The Electric Double Layer at the Semiconductor/Electrolyte Interface[*,+]

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Studies of the structure of the semiconductor/electrolyte solution interface are of interest both for the physics of semiconductors — inasmuch as they throw light on some fundamental characteristics of solids — and for electrochemistry — since the structure of the interface is in many respects the decisive factor in determining the rate of electrochemical reactions on semiconductor electrodes. The object of this review is to give a general idea of recent results obtained in those sections of the electrochemistry of semiconductors which treat the semiconductor electrodes in the equilibrium state. The problems considered are:

1. The electric double layer structure at semiconductor electrodes (potential distribution, charge, relaxation).

2. Methods of investigation. The characteristic features and limits of applicability of basic methods (»field effect«, differential capacity, fast and slow charging curves, electrooptical).

3. Review of experimental results on the electric double layer structure on germanium, silicon and binary compounds.

The double layer studies are no longer the main trend in the electrochemistry of semiconductors (now the interest is centered on the electrochemical kinetics on the semiconductor and insulating electrodes), however, the studies of the double layer structure on semiconductors have yielded some interesting results as well, which can be briefly summarized as follows:

1) development of new methods of investigation,

2) examination of some new effects,

3) examination of some new semiconductors as electrode materials.

We shall confine our treatment to single crystal semiconducting materials with electronic conductivity.

Methods of Experimental Investigation of Surface Properties of Semiconductor Electrodes

Methods applied in electrochemistry of semiconductors may be conventionally divided into two groups. The first one includes the methods which may anyhow relate to the semiconductor surface physics, the second includes those traditionally electrochemical.

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[+] Review of papers published in 1965—1971; for earlier work see Ref. 1.

The electrochemical analogue of »field effect« was the first to be developed widely in the first group. It allows to plot surface conductivity *versus* electrode potential*. Further, the space charge theory is used to calculate potential drop in the space charge layer from the surface conductivity. By subtracting it from the electrode potential one directly obtains the interphase potential drop (accurate to a certain constant) which may be further related to the physicochemical properties of the system under study.

The important fact is that when measuring the resistance of the semiconductor slab submerged into electrolyte, the impedance of the interface rather than bulk resistance of the electrolyte is a limiting parameter which does or does not allow to apply the field effect method. Impedance (mainly, its reactive component) of a semiconductor/electrolyte interface decreases usually with an increase in AC frequency. Therefore, DC measurements produce minimal leakage of the measuring current into the solution. Hence direct current should be used to measure the sample resistance[3,4].

The same is also valid with other methods which require that electric field be applied along a semiconductor/electrolyte interface. In the first place, one must mention here effective lifetime of minority carriers as measured by decay of photo conductivity (the carriers being injected with current or light pulses) or by steady-state photo conductivity. In all such procedures one should use current and/or impedance *vs.* potential plot to ensure that measuring current does not leak to the solution.

Drawbacks of the surface conductivity method made it give up its place to the differential capacity method which retains, however, modulation of surface potential by external field (»field effect«).

Differential capacity is measured very seldom on a »free« surface of semiconductor. The procedure is hindered by the following: the dielectric connected in series with the semiconductor sample has very low capacity whereby the method may not allow to measure higher capacities. Recently, the differential capacity method was often used with the metal-oxide semiconductor system[5] where the series capacity may be of about $0.1 \ \mu F/cm^2$ owing to a relatively small thickness of the oxide layer and its high dielectric constant. In this case, however, semiconductor surface properties are defined by the oxide which is in contact with the semiconductor and they are difficult to monitor which makes the procedure somewhat inconvenient.

In an electrolytic system the whole solution is used as the »field« electrode; the »measuring condenser« *i. e.* the Helmholtz layer has thickness of an order of ion size and its capacity reaches $\approx 10 \ \mu F/cm^2$. Hence very large differential capacities can be measured in a semiconductor-electrolyte system**.

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* Surface potential of a semiconductor electrode can be varied by the change of the solution composition as well (cp. the »Bardeen-Brattain cycle« in gaseous ambients)[2].

** The same facilitates modulation of the semiconductor surface potential in electrolyte by external field. The potential difference applied is localized mainly in the space charge layer in semiconductor. Therefore, voltages of an order of 1 V are sufficient already to give a high induced charge (10^{-8} to 10^{-7} Coulomb/cm^2) and to change potential of the semiconductor surface markedly, even to achieve degeneration of free carriers near the surface.

The capacity *versus* AC frequency dependence (usually measured at 10 to 10^5 cps) informs on the spectrum of surface states and on non-equilibrium processes proceeding in the double layer. Modern instruments automatically measure capacity *versus* the electrode potential, the latter being varied as a certain (mainly, linear) function of time[6-8].

