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VIBRONIC EFFECTS IN SURFACE PHASES AND MOLECULAR ELECTRONICS

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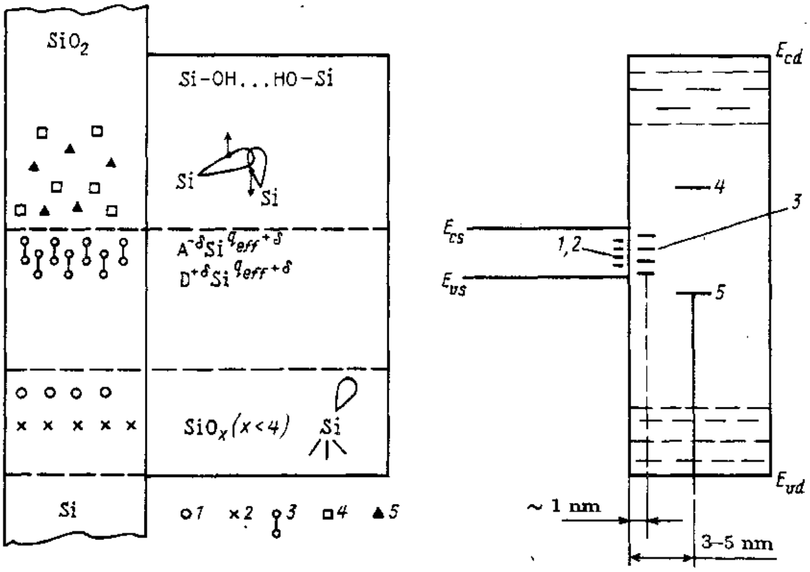
In view of the fast progress in molecular electronics, much attention is being paid during recent years to systems combining the advantages of well studied basic elements of inorganic planar electronics and of elements of purely organic origin. In this work, experimental data are presented that point to the important role of vibronic effects in such structures. Considered are: (1) the role of vibronic effects in the events of trapping and recombination of charge carriers in the structures of semiconductor–insulator–adsorbed molecules, and also in photochemical transformations at the surface; (2) vibronic effects in the systems of semiconductor–insulator–dye molecules and semiconductor–insulator–Langmuir/Blodgett film; (3) some prospects for the utilization of vibronic effects in elements of molecular electronics.

Molecular electronics, which uses associates of organic molecules, polymer films (in particular, the Langmuir/Blodgett films), and liquid crystals as elements of information storage and processing, is expected to compete seriously with the existing semiconductor electronics in the forthcoming decade. Some researchers in the field of molecular electronics believe that its future is related to the development of three-dimensional polymolecular structures all elements of which have an organic origin (see review [1]). However, there are enormous difficulties on this route related to the necessity of developing controlled organic synthesis of such structures. The synthesis must include perfect-quality computer modeling and development of new concepts of self-organization of integrated circuit subcomponents. Nowadays, it seems much more realistic to combine the well-developed and well-studied basic elements of the modern inorganic planar MIS electronics and elements of a purely organic or even biological origin. The first attempts to replace metal coatings of MIS transistors and metal junctions in circuits by the high-conductivity polymer coatings ($\sigma > 10^3$ ohm^{-1} cm^{-1}) opened new prospects in microelectronic engineering [2]. Of no less importance is searching for new informational media that can be used as insulating layers in MIS electronics elements and impart them new functional potentialities. These may be molecular systems with chromophore, electrophorus, ferroelectric, magnetic, and other properties.

In planar elements of MIS devices, of great importance are the properties of well-developed interfaces between the semiconductor–insulator and insulator–metal, as well as the parameters of surface electronic states governing the processes of generation, trapping, and recombination of charge carriers. While in inorganic systems all these surface phenomena have already been studied sufficiently well [3–6], in semiconductor–insulator–molecular system structures these studies have just been started. The problem is complicated by the fact that whereas in the first case the information transfer is largely effected by electrons, holes, phonons, and photons, in the second case these functions can be performed by excited states, in particular, by excitons, plasmons, polaritons, polarons, solitons, etc. In view of the high elasticity of bonds in molecular systems, an important role in information transfer and processing is played by the vibronic effects. These phenomena, due to electron-vibrational interactions, are predominantly governed by individual properties of molecules: their vibrational modes in the surface phase. These effects may considerably extend the functional potentialities of the elements of molecular devices. The study of these effects also has theoretical interest for the physics of surface, since they provide a deeper insight into the elementary mechanism of interaction of charge carriers and excited states with surface electronic states, and also the mechanism of surface defect generation in a structure exposed to powerful electromagnetic radiation.

1. ROLE OF VIBRONIC EFFECTS IN TRAPPING AND RECOMBINATION OF CHARGE CARRIERS IN STRUCTURES OF SEMICONDUCTOR–INSULATOR–ADSORBED MOLECULES

Vibronic effects in molecules and in the bulk of some crystals have already been dealt with in the literature [7]. Information about such effects in surface phases is scarce. Some results may be found [8] only for the surface of some Jahn-Teller crystals and ions of transition metals adsorbed onto the surface. The authors, however, paid practically no attention to the correlation between the vibronic effects and excitations of the electronic system of solids. Very promising for the study of this kind of relationships are systems including a semiconductor, an insulating oxide film, and adsorbed molecules. Particularly convenient are layered Si–SiO_2 and Ge–GeO_2 systems whose bulk and surface properties are studied in more detail in [3–6].



a b

Fig. 1

Schematic representation of spatial localization of basic surface electronic states in the Si–SiO_2 (Ge–GeO_2) structure (a) and its energy diagram (b): fast states (1), recombination states (2), slow states of the interface ($A^{-\delta}Si^{q_{eff}+\delta}$ and $D^{+\delta}Si^{q_{eff}-\delta}$) (3), insulator traps for electrons (4) and holes (5); E_{cs}, E_{vs}, E_{cd}, E_{vd} are the energies of the bottom of the conduction band and the top of the valence band for the semiconductor and dielectric (insulator), respectively.

