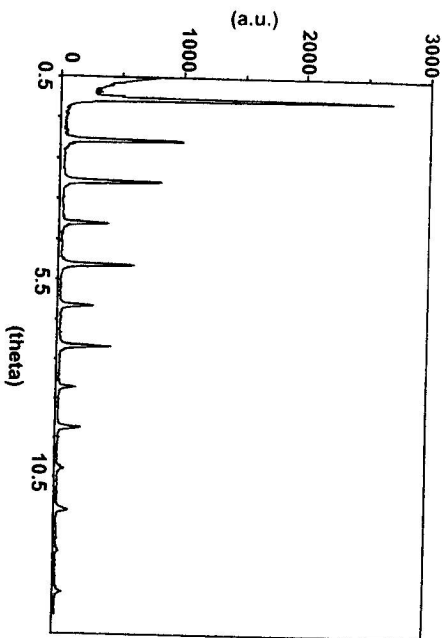


Fig. 3 $\Theta/2\Theta$ X-ray scan of 35 cadmium stearate monolayers deposited on a glass substrate.

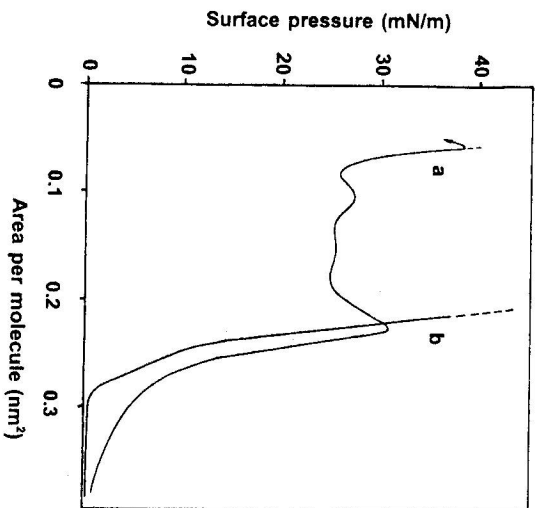


Fig. 4 Dependence of the surface pressure - area isotherms of diacetylene on the subphase temperature. The area per molecule determined from the low-temperature curve (b) is about 0.22 nm^2 . The increased thermal energy prevents the formation of a stable floating film, upon compression at approximately 30 mN/m the film collapses and the further maximum situated at 0.08 nm^2 may be accounted for the formation of a DA trilayer (curve a).

by 180° and they form a bilayer.

3. Diacetylenic amphiphiles

Since the beginning of research in the area of LB films, it was clear that the low chemical, mechanical, and thermal stability of most LB films is a major obstacle for

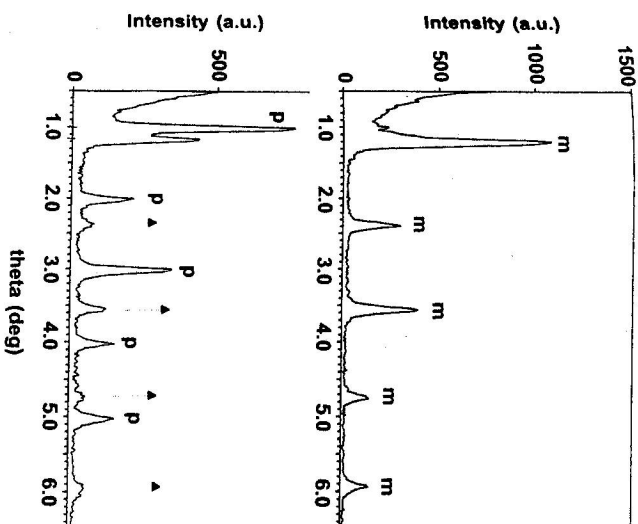


Fig. 5 X-ray diffraction patterns of monomeric and partly polymerized films. In the latter case two sets of the maxima are visible corresponding to monomeric (m) and polymerized (p) regions.

their use in a wide range of technologies. One of the possible approaches to the stability problem is a polymerization of the deposited LB film (the polymerization takes place in the film form).

The utilization of polydiacetylenes (PDA) was proposed for nonlinear guided wave devices [5]. Theoretical calculations showed that 1-dimensional systems of conjugated π -electrons should have nonlinear susceptibilities, and that the magnitude of this nonlinearity is dependent on the conjugation length [6]. Large single crystals of PDA are very difficult to grow, therefore ordered 2-dimensional assemblies that exhibit a high-order parameter are considered and studied as a possible alternative. The polymerization is a topochemical reaction, i.e. requiring that the molecules are regularly packed in a very specific arrangement.

