THE ROLE OF VIBRATIONAL EXCITATIONS OF A MOLECULAR SYSTEM IN THE KINETICS OF SLOW CHARGE RELAXATION ON THE SURFACE OF A SEMICONDUCTOR

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It is shown that the activation energy of the slow relaxation of charge in the field effect depends on the energy of the vibrational modes of absorbed molecules. The reason for the small capture cross sections of the slow electronic states is discussed. A capture model is proposed which explains the temperature dependence of the slow-relaxation kinetics in various gaseous units.

It is well known that the kinetics of slow relaxation of charge on an inhomogeneous surface of a semiconductor is well approximated by the relation

$$\Delta Q_{SS}(t) = \Delta Q_{SS}(0)\exp(-t/\tau)^{a}, \quad (1)$$

where τ is the effective slow-relaxation time, which is close to the mean statistical relaxation time, and a is a coefficient which depends on the degree of inhomogeneity of the surface and is usually equal to 0.3-0.6 [1]. The experiment shows that over a rather wide temperature interval

$$\tau^{-1} = \tau_0^{-1}\exp(-\Delta E_\tau/kT), \quad (2)$$

where ΔE_τ is the so-called activation energy of the effective slow-relaxation time. It was shown in Ref. [1] that the quantity ΔE_τ is close to the average height of the thermal activation of charge carriers in exchange between the slow states and the bulk of the semiconductor.

One of the most often discussed questions in the electronic slow-relaxation model is the question of the large time for the exchange of charge carriers between the slow states and the allowed bands of the semiconductor. In a number of cases, in particular, for real surfaces of germanium and silicon, the value of τ can reach several hours. In many papers it has been assumed that the hindered electronic exchange of the slow states with the bulk of the semiconductor is due to the fact that the slow states are located at the outer surface of the oxide layer. This point of view is not supported by the direct experimental evidence [2,3]. The slow states which are manifested in the field-effect experiments are located near the semiconductor-oxide boundary, but have an extremely small free-carrier capture cross section C. For example, in the case of a real surface of germanium $C \approx 10^{-26} - 10^{-28}$ cm^2 [4]. Slow relaxation is also observed for semiconductors without an oxide layer, for example, binary semiconductors, and also for atomically clean surfaces of germanium with adsorbed molecules (see the review

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Table 1

Parameters of Slow-Relaxation Kinetics on Real Surface of Germanium with Adsorbed Molecules of H_2O, NH_3, and n-bq

Admolecules	Parameters						
	$\hbar\omega_K$, eV	Slow-relaxation parameters in vapors (pressure 1.33 × × 10^3 Pa)			Slow-relaxation parameters after prolonged pumping out of respective vapors		
		τ, sec	τ_0^{-1}, sec^{-1}	ΔE_τ, eV	τ, sec	τ_0^{-1}, sec^{-1}	ΔE_τ, eV
H_2O	0,41—0,45	30	$2,6\cdot10^9$	0,65	180	$5,9\cdot10^3$	0,30
NH_3	0,37—0,42	60	$1,9\cdot10^8$	0,60	210	$7,4\cdot10^1$	0,25
n — bx	0,20—0,21	10	$5\cdot10^5$	0,40	110	2,94	0,15

[5]). These objects are characterized by just as small capture cross sections. For example, in CdS the cross section C is about 10^{-23} cm^2, and in ZnO it is around 10^{-25} - 10^{-26} cm^2 [6]. To explain such small capture cross sections, the author of Ref. [6] hypothesized the existence of a buffer layer of an unspecified nature on the surface of these semiconductors.

We have shown earlier [2-5] by analysis of our own data and data found in the literature, that for the most part the slow states on the germanium-oxide interface and on the surface of binary semiconductors (without an oxide film) have their origins in adsorpbtion. It was mentioned in Ref. [7] that the activiation energy of the slow-relaxation process depends on the type of adsorbed molecule. Using the field-effect method [3,4], we have carried out a detailed investigation of how the adsorption of acceptor (parabenzoquine: n-bq) and donor (water or ammonia) molecules affect the parameters ΔE_τ and τ_0^{-1} of the temperature dependence of the slow-relaxation (2). We investigated a real surface of germanium which had been etched in a peroxide reagent and preliminarily (before the adsorption) evacuated at 470-570 K. The slow-relaxation kinetics was measured in the temperature interval 250-320 K. The parameters τ_0^{-1} and ΔE_τ calculated from the kinetic curves are given in the table.