Figure 1 presents spatial and energy diagrams of such heterogeneous junctions [6]. Located in the near-surface region of the semiconductor are fast surface electronic states (fast states), some of which act as recombination states. They are located on broken bonds of silicon (germanium) in the sp^3 hybridization, the so-called p_B centers. In [9] a vibronic effect was observed upon powerful laser irradiation of the surface. A strong electron–phonon interaction removed the degeneracy of these bonds and the centers underwent transition to a state close to the sp^2–p_z hybridization. The silicon atoms went down by about 0.03 nm with respect to the surface. Simultaneously, the spin-dependent recombination channel vanished completely.

In the systems studied, the energy released in the acts of trapping by neutral fast states is distributed between phonons by the multiphonon or the Lax cascade mechanism. In the case of surface phases, the vibrational modes of adsorption complexes whose energy $h\nu_{\text{vib}}$ generally exceeds the energy of phonons (the electron-vibrational model of surface trapping [10]), can become more efficient acceptors of energy. Such a vibronic effect was observed for germanium in a study of the rate of surface recombination S as a function of the surface potential Y [11]. Substitution of the OH groups ($h\nu_{\text{vib}} = 0.43$ eV) in the recombination states of the OH–Ge_2–Ge type by the OD groups with vibrational modes of lower energy ($h\nu_{\text{vib}} = 0.31$ eV) resulted in deformation of the bell-shaped dependence $S(Y)$ and its shift toward positive values of Y (Fig. 2). This is probably due to lowering of the energy $h\nu_{\mathrm{vib}}$ of the energy acceptor and, accordingly, to a change in the capture cross section for neutral recombination states with respect to trapping of the first charge carrier.

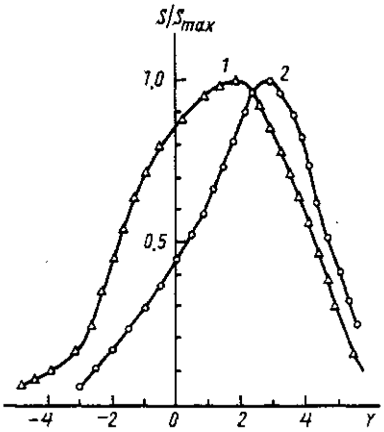


Fig. 2

Relative rate of surface recombination in germanium as a function of surface potential at $T = 295$ K. The surface was hydrated in H_2O (1) and D_2O (2).

The large capture cross sections for fast states and recombination states ($c_{n,p} \sim 10^{-15}$–10^{-12} cm^2) are due to small polarizability of the defects forming their basis and to their good contact with allowed bands of Si(Ge). The vibronic effects are more pronounced when charge carriers are trapped by the slow states of the insulator–semiconductor interface (Fig. 1). The recharging of this group of states occurs largely by the tunnel mechanism, which manifests itself in the field effect. Relaxation of the charge Q_{ss} accumulated at the slow states of the insulator–semiconductor interface upon switching on (off) the field is well described by the Koc equation for heterogeneous surfaces:

$$Q_{ss}(t) = Q_{ss}(0) \cdot \exp\{-t/\tau_s\}^a, \tag{1}$$

where the exponent a depends on the state of the surface and may vary from 0.3 to 0.6. The relaxation rate τ_s^{-1} is given by the Arrhenius law:

$$\tau_s^{-1} = \tau_0^{-1} \exp\{-\Delta E_\tau / kT\}, \tag{2}$$

where ΔE_τ is the effective activation energy for charge carriers trapping.

The slow states of the insulator–semiconductor interface are located at the dipole donor–acceptor complexes of adsorbed molecules with coordinationally unsaturated Si(Ge) atoms within the disordered and nonstoichiometric interphase layer of SiO_x (GeO_x, $x < 2$). The interface slow states of the adsorptive origin show abnormally small capture cross sections: $c_{n,p} = 10^{-28}$–10^{-27} cm^2. This is first of all due to the vibronic character of the interaction between the charge carriers trapped by the interface slow states and soft vibrational modes of adsorbed molecules. Trapping leads to deformation and polarization of the adsorption complex. Upon adsorption, the value of ΔE_τ in (2) was found to be:

$$\Delta E_\tau = E_{cs} - F + h\nu_{\mathrm{vib}}, \tag{3}$$

where E_{cs} is the energy of the conduction band bottom and F is the Fermi energy at the surface. Since the deformation is related to the motion of heavy particles (nuclei), this causes abnormally large values of τ_0 in (2), which at the initial stage of the adsorption exceed by 6 to 8 orders of magnitude the characteristic relaxation times in solids ($\tau_0 \sim 10^{-13}$–10^{-11} s). It is of interest to note that $\ln \tau_0$ was linearly dependent on ΔE_τ [4] (the Constable law).

There is another reason for the appearance of so long-lived (10^{-5}–10^{-4} s) vibrationally excited complexes due to the poor contact with phonons of the crystal. It is well known that in disordered systems to which the surface belongs, their surface phonon spectrum is separated from that of the bulk by the energy gap. The energy exchange between the excited adsorption complexes and the bulk of the solid (channel S) becomes possible only due to anharmonicity of the bonds. As the numer of adsorbed molecules grows, an alternative channel appears due to dissipation of the vibrational energy in the molecular phase (channel M). This is accompanied by a sharp drop in τ_0.