It is significant that if the electrode is charged quickly enough so that relaxation of slow surface states is eliminated, it is possible to attain very high surface potential values. The corresponding capacity value of the space charge region proves to be comparable to that of the Helmholtz layer or even to exceed it. Thus favourable conditions are created for measuring the Helmholtz capacity on the semiconductor electrode. In this way the Helmholtz capacity on germanium has been measured[9].

Semiconductor electrodes may be applied to photo electric measurements using inner photo effect in semiconductor[10,11]. Here as well, the technique of the surface photo e. m. f. measurement with continuously changing electrode potential was developed[12].

In the so-called small-signal version of the method the surface potential is calculated from the photo e. m. f. measured, using the space charge theory. The direct method — the photoeffect at large signals can be also used for this purpose. This method is based on the fact that when nonequilibrium free carriers are injected into the sample, the band-bending near the surface diminishes and at a sufficiently large injection level becomes zero. Thus the limiting value of the photo e. m. f. measured is equal to the initial potential drop in the space charge region.

In practice, however, it is impossible to have the sample sufficiently strongly illuminated (unless lasers are used). But instead of light, it is possible to use, as a source of nonequilibrium carriers, the *p-n* junction on the back side of a thin electrode, biased in the forward direction. The injected minority carriers diffuse from the *p-n* junction to the semiconductor/electrolyte interface and the majority carriers are introduced into the sample through the ohmic contact and are transferred further by the electric field. Using this method, it is possible to obtain high injection levels.

Fig. 1 shows the plot, obtained by this method, of the potential drop in the space charge region *versus* the *n*-type germanium electrode potential. In the limiting anodic current region the potential drop in the Helmholtz layer is practically constant, whereas in the region of ideal polarizability of the electrode it can vary greatly depending on the electrode prepolarization[13].

The limitation of the method is its inapplicability in the case of an accumulation layer and also for semiconductors with a small diffusion lenght of minority carriers.

As regards the surface recombination velocity measurements, apart from conventional methods — the steady-state photoconductivity and the photo-conductivity decay, very popular are now the methods utilizing the *p-n* junction on the back side of a thin germanium electrode. In most cases it is the value of the dark reverse current of the *p-n* junction which is measured. Its value is sensitive to the rate of thermal generation of carriers in the sample, which, in its turn, depends on the surface recombination velocity at the interface with electrolyte. The photo e. m. f. at the *p-n* junction is also measured, the sample being illuminated from the »electrolytic« side[14,15].
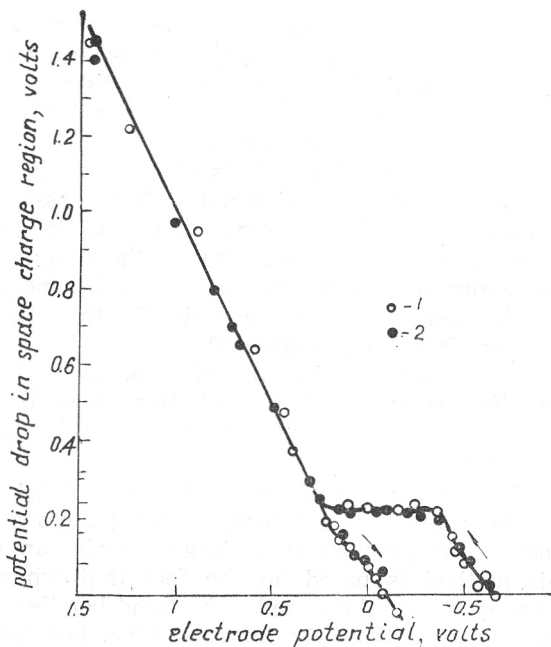
Fig. 1. Dependence of the potential drop in the space charge region on the potential of n-type germanium electrode in 48% HF measured by the injection through the p-n junction method[13]. 1 — direct measurements, 2 — calculated from the differential capacity values.

Finally, IR-radiation attending the recombination processes in the electrode was made use of for determination of the surface recombination velocity[16-18]. The non-equilibrium free carriers are introduced into the germanium sample through the interface with electrolyte (by illumination or by the ferricyanide electroreduction) and undergo recombination in its bulk, the IR-radiation arising being observed from the back side of a thin electrode.

Recently spectroscopic methods have been rather widely spread in electrochemistry of semiconductors. Spectroscopy with internal total reflection in different modifications has been used for investigation of the adsorption layer, diffuse layer and diffusion layer on semiconductor electrodes. A beam of light passes through a sample which is transparent to it and falls on the interface with electrolyte. At a sufficiently high angle of incidence internal total reflection is achieved. The reflection coefficient, and hence the intensity of output signal depends on the structure of the reflecting surface, in particular on the nature of the particles adsorbed on it and on the chemical composition of the phases on both sides of the reflecting interface. For better sensitivity multiple reflection of light beams from the surface being examined is resorted to in electrode systems of different kinds[19], one being presented in Fig. 2.