It can be seen from the table that activation energy ΔE_τ of slow relaxation and the frequency factor τ_0^{-1} depend on the structure of the adsorbed molecules. After removal of the weakly bound molecules from the surface by prolonged pumping at 300 K, a noticeable decrease of ΔE_τ and a simultaneous marked (by several orders of magnitude) increase of τ_0^{-1} were observed (see the Table and Fig. 1). Remaining on the evacuated surface of germanium are molecules which are securely bound by donor-acceptor bonds; these molecules are responsible for the appearance of slow states and the charging of the surface during adsorption [3,5]. We note that the frequency factor τ_0^{-1} in this case (Table) is many orders of magnitude lower than the usual values of τ_0^{-1} for electronic transitions to the bulk (10^{-12}-10^{13} sec^{-1}).

These effects can be explained qualitatively using the basic ideas of the theory of nonradiative electronic transitions in semiconductors (see, for example, [8,9]). An attempt to apply these ideas to the process of capture into electronic surface states was undertaken in [10,11]. The authors of [10] formally connected the large relaxation times of the slow states with the small effective coupling constant of the electron with the phonons of the lattice, leaving aside the

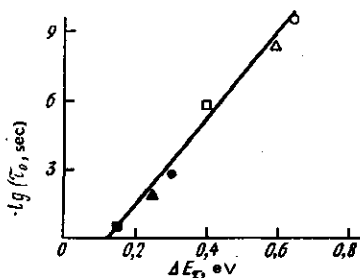

Fig. 1

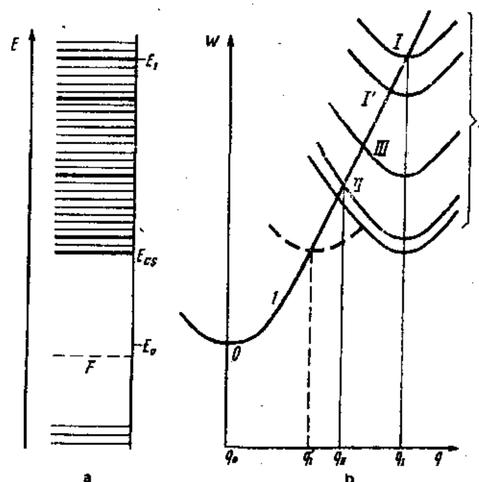

Fig. 2

Fig. 1. Experimental behavior of pre-exponential factor τ_0^{-1} as function of slow-relaxation activation energy. The open points: in water vapor (○), ammonia (Δ), and parabenzoquinone (□). Solid points: after prolonged pumping out of the respective vapors at 300 K.

Fig. 2. Band diagram of a semiconductor (a). Total potential energy of lattice as function of configurational coordinate (b).

questions of the reason for the significant decrease in this constant and the expected temperature dependence of the kinetics of slow relaxation. In Ref. [11] it was assumed that an electron captured into a slow state is located in the orbitals of the adsorbed molecule and therefore interacts weakly with the lattice phonons. In this case the largest times τ should be observed under conditions where there is complete transfer of the electron to the orbitals of the adsorbed molecule. However, the experiments indicate (see Table) that slow relaxation is also observed in cases where the complete transfer of the charge carrier to the adsorbed molecule is impossible (for example, in the adsorption of H_2O and NH_3 [3]).

We will particularize the model of nonradiative electronic transitions [9] to the case of capture into slow states with specific allowance for these facts. To this end we will examine the dependence of the total potential energy W of the crystal lattice on the configurational coordinate q (Fig. 2,b). The potential curve 1 in Fig. 2,b corresponds to an electron localized in a slow state, while the set of curves 2 corresponds to free-electron state, which correspond to the energy levels in the conduction band given by the heavy lines in the band diagram (Fig. 2,a). Suppose that before the capture of the electron the local environment of the slow state is characterized by the coordinate q_I (Fig. 2,b). If during capture the local environment of the slow state does not have time to be restructured (the Franck-Condon principle is observed), an electron from the conduction band should first fall to level E_I (Fig. 2,a), which corresponds to the "unrestructured" center I in the configuration diagram (Fig. 2,b). Then there occurs a restructuring of the environment of the capture center and the electron is in equilibrium state 0 (with coordinate q_0), which corresponds to the energy position of the "effective level" E_0 of the slow state. This level, according to the data of [3], is close to the center of the forbidden band of germanium. In the process of polarization (transition I-0) the energy of the electron usually decreases by

between 0.5 and 1 eV [12]. The difference between the coordinates $q_I - q_0$ characterizes the displacement of the atoms of the lattice during the localization of the electron.