Multilayers of the cadmium salt of diacetylene monomer $\text{CH}_3 - (\text{CH}_2)_9 - \text{C} \equiv \text{C} - \text{C} \equiv \text{C} - (\text{CH}_2)_8 - \text{COOH}$ (tricoso-10,12-diyonic acid) purchased from Dojindo Laboratories, Japan, were deposited on silicon single crystal substrates. The number of monolayers was 39 (the film thickness about 100 nm). These films were polymerized by UV exposure from the mercury UV lamp (the 254 nm line). The exposure time required is of the order of minutes. The polymerization of DA is accompanied by a phase change due to reorientation of the side chains (the extension of the layer thickness). It occurs in two steps:

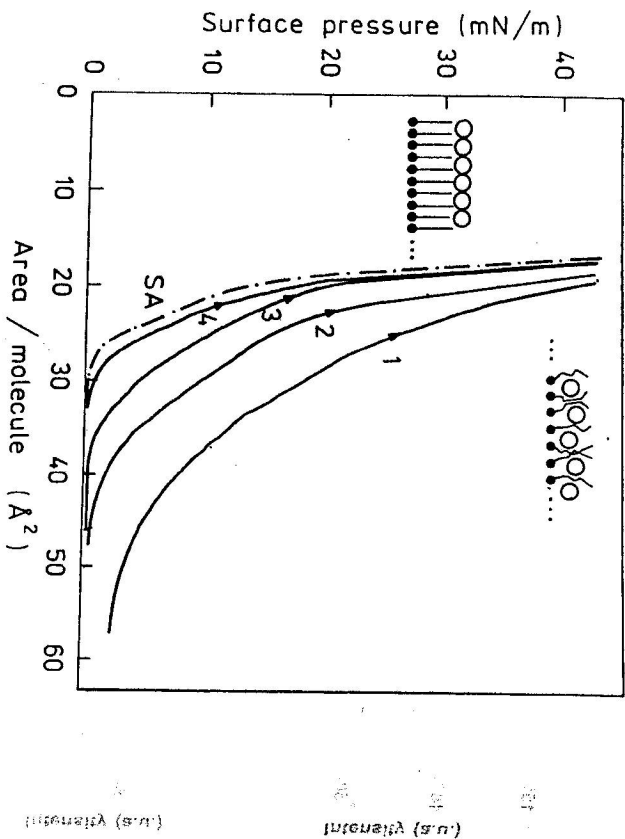


Fig.6 Surface pressure vs. area isotherms of C_{60} mixed with stearic acid on the water surface ($C_{60} : SA = 1 : 4.2$ mol/mol). The numbers indicate a compression sequence. The isotherm of a pure SA is drawn as a dashed line.

- blue phase (the ordered structure is preserved with no register between successive layers),

- red phase (obtained upon annealing above $60^\circ C$ or longer exposure to UV light).

The X-ray scan (Fig. 5) clearly reveals the effect of partial polymerization. The two sets of equidistantly spaced diffraction maxima correspond to two interlayer distances 23.7 nm and 27.5 nm characteristic of monomeric and polymerized assembly, respectively. This attests the existence of a phase separation and enables to calculate the rate of the polymerization reaction.

4. Thin layers of fullerenes

The synthesis of fullerene C_{60} evoked much interest in structural, electronic, and electrical properties of this novel form of carbon in both pure and compound form [7]. There has been considerable effort directed towards the growth of high quality thin films since the samples are ideally suited for physical measurements especially after the news associated with doping of C_{60} which lead to the superconducting transition [10]. These experiments have shown solid C_{60} as the first 3-dimensional organic superconductor. In addition to vacuum deposition and sublimation, the LB technique has been established as an alternative strategy for producing ultra-thin layers containing C_{60} . Although