It should be borne in mind that light penetrates into the solution bulk to the distance of the order of a wavelength (*i. e.* 1 μm). Therefore, the method is sensitive to the properties of the near-the-electrode solution layer and much less sensitive to the structure of the interface proper.
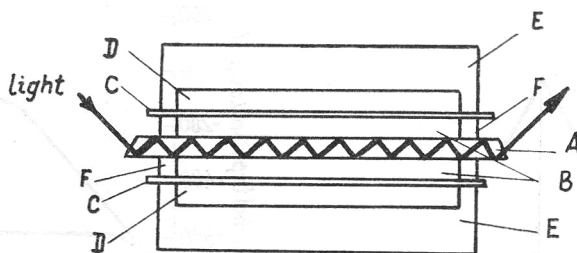
Fig. 2. Transparent electrode for internal reflection spectroscopy[19]. A — germanium plate, B — electrolyte, C — auxiliary palladium electrode, D — hydrogen chamber, C — body of cell, F — teflon gasket.

Osteryoung, Hansen and Kuwana[20] used this method to measure the near-the-electrode concentration of the oxidation product of o-tolidine on a tin oxide electrode; Takamura and Yoshida[21] studied the structure of the diffuse double layer on a germanium electrode in solutions of different composition. Reed and Yeager[22] used IR-spectroscopy for investigation of large organic molecules (for instance, stearic acid) adsorption and also of the space charge region at the germanium electrode. In the latter case, through modulation of the surface potential by alternating current they varied the surface excesses of electrons and holes and thus changed the reflectivity of the electrode surface. In the output signal, a variable component appeared on the frequency of modulation, which is due to absorption of light by free carriers.

The electroreflection method appears to be very promising. For some years it has been applied, in some cases with the use of electrochemical technique, for investigation of the band structure of semiconductors[23]. In recent years it has been used for measuring the surface potential of semi-conductor electrodes. The theory of electroreflection from the space charge layer of the semiconductor electrode has been developed recently by Tyagai et. al.[24,25]

The method is based on the change of optical properties of a solid caused by a local electric field in the space charge region. The intensity of the beam of light reflected from the electrode surface is measured as a function of various parameters characterizing both the incident light (its wavelength, polarization) and the state of the surface (e. g. potential). To increase the sensitivity, the electrode potential is modulated by alternating current and the output signal from the photomultiplier, on which the light from the cell falls, is amplified by a narrow-band amplifier at the modulation frequency. On the germanium electrode this method was used for the surface potential measurements by Gobrecht et al.[26,27] and Konorov[28]. First a calibration curve »reflectivity—electric field strength on the surface« was plotted, for which purpose the differential capacity method has been used (Fig. 3). With the help of this curve the change of the components of the total potential drop was measured at the germanium/sulfuric acid solution interface. Fig. 4 shows the dependence of the Helmholtz potential drop on the electrode potential calculated from these measurements.

It can be supposed that the electroreflection method is applicable also in the presence of appreciable faradaic current, when the capacity measure-
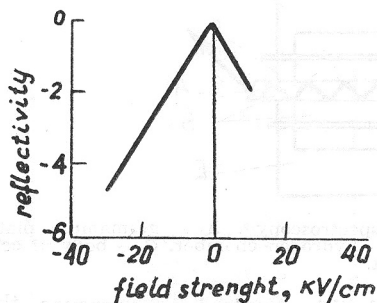
Fig. 3. Relationship between the reflectivity of the germanium/0.1 N H_2SO_4 interface and the electric field strength on the surface[26].
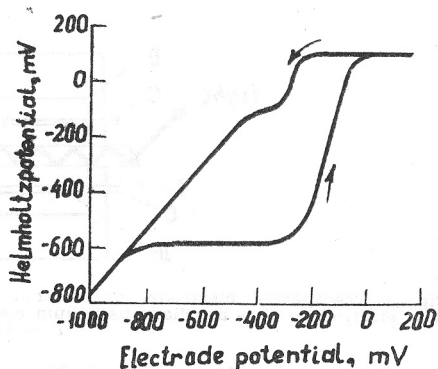
Fig. 4. Dependence of the Helmholtz potential drop on the germanium electrode potential in 0.1 N H_2SO_4 obtained by the electroreflection method[26].

ments become impracticable. However, in some cases, application of this method presents difficulties and the results obtained cannot be readily interpreted. For illustration, Fig. 5 shows the dependence of the differential
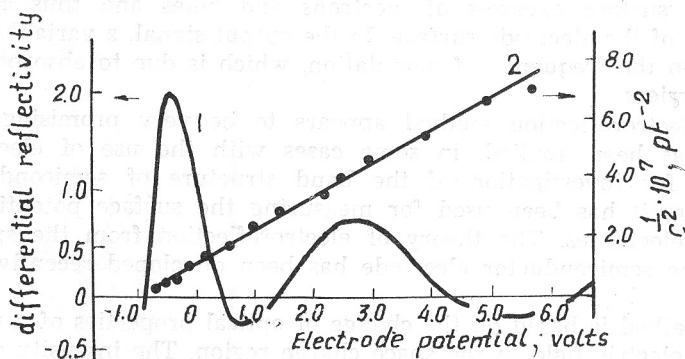