Direct evidence for the important role of the vibronic effects in slow trapping was obtained in measurements of the temperature dependence of the relaxation of $Q_{ss}(t)$ [10]. The derived values of ΔE_τ turned out to be close to the energies of the maximal (accepting) modes of various adsorbed molecules. For example, on going from H_2O molecules to D_2O molecules, the equilibrium surface charge (and therefore the curvature of the energy bands Y and the surface conductivity σ_s) does not change, the two types of molecules form an effective adsorption energy level ε_t at the same depth in the forbidden band (for germanium, $\varepsilon_t \sim -1kT/q$ [4]). The same level ε_t is formed upon adsorption of NH_3. In view of the quasicontinuity of the spectrum of the adsorptive surface electronic states at a nonuniform surface, measurements of the equilibrium surface parameters (Y, σ_s) are unable to provide adequate information about the individual structure of the adsorbed molecules. The vibronic spectrum characteristic of a given type of molecules is manifested only in variations of the kinetic parameters $c_{n,p}$, τ_s, and ΔE_τ. The isotopic shift of ΔE_τ observed upon deuteration of the surface turned out to be close to the difference between the modes of valence vibrations of the OH and OD groups of adsorbed molecules: $\Delta h\nu_{\text{vib}} = 0.10$–$0.11$ eV.

It should be noted that the presence of soft localized modes of prehistory defects and many-body adsorption complexes at the disordered surface may account for the appearance of two-tier atomic potentials, tunnel modes, and an electric instability. These effects are responsible for some nonlinear properties of amorphous materials [12]. In view of this, the newly arising methods of nonlinear optics, such as second-harmonic generation, giant Raman scattering, and electrical reflection (see, e. g., [13, 14]), seem to be promising for use in surface studies.

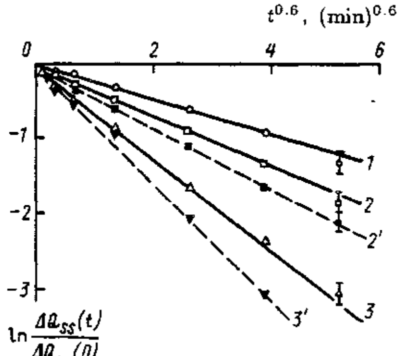


Fig. 3

Relaxation of the charge ΔQ_{ss} at the Ge surface in a transverse electric field in the dark (1–3) and upon IR irradiation (2′, 3′) at temperatures 295 K (1), 310 K (2, 2′), and 325 K (3, 3′).

So far, we considered the vibronic effects arising upon excitation of the electronic subsystem. Similar effects also take place upon excitation of phonons. The Ge–GeO_2 system turned out to be quite convenient. Frequency of emission from the infrared CO_2 laser ($\nu_l = 946$ cm^{-1}) falls within a broad band of optical phonons in a disordered GeO_2 film with a maximum at $\nu_p = 935$ cm^{-1} [15]. To eliminate any noticeable influence of heating of the system (due to nonresonant light absorption by free charge carriers and bulk phonons), measured were the temperature dependencies of the slow charge relaxation in the system of slow states of the interface in the field effect, $Q^0_{ss}(t)$, (i) in the absence of irradiation and (ii) under conditions of irradiation by the CO_2 laser, $Q^{IR}_{ss}(t)$. As is seen in Fig. 3, at the same mean sample temperatures T_m, after switching on a static electric field (−100 V at a field electrode), the relaxation occurs faster in the field of IR radiation ($Q^{IR}_{ss}(t)$) than without irradiation ($Q^0_{ss}(t)$). The relaxation curves linearized within the coordinate system of Eq. (1) show different slopes. Acceleration of relaxation is caused by resonant excitation of soft local vibrational modes of Ge–O bonds in adsorption complexes. The latter leads to a decrease of mean activation energies ΔE_τ from 0.3 to 0.25 eV, which is equivalent to a change of the capture cross section $c_{n,p}$.

2. ROLE OF VIBRONIC EFFECTS IN PHOTOCHEMICAL TRANSFORMATIONS AT THE SURFACE

The vibronic energy accumulated in a relatively long-lived (10^{-5}–10^{-4} s) excited adsorption complex can stimulate the processes of defect generation [16], photoadsorption, desorption, and catalysis in the surface phase [17]. Let us consider the more vivid example of a vibronic effect during photodissociation of H_2O and D_2O molecules adsorbed to the real silicon surface. The surface was pulse-illuminated and the yield of the photodissociation products was monitored mass spectrometrically. As is seen from the spectral dependence of the quantum yield $\eta_{H_2}(h\nu)$ for the main reaction product (hydrogen), the value of η_{H_2} grows together with the photon energy $h\nu$ (Fig. 4). Photodissociation of water was not found [18] to be related to surface heating and direct photolysis of water molecules. Within the range of $h\nu \simeq 1.5$–3.5 eV, η_{H_2} grows whereas the quantum yield $\eta_{n,p}$ of photogenerated electron–hole pairs remains constant. Therefore, the occurrence of photodissociation cannot be explained only by a change in the charge of surface electronic states, i.e., by purely electronic transitions. The fact that η_{H_2} increases for $h\nu > E_g$ (the width of the forbidden band) points to the involvement of "hot" charge carriers in the event of dissociation. In such a case, the barriers separating the slow states of the insulator–semiconductor interface from the allowed bands of the semiconductor are lowered. The sharp increase of η_{H_2} at $h\nu > 3.5$ eV is related to the beginning of the collision ionization.