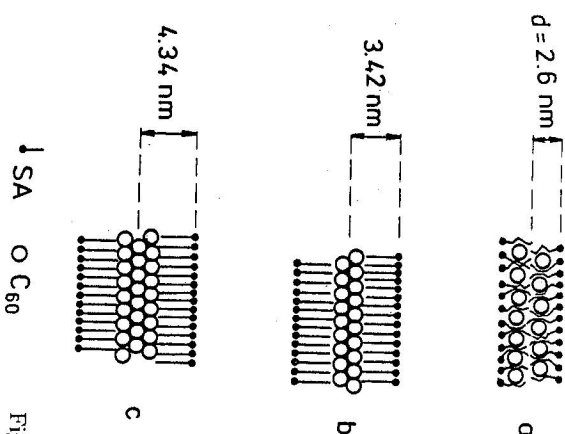


Fig.7 Schematic arrangement in the LB bilayer composed of C_{60} and stearic acid.

fullerene is not a typical amphiphilic material usually used to form LB films, recent studies reported that C_{60} forms a monolayer at the air-water interface with the area per molecule 0.87 nm^2 [8]. However, this highly ordered layer can not be transferred onto any substrate without disrupting its order and as reported by Long et al. [9] the transferred layers are inhomogeneous and most of the parts are in an amorphous state. Yet these functional molecules can be incorporated into LB films by mixing with a film-forming material, e.g. with stearic acid whose properties as a surfactant were described in the preceding sections.

Our experiment was focused on the characterization of fullerene C_{60} molecules at the air-water interface and the study of the films deposited by the LB technique. The C_{60} material was chromatographically purified fullerene powder. The compounds (C_{60} and stearic acid) were dissolved in benzene in a molar ratio $C_{60} : SA = 1 : 4.2$ which is the inverse ratio of the respective areas per one molecule in the monolayers (0.87 nm^2 for C_{60} and 0.21 nm^2 for SA). The solution was added onto the surface of distilled water (12 M O cm). The volatile solvent was left to evaporate and the floating film was then compressed at a rate $10 \text{ cm}^2/\text{min}$ which corresponds to $0.01 \text{ nm}^2 \text{ s}^{-1} \text{ molecule}^{-1}$. Upon the first compression the π -A isotherm was situated at 0.31 nm^2 per one stearic acid molecule (Fig. 6). A stable, repeatable isotherm was obtained after completing 3 - 4 successive cycles of compression and expansion of the monolayer, indicating the limiting area of 0.23 nm^2 . The addition of C_{60} molecules to the stearic acid monolayer results in increase of the area by approx. 10%. This supports a suggestion that although there are some C_{60} molecules intercalated between the close-packed hydrocarbon tails of SA,

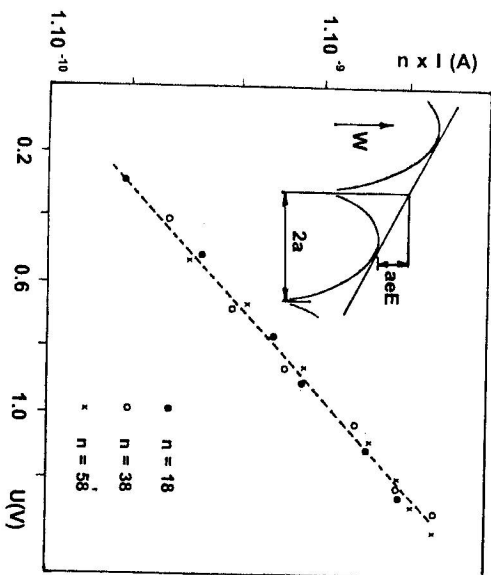


Fig. 8 I - V dependence of phthalocyanine multilayers. The value calculated as a product of the number of monolayers (n) and the current (I) enables to compare directly the results detected on the samples with various numbers of monolayers. Gold contacts of 0.36 nm^2 were used in experiments. Insert: Barrier lowering by a high field in closely spaced coulombic centres ($2a$ - the separation of the centres).

a majority of the molecules are squeezed out of the floating SA film and they form a separate uniform molecular sheet above (see insert in Fig. 6) [11].

The mixed C_{60} : SA floating film was deposited onto substrates of single crystal silicon, a number of layers ranging from 19 to 39. For the determination of thickness of the transferred films ellipsometry measurements were accomplished (Präzision Mechanik SGO1-01, Germany). The average value of the thickness per one layer was found $3.4 \pm 0.1 \text{ nm}$. This would imply that the bilayer heterostructure formed at the air-water interface was transferred into the multilayer structure on the solid substrate. The repeat unit found by ellipsometry exceeds the length of a stearic acid molecule by approx. 1 nm which is the thickness of the separate C_{60} monomolecular sheet. As shown in [12] this ideal configuration is partly disrupted during the deposition and beside the quasi-2-dimensional molecular stacks of C_{60} in the stearic acid bilayer there are large domains of C_{60} embedded into the layered system.