Fig. 5. Differential reflectivity (1) and inverse differential capacity squared (2) vs. potential of the cadmium sulfide electrode in 1 N KCl[29].

electroreflection signal on the potential of a cadmium sulfide electrode. It presents also a curve of the inverse capacity squared, which intersects the potential axis near the point of zero charge. It can be seen that electro-reflection signal is zero not only at the flat-band potential, when the electric field on the surface is zero: during anodic polarization there appear also spurious electroreflection zeroes. Tyagai and coworkers[29] ascribed these zeroes to the oscillating nature of the dependence of the local value of dielectric constant on the field strength and also to light interference in the space charge region.

At any rate, this method deserves further experimental and theoretical refinement.

The second group of methods are purely electrochemical ones. Surface oxides, adsorbed hydrogen etc. may be readily determined by electrochemical

oxidation or reduction of the chemisorbed or phase layers located on the electrode surface. This may be exemplified by the galvanostatic charging curves method[19]. Duration of charging may be several microseconds to several hours. In the first case, one observes relaxation of the space charge and of the trapped charge which relates to fast surface states only, in the second case, relaxation of the charge trapped in slow surface states is observed as well.

Potentiodynamic i-φ curves method can be also used for the same purpose. Integration of the current *vs.* time curve produces amount of the substance adsorbed on the surface.

Finally, radioactive tracer method may meaningfully inform on the adsorption proceeding at a semiconductor electrode.

Main Results of the Experimental Investigation of the Surface Properties of Semiconductor Electrodes

Electrochemistry of semiconductors deals mainly with germanium so far. Silicon, cadmium sulphide, zinc oxide, gallium arsenide were studied in much less detail. More recently, nickel oxide, gallium phosphide and other substances became subject to investigation.

A. Germanium, Silicon

Quite a number of papers are concerned with the effect of chemisorbed oxygen on the surface properties of the germanium electrode.

Ellipsometry[30,31] as well as potentiodynamic charging method show that germanium electrode when placed into an electrolyte which is a fair solvent for germanium oxides (concentrated alkali or hydrofluoric acid) is covered by approximately one monolayer of oxygen under steady-state conditions. Anodic oxidation, even if fast anodic dissolution of electrode takes place, does not increase this quantity markedly. By cathodic polarization the chemisorbed oxygen can be reduced; further, the electrode becomes covered by a monolayer of chemisorbed hydrogen.

Transfer from oxidized to reduced state of the germanium surface is accompanied by the variation (of ≈ 0.5 V) in the interphase potential drop, which was traced by the variation in potential of minimum of differential capacity. It was shown[32,33] that the interphase potential drop related to chemisorbed oxygen is accounted for both by polar nature of $Ge^{(+)}$—$O^{(-)}$ bond and by partial dissociation of the surface oxides with formation of ionic double layer.

Gerischer, Gobrecht, Mehl, Memming and others[6,26,27,32-44] have investigated the relationship between the total amount and the individual forms of oxygen adsorbed on germanium, the potential distribution and the surface recombination velocity. The amount of oxygen was determined mainly by means of the potentiodynamic i-φ curves, the initial surface coverage with oxygen and solution pH being varied in the experiments. As can be seen from the polarization curve for adsorbed oxygen reduction taken during linear sweep of potential and presented in Fig. 6, oxygen is present on the surface in several (two or three) energetically different forms. Such resolving maxima on the i-φ curves are well-known also for other electrode materials, *e. g.* the platinum group metals. It was suggested[40] that on germanium different oxygen
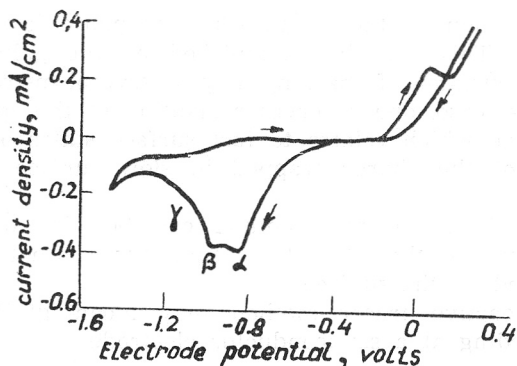
Fig. 6. Potentiodynamic i-φ curves measured on *n*-type germanium electrode in the 1 *N* Na₂SO₄ +
+ 0.01 *N* H₂SO₄[40].

forms correspond to its adsorption on surface microfaces with different crystallographic indices.