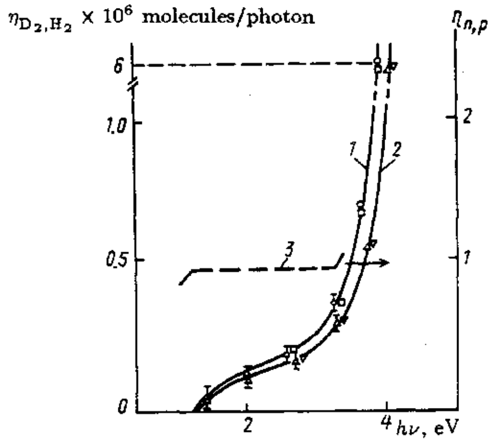
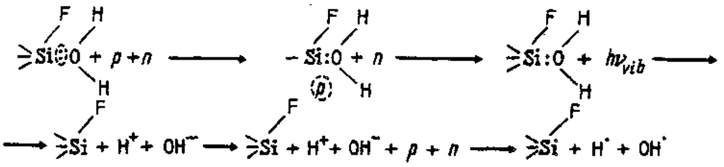


Fig. 4

Spectral dependence of the mean quantum yield of water photodissociation products at the silicon surface: D_2 for the deuterated surface (1), H_2 for the hydrated surface (2); quantum yield of electron–hole pairs (3).

According to the donor–acceptor mechanism of adsorption suggested by us [4, 19], $(H_2O)_k$ molecules at the Si–SiO_2 boundary that are coordinationally bound with Si atoms are the source of H_2. Such dipole slow states of the interface capture a hole (p), which is accompanied by a weakening of the O–H bonds, i.e., by protonation of the $(H_2O)_k$ molecule and by an increase in the capture cross section c_n with respect to the second photogenerated carrier, the electron (n). The energy released in the recombination of $n + p$ produces an additional excitation of the vibrational modes of the ($h\nu_{\text{vib}}$) complexes and their heterolytic dissociation:



Then apparently

$$H^{\cdot} + H^{\cdot} \rightarrow H_2; \quad OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2.$$

Peroxide undergoes dissociation under the action of the third pair of n and p. No less than three photons are involved in the cycle, which is supported by the power dependence of η_{H_2} on illumination intensity that is close to cubic [18]. The effect is bipolar, for both types of carriers (n and p) are involved. We have also observed a monopolar effect of proton accumulation when holes moved closer to the surface in the presence of a field [4].

Direct evidence for the presence of vibronic interactions in these reactions was obtained in the experiments with D_2O. As is seen in Fig. 4, the curve $\eta_{D_2}(h\nu)$ is shifted toward smaller photon energies. The magnitude of the isotopic shift is close to the difference between the energies of the accepting modes for the O–H and O–D vibrations: $\Delta h\nu_{\text{vib}} = 0.11$ eV.

The occurrence of strong protonation of $(H_2O)_k$ molecules, which form the basis of the interface slow states and are responsible for the processes mentioned, is confirmed by the observation in [18] of a considerable Stark shift in the fluorescence spectra of the probe molecules (dye molecules showing proton-accepting properties) as well as by the catalytic decomposition of CCl_4, HCOOH, and CO_2 stimulated by photogenerated charge carriers and vibronic interactions. Protonated $(H_2O)_k$ molecules serve as catalytic sites. Now let us consider only the reaction of decomposition of CO_2 molecules adsorbed to the Si surface. Pulsed illumination of the deuterated Si surface induced release of CD_4, CHD_3, CH_2D_2, and CH_3D, which was detected mass spectrometrically [18].

As mentioned above, the slow states of the insulator–semiconductor interface of adsorptive origin show very small cross sections of charge carrier trapping. The rate of charge carrier recharging is given by:

$$dQ_{ss}/dt = nNv_Tc_{n,p}, \tag{4}$$

where n is the concentration of charge carriers in the region of space charge, v_T is the velocity of their thermal motion, N is the concentration of trapping sites. At constant values of N, v_T, and $c_{n,p}$, the magnitude of the effects observed is determined by the injection intensity for nonequilibrium charge carriers, i. e., by n. In our experiments, the intensity of pulsed illumination of the surface I reached 10^{19}–10^{20} photons $cm^{-2}\ s^{-1}$.

The decisive role of the vibronic effects was also observed when local phonons were excited by the CO_2 laser irradiation of the surface of Ge–GeO_2 structures [15]. Under these conditions, the formation of new vacancy defects (of the type of E' centers) in the insulating GeO_2 film [20] and desorption of "resonant" preadsorbed CO_2 molecules [18] were found to occur. Just as in the case of excitation of the electronic subsystem of the semiconductor by the IR radiation of the deuterated Ge surface, methane molecules with atoms isotopically substituted to a variable extent were found in the desorption spectra [15].

3. VIBRONIC EFFECTS IN SYSTEMS OF SEMICONDUCTOR–INSULATOR–DYE MOLECULES

Photoexcitation of singlet–singlet $S_0 \rightarrow S_1$ transitions in the adsorbed dye molecules is known to initiate electronic transitions in solids [21]. Two pathways of such a spectral sensitization are feasible: (i) resonant transfer of the energy of the reverse $S_1 \rightarrow S_0$ transition in a relaxing molecule to charged surface electronic states and their recharging (Fig. 5 a) and (ii) electron transfer from an excited molecule thereby converted into an ion radical, which subsequently regenerates into a neutral molecule due to charge carrier tunneling

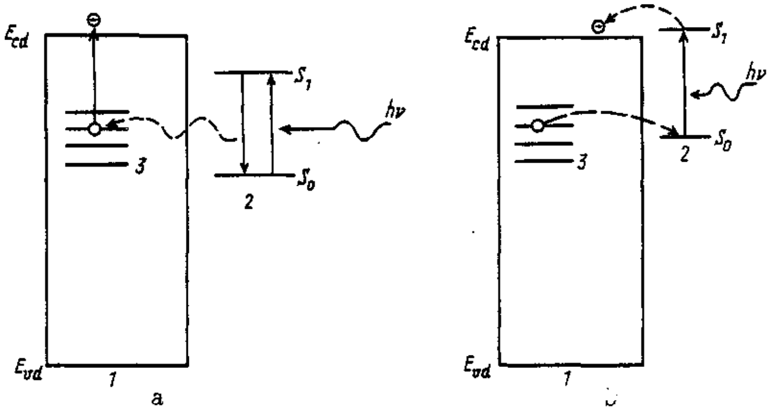


Fig. 5

Schematic representation of two alternative mechanisms of spectral sensitization of the surface phase of a solid by adsorbed photoexcited dye molecules: (a) energy transfer, (b) electron transfer; E_{vd} and E_{cd} are the edges of the valence band and conductivity band in the dielectric (insulator); (1) insulator, (2) adsorbed molecule, (3) insulator traps.

from the semiconductor (Fig. 5 b). It was found in [18, 22] that in the insulator–semiconductor structures based on Ge and Si, only the first mechanism is taking place.