As we have already pointed out, the origin of most of the slow states is in donor-acceptor complexes of adsorbed molecules with the active centers of the surface. The structure of these complexes is known [5,13] to be extremely sensitive to their state of charge. In other words, the chemical bonds of the complexes have a high polarizability. This is evidently the main characteristic of slow states which distinguishes them from fast states. In the configuration diagram this difference is reflected in the sizes of the displacements of the equilibrium coordinates $q_I - q_0$. If the level E_0 belongs to a fast state, the displacement $q'_I - q_0$ of the minima of the potential curves for localized and free electrons (dashed curves) will be significantly smaller than for localization in a slow state ($q_I - q_0$).

The energy liberated during the transition of the system from state I to the equilibrium state 0 (curve 1 of Fig. 2,b) should be dissipated by the emission of a rather large number (tens and more) of lattice phonons. In a number of cases such multi-phonon processes are characterized by small probabilities [8]. In the situation under study it is necessary, in addition, to take into account the significant probability of the transition of the system from metastable states on curve 1, for example I', to one of the potential curves 2 after emission of one or two phonons (the "failure" of the capture). For this reason the ulitmate capture of an electron (i.e., its localization in state 0) after the transition from state I is an impossible event. Apparently the original capture of the electron into an intermediate state II in which its energy is higher than the bottom of the conduction band at the surface E_{CS} by an amount of the order of the phonon energy $\hbar\omega_p$ is more probable in this case. Then after the emission of one phonon the energy of the electron will be close to E_{CS} and the probability that the capture will be interrupted is sharply diminished. It is clear that the local environment of the capture center in state II is already somewhat distorted due to thermal fluctuations in the lattice.

In the general case the probability of localization of the electron at the capture center can be written in the form

$$\nu = \nu_0 \exp\left[-\frac{E-F}{kT} - \frac{(E-B)^2}{2\delta^2} - \alpha (V_0 - E)^{1/2}\right], \qquad (3)$$

where ν_0 is a pre-exponential factor, F is the Fermi energy, B and δ are the effective coupling constants of an electron at a local center with vibrations of the crystal lattice [9,11], and α and V_0 are constants (see below).

The first term in the exponential in Eq. (3) corresponds to the probability of exciting an electron to a level of the conduction band with energy E, the second term describes the decrease of the capture probability owing to the restructuring of the immediate environment of the local center [9,11], and the third term takes into account the probability of tunneling through a potential barrier of height V_0, which can be due, for example, to the presence of an oxide layer of tunneling thickness on the surface of the semiconductor [14] (the coefficient α depends on the shape of the potential barrier and on the effective mass of the tunneling electron). In one-phase systems the tunneling factor in Eq. (3) is absent, and the small cross sections for capture into slow states are governed by the first and second terms of Eq. (3). In the case of a real surface of germa-

nium, an appreciable fraction of the slow states are located near the semiconductor-oxide interface, and tunneling is not the controlling factor here either [3,5].

If the temperature dependence of the second term $((E-B)^2/2\delta^2)$ in Eq. (3) is small, the activation energy of slow relaxation in first approximation is equal to $\Delta E_\tau \simeq E-F$ (the tunneling factor does not depend on temperature).* The product $\nu_0 \exp[-(E-B)^2/2\delta^2-\alpha(V_0-E)^{1/2}]$ in Eq. (3) in essence plays the role of the frequency factor τ_0^{-1} that is measured in the experiment (formula (2)).

In the case of capture into an intermediate state II (Fig. 2,b), $E-E_{CS} \simeq \hbar\omega_p$, and therefore $\Delta E_\tau \simeq (E_{CS}-F)+\hbar\omega_p$. In our experiments with germanium $E_{CS}-F \simeq 0.2$-0.3 eV and, consequently, the values of ΔE_τ (Table) observed for evacuated samples are close to the expected values. It is clear that the smaller the activation energy ΔE_τ the more strongly the configurational coordinates q_I and q_{II} differ (Fig. 2,b) and the larger the quantities $(E-B)^2/2\delta^2$ and (V_0-E) become. This is manifested experimentally by the significant decrease in τ_0^{-1} accompanying the decrease of the activation energy ΔE_τ of the slow-relaxation process (see Fig. 1).