The potential distribution at the interface under steady-state conditions can be accounted for by assuming the oxidized electrode surface to be covered by hydroxyl groups, which dissociate, depending on *p*H, like acid or base. The calculation carried out by Gerischer, Hoffmann-Perez, and Mindt[34] leads to a linear *p*H dependence for the value of the Helmholtz potential drop:

$$\Delta \varphi_0 = - 2.3 \, RT/F \, pH - \lg (fx) + C$$

Here x and f are molar fraction and activity coefficient of the ionized surface oxide groups (GeO⁻), C — a constant. At the flat-band potential there is no potential drop within the semiconductor, hence the *p*H dependence of the flat-band potential is the same as that of the $\Delta \varphi_0$. As is clear from Fig. 7
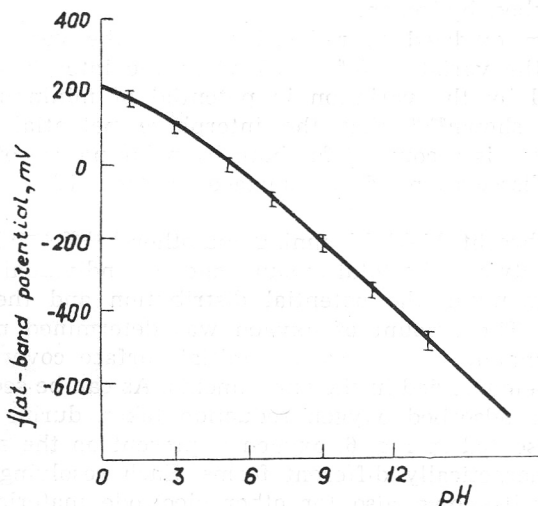

Fig. 7. Flat-band-potential of intrinsic germanium *vs.* pH[34].

the flat-band potential of oxidized germanium is actually a linear function of the pH (at constant x and f).

In concentrated hydrofluoric acid solutions dissociation of surface hydroxyl groups seems to be suppressed[37].

Much less is known about the cathodically reduced germanium surface. Here one encounters experimental difficulties associated with the dual effect of adsorbed hydrogen: on the potential drop in the Helmholtz layer and on surface recombination velocity. The former effect is more pronounced at large cathodic polarization, the second — at moderate one[45]. It can be considered proved, at any rate by indirect methods, that electrolytic hydrogen penetrates to some depth into the germanium crystal lattice[46]. It is a radical species formed intermediately when an »oxide« surface is transformed to a »hydride« one which monitors, along with chemisorbed oxygen or hydrogen, surface properties of a germanium electrode[35,39]:

$$\diagdown \text{Ge--OH} \xrightarrow[\text{+ H}^+]{\text{+ e}^-} \diagdown \text{Ge} \cdot \xrightarrow[\text{+ H}^+]{\text{-- h}^+} \diagdown \text{Ge--H}$$
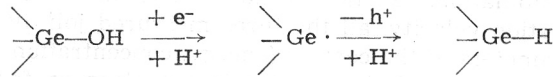
A number of papers is concerned with relaxation properties of the germanium/electrolyte interface. When potential varies relaxation of the space charge in semiconductor and of the ions electrostatically adsorbed in the double layer is practically instantaneous as long as the process does not involve diffusion. On the contrary, adsorption and desorption are rather slow, therefore the equilibrium state is reached in a longer time when adsorption layer is present on the electrode.

Slow relaxation proceeding on the surface of germanium electrode relates, at least partially, to chemisorbed oxygen. The investigation of the kinetics of cathodic oxygen reduction by means of the potentiodynamic i-φ curves has shown[47] that the amount of reduced oxygen depends essentially on the rate of potential sweep (Fig. 8). At large sweep rates only an insignificant fraction of adsorbed oxygen is reduced, regardless of the sweep amplitude.
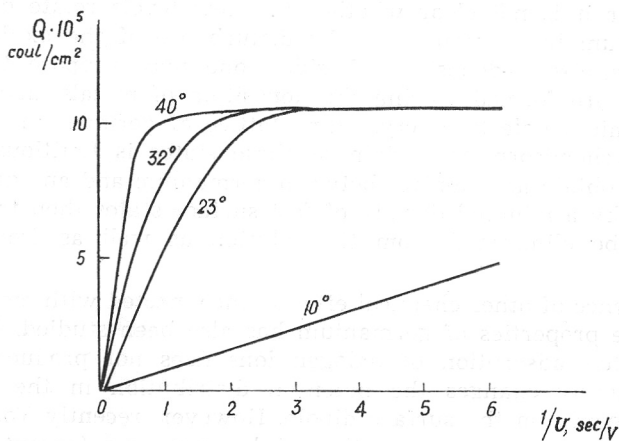

Fig. 8. Dependence of the amount of electroreduced oxygen chemisorbed on germanium in 48% HF (in electrical units) on the inverse rate of cathodic potential sweep. The temperature (°C) is shown on the curves[47].