5. Electrical properties

The fact that the extensive and systematic research in the field of LB films at its outset was focused on classical amphiphilic materials - fatty acids and their salts, has lead to a general conception that LB films were considered, from the electrical point of view, insulators. However, the variety of materials suitable for LB deposition has enormously increased in the last ten years. These specially designed and synthesized molecules cover a very broad interval of electrical conductivity: from insulators with resistivity comparable with teflon [13] up to LB layers with conductivity approaching that of metals [14]. As regards the practical utilization, LB films as insulators remain

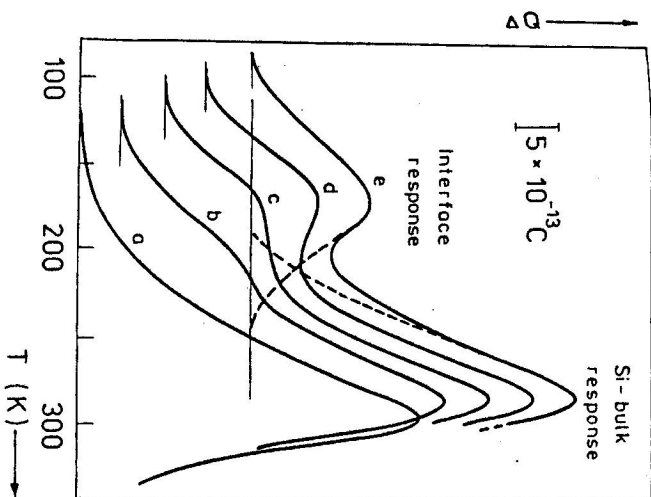


Fig. 9 Typical set of QTS responses obtained on an M - LB - Si structure with 58 phthalocyanine layers as a function of gate voltage U_g : (a) $U_g = 0.2$, (b) 0.4 , (c) 0.5 , (d) 0.55 , (e) 0.6 V .

of prime interest and the results presented here belong to this type of materials. The tunnelling effect accounts for the transport of electrons through a single molecular layer. B. Mann and H. Kuhn long ago [15] published a measured exponential dependence of electric current on the thickness of the sample composed of several monolayers and found that the tunnelling is a dominant mechanism of d. c. conduction in very thin structures up to the dimensions equivalent to 5 - 6 monolayers. In the case of thicker films (from about 20 layers) the experimentally observed behaviour typically fits the dependence of the form:

$$I \sim \exp\left(\frac{e a E}{k_B T}\right),$$

which is consistent with the model of the charged donor centres spaced sufficiently closely to give a significant overlap of their coulomb fields ($2a$ is the distance between the centres) - Fig. 8 [22]. The analysis of the experimental curves obtained from the samples of various thickness provides the value of $a = 1.61 \text{ nm}$. This corresponds to the thickness of one monolayer of copper-phthalocyanine which was the material used in the I - V measurements.

A considerable effort aiming at practical applications of LB films is based on MIS FET structures with incorporated central LB layer. The need for a systematic investiga-

tion of the properties of M - LB - S structures is therefore very actual. The study of the properties of metal / Langmuir-Blodgett film / GaAs structures [16] was regarded as the first use of deep level transient spectroscopy (DLTS) [17] in the charge modification mode (QTS) [18] on such materials. The effectiveness of the QTS method was proved in [19], it enabled to study the distribution and the concentration of fixed charge at the LB/semiconductor interface in a relatively wide interval of energy levels throughout the energy gap.

The set of the QTS signals is presented in Fig. 9. The M-I-S structure under investigation consisted of a top gold contact (gate), LB-phthalocyanine film, and n-Si substrate. The QTS measurements were carried out at various values of the gate voltage U_g . At higher gate biases the QTS response is composed of two distinctly resolvable signals while proceeding towards lower biases the low-temperature maximum merges into the high-temperature dominant peak. According to the theoretical analysis in [20] the various values U_g applied to the gate electrode adjust such a condition that the energy levels picked out from different intervals of the continuous spectrum of the surface states dominantly contribute to the origin of the low-temperature QTS signal. If the M-LB-Si structure is excited by low voltage pulses the energy spectrum is scanned with a narrow window ΔE_i in the energy interval from $E_m = 0.3$ eV (measurement at $U_g = 0.2$ V) to $E_m = 0.15$ eV ($U_g = 0.6$ V). E_m represents the energy of levels with respect to the centre of the Si band gap.