It is extremely probable that the above processes play a significant role in a number of phenomena. In particular, they can lead to the well known "compensation effect" in catalysts, which consists of cymbiform variations in the activation energies and frequency factors of various catalytic reactions on the surfaces of semiconductors. We note that a linear relation between the logarithm of the pre-exponential factor and the activation energy of a process, such as that shown in Fig. 1, has been noticed repeatedly in catalysts phenomena on semiconductors (the empirical law of Constable).

We will now look at the situation when the surface of the semiconductor is in equilibrium with the adsorbate vapors. In this case the primary donor-acceptor adsorption complexes forming the basis of the slow states are surrounded by clusters of adsorbed molecules, bound to each other by weaker hydrogen (H_2O and NH_3) or Van der Waals (n-bq) bonds. It is important that the energy of the vibrational modes ($\hbar\omega_v$) of these molecules is significantly higher than the energy of the phonons ($\hbar\omega_p$) of the semiconductor (Table). In this case it becomes possible for the excess energy to be transferred from the electron - capture-center system to the vibrational modes of the adsorbed molecules.** For this reason the initial capture of an electron from the higher levels of the conduction band to some intermediate state III (Fig. 2,b) whose energy is higher than that of state II by an amount of the order of $(\hbar\omega_k - \hbar\omega_p)$ becomes extremely probable. Since this requires less restructuring of the environment of the slow state (the coordinate q_{III} is closer to q_I than q_{II} is), the pre-exponential factor τ_0^{-1} increases sharply (Fig. 1 and Table). This leads to an increase in the probability of localization of the electron in the slow state and a decrease in the slow relaxation time τ (see Table). The activation energy of the slow relaxation process under these

*Here it is assumed that the Fermi level on the surface of the semiconductor does not depend on the temperature (the Fermi level is "stablized" by the system of surface states)

**The possibility of energy exchange between the electrons and vibrational modes of the adsorbed molecules has been demonstrated by experiments on inelastic tunneling through thin dielectric layers [15].

conditions increases by approximately ($\hbar\omega_k - \hbar\omega_p$), reaching $\Delta E_\tau \approx (E_{CS}-F) + \hbar\omega_k \approx$ $\approx$ (0.2-0.3 eV) + $\hbar\omega_k$. The values given in the table for the energies of the most intense vibrational modes of the adsorbed molecules $\hbar\omega_k$ and the activation energy ΔE_τ indicate that this relation is rather well satisfied.

It can be assumed that by extrapolating the dependence of τ_0^{-1} on ΔE_τ given in Fig. 1 to values of the frequency factor typical of solids ($10^{12} - 10^{13}$ sec^{-1}) one can estimate qualitatively the activation energy $\Delta E_{\tau 0}$ corresponding to the transition of the system into state I (without restructuring of the immediate environment). In our case such an extrapolation leads to the value $\Delta E_\tau \approx 0.8$ eV, which agrees in order of magnitude with the theoretical estimates [12].

If the value of $E_{CS}-F$ is around 0.2 to 0.4 eV, then according to the proposed model the temperature dependence of the slow relaxation for other semiconductors should be about the same as for germanium. This is evidently the case in the experiments on ZnO reported in Ref. [16]. Under conditions where there were weakly bound water molecules on the surface, the activation energy of slow relaxation in ZnO was equal to 0.6 eV. After the adsorption on the ZnO surface of molecules of the aromatic compound erythrosine (whose vibrational mode energies are similar to $\hbar\omega_k$ for n-bq), the activation energy of slow relaxation fell to $\Delta E_\tau \approx 0.35$ eV.

In conclusion, we will remark that the proposed model for the capture of electrons into slow states enables one not only to explain the existing experimental data on the temperature dependence of slow relaxation, but in a number of cases can predict the expected dependence of the kinetics of relaxation on the nature of the adsorbed molecules and on the temperature. It is also of no little importance that the model predicts substantial vibrational excitation of the adsorbed molecules during electronic transitions to the slow states, which can lead to desorption of the molecules or the breaking of some of the intramolecular bonds. Under certain conditions such "electrically controllable" excitation of the adsorbed molecules can be used in heterogeneous catalysts in semiconductors and in semiconductor-dielectric systems. The proposed model also implies that it is in principle possible to use excitations in a system of adsorbed molecules to stimulate electronic transitions in solids. The validity of this conclusion is confirmed by experiments on the photosensitization of electronic transitions in the surface region of solids in the presence of adsorbed dyes molecules [17]. The joint investigation of slow relaxation and photoexcitation of adsorbed molecules will disclose the complex mechanism of energy exchange between the surface excitations of the solid and the adsorbed molecules.

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