This indicates that the slow step is a nonelectrochemical one. It was supposed that oxygen adsorption occurs over the whole surface of the germanium electrode, whereas electroreduction only on its active sites, the area of these being no more than some per cent of the total electrode area. It is the surface diffusion of oxygen towards active sites which is likely to be the slow step of the electroreduction reaction.

As to the fast surface states, several semiconductor electrodes were shown to have no surface charge characterized by small relaxation times. E. g., zinc oxide (as well as cadmium sulphide) usually contains practically no fast surface states. Germanium electrode contains, contrary to the preceding case, fast states of two types: those characterized by a discrete level near the middle of the forbidden band, and those characterized by continuous energy distribution near the edges of the forbidden band[48,49].

The levels which lie in the middle of the forbidden band perform as centres of recombination. Surface conductivity, differential capacity and surface recombination velocity, all the three measured jointly *versus* potential, allow to find parameters of the centres (energy, concentration, and two capture cross-sections). The origin of the centres is not clear so far. Some of them arise after »conventional« treatment of a semiconductor (etching in oxidizing solutions) and they may relate to »inherent« defects of crystalline lattice of the semiconductor. It is interesting that parameters of the levels correlate with fine structure of germanium surface. Thus, the number of defects per unit surface in its order of magnitude is near to the number of surface levels determined by the differential capacity method at the frequency 10—100 kcps ($\approx 10^{10}$ per 1 cm^2). The number of defects is determined by means of an electron microscope or by the »decoration« method (by copper electro-deposition)[50,51].

Electropositive metals (gold, silver, copper) deposited on germanium from solutions of their salts also cause fast surface states, *inter alia* recombination ones, whose levels lie near the middle of forbidden band[52-54]. Their concentration is close to that of the metal microcrystals formed on germanium surface. So far it is not clear whether the new levels relate directly to the metal-germanium interaction or to the disturbance of the oxide layer being caused by the electro-deposition. Besides, one may suppose that nuclei of crystallization are formed, during the deposition of metals, actually at those spots where micro defects of crystalline lattice of germanium appear on the surface, *i. e.* »chemisorption« origin of these states is fictitious. Anyhow, if one desires to obtain an interface between germanium and an aqueous solution characterized by a minimal density of fast surface states then traces of heavy metals must be eliminated from the solution as well as from the crystal surface.

The influence of other chemical effects, unconnected with metal deposition, on the surface properties of germanium has also been studied. Earlier it was believed[55-57] that adsorption of halogen ions does not produce fast surface states, but merely changes the potential distribution in the double layer, acting, as it seems, on the surface dipole. However, recently Toshima, Uchida *et al.*[58-60] found that after adsorption of halogen ions (except fluorine) the differential capacity of a germanium electrode shows frequency dispersion. They associated this effect with formation of fast surface states. From the

frequency dependence of the phase shift angle they determined the relaxation time and then attempted to estimate the adsorption rate constant.

In some cases the surface recombination velocity proves to be rather large. But at the same time, the differential capacity method does not reveal any appreciable density of the fast surface states with levels lying near the middle of the forbidden band of germanium. To eliminate this contradiction, Gobrecht and Blaser[61] proposed a model for recombination at the semi-conductor/electrolyte interface which is not associated with the existence of special recombination centers on the surface of semiconductor. According to this model, the disappearance of non-equilibrium free carriers in the sample is the result of the redox process occurring on its surface, the carriers of opposite signs participating in the forward and back electrochemical reactions. This process seems not to contribute to the differential capacity, provided that the faradaic component of impedance is correctly taken account of. Naturally, this model is applicable only in solutions of appropriate redox systems. Probably, it should be made use of when accounting for the surface properties of a germanium electrode in nitric acid solutions, investigated by Konorov et al.[62,63].

On the whole, it should be concluded that the surface electronic states concept, so widely used both in the physics and in the electrochemistry of semiconductors, is largely only a formal method of description of the electric and relaxation characteristics of the electrode. Only in a few cases has it been possible to interpret to any satisfactory degree the physico-chemical sense of these states. And yet a formalism of surface states allows to explain several peculiarities of a semiconductor electrode surface.

To conclude this Section dealing with germanium electrode let us mention the non-equilibrium charging of the double layer on semiconductor electrodes, a phenomenon investigated by Roolaid et al.[64,65] on a germanium/electrolyte contact and observed also on a surface of silicon in vacuum[66]. This phenomenon may influence the parameters of semiconductor devices operating a »large signal« mode. If a semiconductor surface enriched in minority carriers (inversion layer) is charged by a sufficiently strong current (so that amplitude of the variation of surface potential be an order higher than 25 mV), then the limiting step of the process is diffusion of minority carriers in the semi-conductor bulk to or from the boundary of the space charge layer. As carriers transport is slow, therefore actual variation in the space charge is less than that required by the space charge theory for the given value of the potential amplitude, and an experimental (dynamic) charging curve declines from an equilibrium (static) charge vs. surface potential curve. Naturally, if duration of charging is higher than life-time of minority carriers, then recombination-generation contributes to the charge exchange between the semiconductor bulk and the space charge layer, and the charging occurs under equilibrium conditions.