The analysis of the measured low-temperature QTS signals (for details see [19]) provided the spectrum of surface states depicted in Fig. 10 by circles. It has become evident that the surface states at the LB/Si interface form a continuous U-shaped spectrum in the gap of the semiconductor. The experimental dependences shown in Fig. 10 (traces 1 to 5) obtained by other authors [21] clearly demonstrate the fact that the surface states at the insulator/semiconductor interface depend not only on the properties of the solids in contact but to a high degree on the technological process producing the junction. It suggests that the high density of surface states and the U-shaped spectrum originate to a certain extent in the specific "wet" technological steps involved in the surface preparation before the LB deposition.

These findings approved the suitability of QTS for investigation of the technology influence on basic parameters of M - LB - S structures and enabled to monitor the changes accompanying modifications in the LB technique which are aimed at reduction of the density of undesirable surface charge.

6. Conclusions

When defining the role of LB films research in materials science in the 1990s and beyond not only should potential applications be considered but first of all the understanding of the molecular assembly in two dimensions at the molecular level is the basis in the technique of materials. More than anything else the interest is given to the systems composed of several types of molecules where the molecular interactions play a key role in the determination of the resultant system properties. But the interactions depend on the way how the molecules are spontaneously organized in the system depend on the self-organization. From this point of view LB films can be regarded as

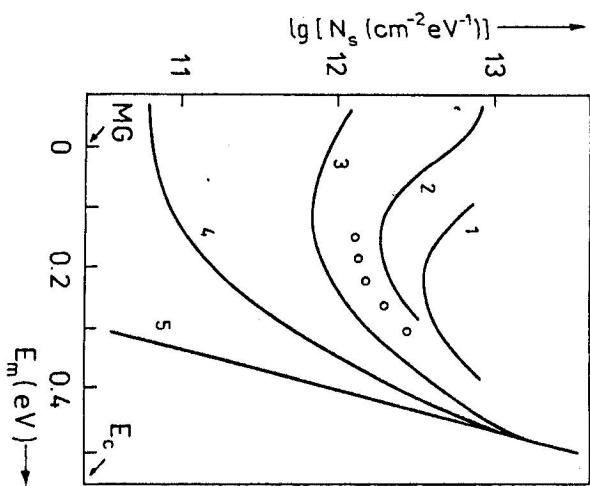


Fig.10 -Interface state distribution in the band gap of n-Si obtained by QTS technique on the M - phthalocyanine - Si structure (circles). For the sake of comparison this dependence of states is shown for (1) p-Si surface etched in HF liquid, (2) p-Si etched in HF vapour, (3) n-Si wet oxidized at 1150 °C, (4 and 5) as (3) with additional annealing in H_2 [21].

an ideal technological tool for modelling basic physical processes in the systems with molecular organization and this impact of the research should be understood and put forward in any proposal.

The particular role of LB films can be defined as follows:

- a - The study of mixed monolayers where the self-organization effect is obtained due to H-bonding and dipole-dipole interactions.
 - b - The study of supramolecular structures, i.e. a deposition of different kinds of monolayers in a planned sequence, thus creating desired physical phenomena and devices (tunnelling effect, donor - acceptor pairs with desired spatial configuration, etc.).
 - c - The study of highly selective chemical reactions with the aim at the understanding of the phenomena associated with molecular recognition (substrate-enzyme, antibody-antigen, etc.).
 - d - The study of the physics and chemistry of complex systems at reduced dimensionality (magnetization, biochemical reactions, electrical transport in polymers).
- More direct goals of the LB research can be expected in these areas:
- a - Nonlinear optical systems (the use of spontaneous orientation of molecules in the layers, molecular-level control on film thickness, generation of higher harmonics).
 - b - Development of novel materials for the control of friction and wear (tribology).
 - c - Development of microsensors (the use of selective reactions of organic molecules in the ordered systems, simulation of processes in biological membranes).

d - Development of novel materials for solar energy conversion.

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