The overall rate constant (k) for deactivation of the photoexcited molecules is known [23, 24] to be determined by energy transfer through the following five channels: (i) radiative losses via luminescence (k_r); (ii) nonradiative energy transfer to neighboring molecules by the Förster-Dexter induction-resonance mechanism (k_{FD}); (iii) singlet–triplet intersystem crossing (k_{st}); (iv) internal conversion to vibrational modes (k_{ic}); and (v) nonradiative energy transfer to the solid (k_s), i. e.:

$$k = k_r + k_{st} + k_{ic} + k_{\mathrm{FD}} + k_s . \tag{5}$$

For semiconductors, k_s is determined by the efficiency of charge exchange for different groups of surface electronic states (see Fig. 1) and by interband transitions (k_{IB}):

$$k_s = k_{\mathrm{IT}^-} + k_{\mathrm{IT}^+} + k_{\mathrm{SSI}} + k_{\mathrm{FS}} + k_{\mathrm{IB}}, \tag{6}$$

where the subscripts "IT$^+$" and "IT$^-$" denote the insulator traps for holes and electrons, respectively.

The experiments with the insulator–semiconductor structures based on Ge and Si show that energy transfer from donors (the excited dye molecules) to acceptors in a solid occurs by the dipole–dipole Förster-Dexter mechanism at a rate constant k_{FD} given by:

$$k_{\mathrm{FD}} = (R_0/R)^6 \tau_0^{-1}, \tag{7}$$

where R is the distance from donor to acceptor, R_0 is the critical radius (about 50 Å), and τ_0 is the lifetime of the excited state of an isolated dye molecule. Depending on the extent of dimerization of dye molecules in their adsorbed state, τ_0 varies from 1.2 ns for monomers to 250 ns for dimers (of rhodamine B) [24]. At a low concentration N_A of adsorbed dye molecules of the same type, this mechanism also governs the energy transfer in the molecular phase (channel M).

Combined measurements of the charge of surface electronic states and of its relaxation by electrophysical methods (the field effect, C-V characteristics), on the one hand, and spectral measurements of the parameters of molecular luminescence (its quenching and spectral features), on the other hand, provide two independent channels of information, which open up unique possibilities for the study of fine vibronic effects in the semiconductor–insulator–dye structures. In view of the two competing channels of energy migration (M and S), the response of the semiconductor electronic subsystem may be quite sensitive to any changes in the adsorbed phase. Even the first experiments [22] showed that the dependence of the charge ΔQ_{IT} ejected from the insulator traps of the insulator–semiconductor structure on the concentration of the dye molecules adsorbed on the surface has an extremum at $N_A \simeq (1\text{–}3) \times 10^{13}$ molecules/cm^2 when the efficiency of the channel S is greater than that of the channel M. When the energy transfer is determined solely by k_{IT}, other channels of energy migration in (5) and (6) being constant, there exists a nearly linear dependence between the charge ΔQ_{IT} and the extent of luminescence quenching ΔI. When both donating and accepting molecules are present on the surface (e. g., erythrosine and rhodamine B on Ge–GeO_2) whose bands of luminescence and absorption overlap, an additional fluorescence quenching occurs, and the charge ejection from the insulator traps diminishes. When there is no resonance between the donor and acceptor molecules ($k_{\mathrm{FD}} \to 0$), the energy can migrate by other alternative pathways through channel M: reabsorption of the emitted photons and the vibronic effects. In the latter case, the energy of the electron-excited donor molecule excites vibrational modes of the molecule via internal conversion (k_{ic}) and then is transferred to neighboring acceptor molecules if their vibrational spectra overlap [25]. Such a mechanism was repeatedly observed in three-dimensional molecular systems. Its specific features for the semiconductor–insulator–dye system were considered by us in [26].

We studied the system of Ge–GeO_2–rhodamine B–impurity molecules. Molecules of H_2O, D_2O, naphthalene and perdeuterated naphthalene were used as impurity (guest) molecules. Their electronic spectra differ substantially from those of donor molecules over the frequency scale. But the vibrational spectra of H_2O and naphthalene partially overlap with the vibrational modes of some molecular groups of rhodamine B. In the case of adsorbed H_2O molecules, these are vibrations of the OH groups ($\nu_{\mathrm{vib}} = 3540\text{–}3650$ cm^{-1}) and vibrations of the respective groups in rhodamine B molecules. The band of the vibrational modes of the CH groups in rhodamine B molecules and the respective bands of naphthalene molecules are partially overlapping. For deuterated molecules, such an overlapping is absent.

As follows from Figs. 6 and 7, admission of H_2O and naphthalene vapors is accompanied by a noticeable quenching of the fluorescence intensity I of rhodamine B molecules. Since the singlet–triplet intersystem crossing in rhodamine B molecules is small ($k_{st} \to 0$) and the Förster-Dexter mechanism is inefficient ($k_{\mathrm{FD}} \to 0$) at mean distances between molecules greater than 50 Å, the observed quenching is determined entirely by the internal conversion of the electronic excitation into vibrational modes (k_{ic}) followed by energy transfer to the guest molecules. For deuterated molecules, the quenching ΔI is absent due to an insignificant difference between the vibronic bands.