Theory of non-equilibrium galvanostatic charging curves was given by Tyagai and Gurevich[67]. In Fig. 9 the calculated curve of the surface potential change versus the space charge change (in the dimensionless units) is shown by solid line and the experimental data for anodic charging of n-type ger-manium electrode are shown by dots[64]. The results may be summarized in the following way. Charging curves taken in the time interval less than
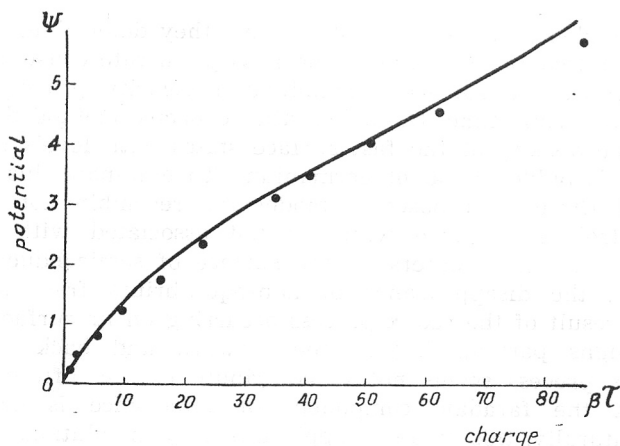
Fig. 9. Non-equilibrium anodic charging curve of the n-type germanium electrode in N-methyl-
formamide KBr solution: solid line — calculation, points — experiment[64].

approximately 15—20 μsec coincide quantitatively with those calculated from
the Tyagai-Gurevich theory and decline markedly from the well-known
equilibrium curves. If the charging pulse duration exceeds 15—20 μsec, the
experimental curves deviate from the calculated ones and lie between the
non-equilibrium (or »dynamic«) curve and equilibrium (or »static«) one.
Obviously the discrepancies observed are due to the charging of the electronic
surface states, the relaxation time of which is comparable with the charging
pulse duration.

It is much more difficult to prepare the surface of a silicon electrode
with reproducible properties than that of a germanium electrode. This is
accounted for by high reactivity of silicon. However, in concentrated hydro-
fluoric acid solutions it is possible to realize the simple case when the
differential capacity of the electrode is equal to the space charge region
capacity, and the potential drop change during electrode polarization in a
certain range is also localized in this region[68-70]. In the majority of other
solutions (KOH, H_2SO_4, etc.) the surface properties of the silicon electrode
are determined by fast and slow surface states whose density seems to be
very large[71-74]. Some papers are concerned with the measurements of the
heavy metals adsorption on silicon (by the radioactive tracer technique)[75,76].

B. Binary Compounds

Among relatively new materials which have attracted attention in the
electrochemistry of semiconductors are binary compounds: titanium di-
oxide[77,78], potassium tantalate[79], cadmium selenide and telluride[80], nickel
oxide[81,82]. Simultaneously, further studies have been made on zinc oxide[83-86],
cadmium sulfide[87,88], gallium arsenide and phosphide[89,90].

Perhaps, one may say that investigation of the double layer structure
at »new« semiconducting electrodes, at any rate in the cases where reliable
and conclusive data have been obtained, has not revealed any new effects
which would differ fundamentally from those already known. On materials
with a wide gap the space charge is formed by ionized impurities (depletion

layer), or by majority carriers (accumulation layer), which is conclusively proved by the differential capacity method. As an example, Fig. 10 shows
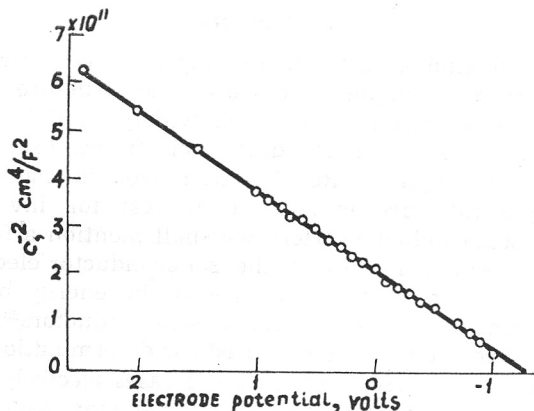

Fig. 10. Inverse capacity squared *vs.* potassium tantalate electrode potential[79].

the dependence of the inverse differential capacity squared on the potential of the potassium tantalate electrode at moderate polarisation (according to Boddy *et al.*[79]). At higher field strength this dependence becomes nonlinear, which has been attributed to the change in the dielectric constant of the crystal in a strong field. Note that estimates of the Helmholtz capacity on potassium tantalate (as well as on germanium[9] and zinc oxide[91]) gave very low values — 3 to 6 $\mu F/cm^2$.

On lithiated nickel oxide the concentration of fast surface states seems to be high[81,82].

On zinc oxide[83] as earlier on germanium (see above), the dependence of the flat-band potential on the solution pH has been found to be linear, with the slope close to 59 mV. By analogy with germanium, it has been explained by formation of a »hydroxide« surface, *i. e.* a monolayer of adsorbed hydroxyl groups which dissociate like acid or base. The potential drop in the Helmholtz layer is determined by the dissociation type and degree which, in its turn, depends on pH. Here we also find similarity in the double layer structure on different semiconducting materials whose common feature is their surface oxidizability.

Zinc oxide crystals, just as other polar compounds of the type A^3B^5, have not shown any difference in the equilibrium properties of the surfaces formed mostly by atoms of an individual component — »zinc« or »oxygen« surfaces[83]. Such differences seem to exist only in the kinetic properties and manifest themselves *e. g.* in processes of anodic or chemical etching.

In conclusion, one should mention the investigation of the nature of the quasi-equilibrium (*i. e.* unconnected with any electrochemical reactions) photo e. m. f. on binary semiconductors with a wide gap. Tvagai[92] on cadmium sulfide and Eletsky *et al.*[93,94] on gallium arsenide and gallium phosphide showed the photo current to be associated with the separation, in electric field near the surface, of electrons and holes injected by light. The photo e. m. f. can be conceived as being the result of charging of the semiconductor surface capacity

with this photo current. Thus, photoelectric measurements can give the values of the differential capacity and »parallel« resistance of the electrode.

CONCLUSIONS

Not only have the studies on the double layer at the semiconductor/electrolyte interface afforded a complete picture of the structure of this interface, but the results of these studies have been widely used for investigation of the kinetics of reactions at semiconductor electrodes (a review of kinetic studies is given, for example, in Ref. 95). Moreover, in many cases the semiconductor/electrolyte interface is also of interest for investigation of the bulk properties of semiconductors. Here we shall mention a few of such cases. Thus, the electroreflection studies at the semiconductor/electrolyte interface have afforded information on the structure of the energy bands and nature of the interband transitions in a number of semiconductors[23]. A measurement of photo e. m. f. at such interface can be used for determination of the diffusion length of holes in gallium arsenide[96]. In these cases electrolyte has been used as a convenient blocking contact to a semiconductor which is transparent to light, has a low ohmic resistance and readily allows to modulate electric field on the surface.

Summing up, we can say that as regards the double layer structure at semiconductor electrodes, we are, as it were, at crossroads. Traditional methods have largely exhausted themselves, at any rate for traditional objects. At the same time, some fundamental questions have not been answered as yet. Among the most interesting problems are the following*:

1. Elucidation of the nature of the surface states (making use of the data on electrochemical kinetics at semiconductor electrodes).

2. Elucidation of the role of quantum effects in the space charge region, which appear to be of great importance in electrooptical phenomena.

3. Investigation of the behaviour of thin semiconductor films (those thinner than the Debye length included) as well as of dielectric films on semiconductor electrodes.

4. Extension to the semiconductor electrodes of the electrocapillarity theory developed recently for solid metals[98] and elucidation of the nature of the zero charge potential of semiconductor electrodes.

It would be expected that development of new methods and investigation of new phenomena, of the electrooptical properties of the semiconductor surface, in particular, should stimulate new ideas and make for further progress in this field.

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IZVOD

Električni dvosloj na granici faza poluvodič—elektrolit

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Prikazani su rezultati istraživanja granice faza poluvodič elektrolit opisani u svjetskoj literaturi u periodu između 1965. i 1971. godine. Posebna je pažnja posvećena istraživanjima strukture električkog dvosloja na poluvodičkim elektrodama u smislu podjele potencijala i relaksacije naboja, zatim metodama istraživanja i konačno prikazu eksperimentalnih rezultata dobivenih za germanij, silicij i binarne spojeve. Pregled literature upućuje autora na zaključak da su istraživanja doprla do prekretnice. Klasične metode su se iscrple barem u smislu istraživanja na tradicionalnim objektima. U isto vrijeme neki osnovni problemi još uvijek zahtijevaju odgovore. Među njima se kao najvažniji postavljaju ovi: (1) Razjašnjavanje naravi površinskih stanja; (2) razjašnjavanje uloge kvantnih efekata u području prostornog naboja (što je od osobite važnosti u elektrooptičkim fenomenima); (3) ispitivanje ponašanja tankih poluvodičkih filmova i dielektričkih filmova na poluvodičkim elektrodama, te (4) primjena teorije elektrokapilarnosti na poluvodičke elektrode i objašnjenje naravi potencijala nula naboja na njima.

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