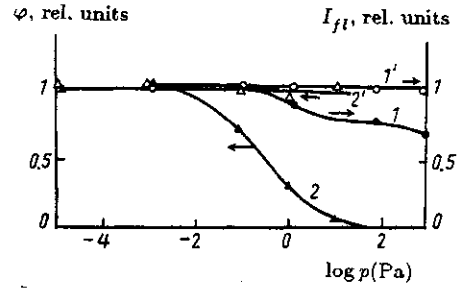


Fig. 6

Fluorescence intensity of rhodamine B (1, 1′) and efficiency of IT$^-$ photodepletion (2, 2′) in the semiconductor–insulator–dye system as functions of the H_2O (1, 2) and the D_2O (1′, 2′) vapor pressure.

At the system parameters chosen ($N_A^{\max}$ and thickness d of the GeO_2 layer), the response of the electronic subsystem (change of the charge Q_{IT} on the IT$^-$ traps) turned out to be rather strong according to field effect measurements. It is convenient to express these changes in terms of the efficiency of sensitized photoejection:

$$\varphi = (Q^0_{\mathrm{IT}} - Q^{\mathrm{ph}}_{\mathrm{IT}})/Q^0_{\mathrm{IT}},$$

where Q^0_{IT} is the equilibrium dark charge of IT, $Q^{\mathrm{ph}}_{\mathrm{IT}}$ is the charge after photoexcitation of a dye molecule. As is seen in Figs. 6 and 7, adsorption of H_2O and naphthalene resulted in a drop of φ, while adsorption of

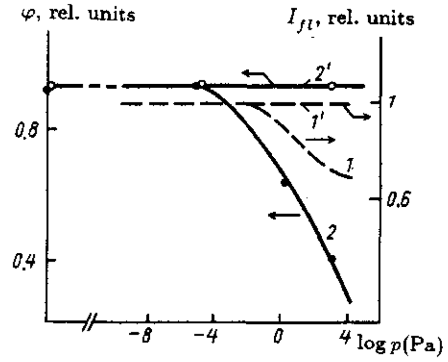


Fig. 7

Fluorescence intensity of rhodamine B (1, 1') and efficiency of IT^- photodepletion (2, 2') in the semiconductor–insulator–dye system as functions of the naphthalene (1, 2) and the deuterated naphthalene (1', 2') vapor pressure.

deuterated molecules had no influence on φ. Increase in the efficiency of channel M (growth of k_{ic}) due to vibronic effects led to suppression of channel S, i.e., to a decreased φ with unchanged charge of other surface electronic states.

The observed influence of vibronic effects in the semiconductor–insulator–dye system on its electronic subsystem was found to be rather strong. We have performed similar experiments [21] using a popular material for photosensitization studies: a zinc oxide single crystal with rhodamine B molecules adsorbed to its surface. We have chosen the efficiency of change of the photoconductivity (G) at maximum absorption of dye molecules as an electrophysical parameter: $\Phi = (G_{\mathrm{ph}} - G_0)/G_0$. As follows from Fig. 8, the character of the influence produced by adsorption of guest molecules on Φ is essentially the same as that on φ for the semiconductor–insulator–dye structure. Similar dependencies were observed also for films of polycrystalline ZnO, where changes in transport of nonequilibrium charge carriers are related entirely to the barrier phenomena.

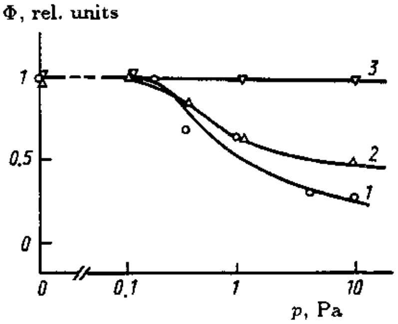


Fig. 8

Efficiency of conductivity photosensitization as a function of naphthalene vapor pressure for the systems: ZnO single crystal–rhodamine B (1); polycrystalline ZnO–rhodamine B (2); the same after admission of deuterated naphthalene vapor (3).

Now let us return to electronic processes in the IS structures. To discharge the surface electronic states, the energy of the photoexcited dye molecule, K ($h\nu_l$), must be greater than the effective depth (ε_t) of these states in the energy diagram of a disordered heterogeneous junction (see Fig. 1), i.e., $h\nu_l > \varepsilon_t$. A photosensitized ejection of electrons from the electronic states is determined by the Franck-Condon vertical optical transition that characterizes the optical depth ε_t^O of the level of surface electronic states.

Unfortunately, its exact determination is impossible because of the extremely small photon capture cross section for electronic states. The optical depth ε_t^O is always greater than the energy of thermal ejection ε_t^T, especially for disordered semiconductors with strong ionic bonding. The Stokes shift $\Delta\varepsilon = \varepsilon_t^O - \varepsilon_t^T$ is determined by the rate constant of electron–phonon interactions. For SiO_2, the optical phonons ($h\nu_p = 0.15$ eV) are responsible for vibronic interactions. Using the available data on ε_t^O derived from measurements of the efficiency of photosensitized ejection and the data on ε_t^T derived from studies on thermostimulated depletion of IT [6], and taking account of the high density of localized states in the forbidden band of SiO_2 (tails of the state density) chipped off the edges of the allowed bands of the disordered SiO_2 (the dashed line in Fig. 1), we obtained $\Delta\varepsilon \simeq 0.2$–$0.4$ eV, which does not differ too much from the theoretical predictions ($\Delta\varepsilon \simeq 0.13$ eV)* [27].

It should be noted that vibronic interactions of a trapped electron with soft local modes of a defect that includes either an adsorbed molecule or its fragment must also manifest themselves with the reverse process of IT$^-$ charging [6]. Part of energy released upon transition of an electron photoinjected from the conduction band of SiO_2(GeO_2) to deep IT$^-$ may be spent on the vibrational excitation of a defect. This may probably account for the transition of part of adsorbed acceptor molecules of *para*-benzoquinone (pBQ) (which enter into the composition of IT$^-$ in the Ge–GeO_2–pBQ–rhodamine B system) to the radical state (pBQ)$^{\cdot}$ and the accompanying growth of the ESR signal from these spin species [28]. By the way, in this case we managed to observe directly the sensitized ejection of electrons from the IT$^-$ upon illumination of the system within the spectral range of dye absorption from a decrease of the ESR signal from these spin species. For some semiconductor–insulator–dye systems, the energy released upon trapping may be transferred resonantly to dye molecules thus causing their excitation. We have observed slowing down of the dye molecule fluorescence quenching upon photocharging of the IT$^-$.

So far we considered situations when the dye molecules do not form their own surface electronic states in the semiconductor–insulator–dye system. They are retained at the surface largely by the Van-der-Waals forces and in their excited state they play only the role of energy donors. In all the experiments mentioned above, we verified that there is no influence of dye adsorption on the electrophysical parameters of the surface. However, one cannot rule out that there exist systems in which sensitization of electronic transitions is mainly achieved by the mechanism of electron transfer from dye to solid (Fig. 5 b). Such mechanisms have been discussed in the literature [29]. But in these cases, too, the vibronic effects must play a major role in the dynamic polarization of electron spins of the ion radicals formed and in their variable interactions in the adsorbed phase, which no doubt will have response in the electronic subsystem of the semiconductor.

4. VIBRONIC EFFECTS IN THE SYSTEM OF SEMICONDUCTOR–INSULATOR–LANGMUIR/BLODGETT FILM

We studied Langmuir-Blodgett (LB) films formed by molecules of zinc ethylaminemethyl phthalocyanine and deposited onto a real silicon surface (Si_r), onto a Si–SiO_2 structure with a thick oxide film (about 50 nm), and onto a quartz surface. The number of monolayers in the films was always equal to 10. As might be expected (Fig. 9 a), the absorption spectra (I_a) for the samples of quartz and silicon with a thick oxide film turned out to be the same, which indicates the identity of the adsorbed phase structures and a markedly oriented j-packing of molecules in the vicinity of the interface. This is also supported by the small Stokes shift $\Delta\lambda_S = \lambda_{fl} - \lambda_a$ (λ_a and λ_{fl} are the wavelengths at the adsorption and fluorescence maxima of the films, respectively). A different picture is observed for the real silicon surface Si_r partially coated with an oxide film [6]. The absorption spectrum of phthalocyanine on the surface is shifted by 170 nm to the UV region (Fig. 9 a). This is explained by the formation of dimers on unoxidized surface regions of Si [30], which leads to film disordering (Fig. 9 b).

Studies of photocharging of the semiconductor–insulator–LB film structures showed that the majority of electrons injected from the semiconductor to the insulator of the structure are localized at the traps in the LB film (T^-_{LB}). Capture of charge carriers by these traps is accompanied by the following two changes in the spectra (Fig. 9 a): (i) a decrease in the fluorescence intensity due to ejection of electrons from part of T^-_{LB} to SiO_2 and the semiconductor; and (ii) a large shift (by about 170 nm) of the absorption maximum to

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* The difference is probably due to the fact that in the theoretical calculations of $\Delta\varepsilon$ [27] use was made of the values of the corresponding parameters typical of a three-dimensional phase.

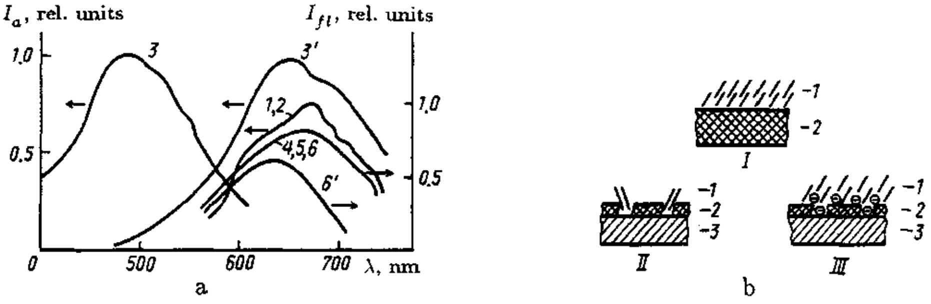

Fig. 9

(a) Absorption spectra I_a (1–3) and fluorescence spectra I_{fl} (4–6) of Langmuir-Blodgett phthalocyanine films ($n = 10$) on the surface of quartz (1, 4), Si–SiO$_2$ (2, 5), and Si$_r$ (3, 6). Also shown are the spectral changes occurring in the samples of Si$_r$ (3', 6') after optical charging of the semiconductor–insulator–LB film structure up to $Q_{ss} = 5 \times 10^{11}$ el.charge/cm^2. (b) Packing of phthalocyanine molecules (1) at the surface of SiO$_2$ (I), Si$_r$ (II), and charged Si$_r$ (III) (SiO$_2$ is denoted by 2, Si by 3).

the red region. The absorption spectrum becomes nearly coincident with the spectra of molecules adsorbed to quartz and to the Si–SiO$_2$ structure. The Stokes shift drops sharply.

These marked changes in the absorption spectrum and in the Stokes shift are related to the ordering of molecules in the LB film, to its j-packing (see Fig. 9 b). As was mentioned above, the possibility of using the synergism principle to develop the integrated circuits of molecular electronics is being widely discussed in the literature. As follows from the previous discussion, due to their bond elasticity LB films can be a convenient material for the study of self-organization of circuit fragments.

5. ON SOME PROSPECTS OF UTILIZATION OF THE VIBRONIC EFFECTS IN MOLECULAR ELECTRONICS ELEMENTS

We shall confine ourselves to the consideration of only two aspects of utilization of electron-vibrational interactions in the semiconductor–insulator–dye and semiconductor–insulator–LB film systems.

Selective Sensors for Analysis of Gaseous and Liquid Mixtures

The ideas of utilization of semiconductor structures for this purpose appeared as early as the 1960s but received particular attention only in recent years (see, e. g., reviews [4, 31]). Most of these ideas are based on the fact that the molecules to be analyzed form their own electronic states at the surface. This, in turn, leads to a change in the electrophysical parameters of the surface or interphase boundaries in IS and MIS structures, which is manifested in changes of the potential Y and the surface conductivity σ, the mobility of charge carriers, etc. Sensors utilizing these principles may be highly sensitive, particularly in the case of polycrystalline films containing a great many barriers between particles [4]. Such sensors, however, cannot in principle be selective with respect to different molecules. Different molecules containing the same active fragments will form surface electronic states of the same equilibrium parameters. As was mentioned in Section 1, the new adsorption-related electronic states or changes in the existing prehistory electronic states on a disordered surface, to which the real surface of all semiconductors belongs, do not reflect at all the individual features of the molecules.

To improve the selectivity, we suggested, as early as 1973 [32], a chemical and a radiation-induced modification of the surface, the use of selective membranes as an insulator layer, setting up at the insulator–semiconductor interface a topography of active sites that would correspond to the position of active groups in the molecules to be analyzed, etc. All these suggestions, however, are of a technological nature.

We believe that the purely physical concepts of developing highly selective sensors must include the utilization of the vibronic effects described above. The vibrational spectrum is the most unambiguous characteristic of a given molecule. Proceeding from the vibronic mechanism of interaction between the adsorptive interface slow states and the charge carries trapped by them, a novel principle of selective analysis was suggested in [33] based on measurements of the kinetics of charge relaxation at varied temperatures and on the determination of ΔE_T and τ in Eqs. (1) and (2). Apparently, the authors of [34], leaving aside the elucidation of the physical reasons responsible for the selectivity of the kinetic parameters, intuitively improved the selectivity by statistical processing of the kinetic curves of charging during adsorption in which these parameters are present in an implicit form [4].

Still more promising seems to be the utilization in selective analysis of semiconductor–insulator–dye and semiconductor–insulator–LB film structures. As follows from Section 3, the efficiency of energy dissipation for photoexcited dye molecules in the molecular phase (channel M) is strongly dependent on the extent of overlapping of their molecular spectra with the vibronic spectrum of adsorbed guest molecules. This effect has already been used for selective analysis of gaseous mixtures according to quenching of the fluorescence of dye molecules at the insulator surface or in polymer matrices (see, e. g., [35]). In metal–LB film systems, one can detect the guest molecules from the shift of the plasmon resonance [36]. In all the cases, optical equipment is needed for monitoring the response of the system.

We used the competitive channel S to record the molecules in question in the semiconductor–insulator–dye system, i. e., the response of the electronic subsystem of the semiconductor, which has undoubted advantages in developing microelectronic circuits. As is seen in Figs. 6, 7, the selectivity of these systems is sufficient even for the isotope analysis of molecular mixtures. Taking into consideration the enormous potentialities of organic synthesis, it seems quite possible to prepare dye molecules that would be suitable (by their vibronic spectra) to every kind of analyzed molecules, have large photon trapping cross sections, and have suitable (for a given semiconductor) energies of fluorescence photons. Very helpful in this search may be systematic studies of the electron-vibrational processes in polyatomic molecules [37].

As a convenient molecular matrix, use may be made of LB films or immobilized enzymes [32]. The selectivity of the latter is well known in cytology. Adsorption of molecules to be detected will result in conformational transitions in the enzymes or in molecular reorientation in the LB films, which will finally affect the vibronic effects responsible for the dark trapping, for polariton processes at the insulator–semiconductor interface, and for the photosensitization of electronic transitions in this interphace region.

Modeling of Some Biological Processes

A specific feature of many biological systems is combination of electronic and ionic, in particular protonic, processes taking place in cell membranes. The semiconductor surface and the insulator–semiconductor interphase boundary may be used as a convenient place to model individual stages of these processes [32]. Trapping by adsorptive slow states of the interface and recombination of charge carriers change the activity of the electron-accepting and proton-donating centers of the redox and acid-base catalysis, as well as of biocatalysis [38, 39]. These processes could be stimulated by pulsed illumination and transverse electric fields. They may be intensified by means of additional excitation of local soft phonons in the region of the interface slow states. As follows from Sections 2 and 3, vibronic interactions play an important part in the dissociation of adsorbed molecules and in their catalytic transformations. Even in inorganic insulator–semiconductor and metal–insulator–semiconductor systems, one can model some separate stages of photosynthesis (decomposition of water and catalytic conversion of CO_2) by excitating the electronic and phonon subsystems of the IS structures. This analogy may be made more accurate if LB films and immobilized enzymes containing atoms of transition metals are used as the insulator layer. These aspects of the problem are discussed in more detail elsewhere [17, 18, 39].

The applications of elements of molecular electronics, such as semiconductor–insulator–dye and semiconductor–insulator–LB film structures, may open up new possibilities in the study of various photochemical and photobiological reactions: their carrying out under conditions of injection of nonequilibrium charge carriers and vibronic interactions. These issues belong to the group of problems associated with the conversion of solar energy to the electric or chemical energy. Of interest to microelectronic engineering may be the possibility of control of photopolymerization in submicron photolithography processes. Also quite appropriate at present is research into the vibronic effects in elements of the memory and information processing using semiconductor–insulator–LB film and semiconductor–insulator–liquid crystal structures.

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