# ELECTRICAL STRUCTURE OF BOUNDARY LAYERS

1969

SovietRxiv

## Abstract

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UDC 541.183+548.4+620.187

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# ELECTRICAL STRUCTURE OF BOUNDARY LAYERS

*(Presented by Academician A. V. Shubnikov, 17 IX 1968)*

The formation and properties of liquid and solid boundary layers are determining factors in many problems of physics, physical chemistry, and biological physics. One may mention, selectively, adhesion, crystallization from solution and melt, boundary friction, and also induction processes in the intercellular medium. In the works of B. V. Deryagin and his school, G. I. Fuks, A. S. Akhmatov, I. F. Efremov, and others it was established ($^1$) that in thin layers of liquids adjacent to the surface of solids, their structure-sensitive characteristics change, such as viscosity, density, dielectric permittivity, mechanical properties, etc. P. A. Rebinder ($^2$) showed the role of adsorption-solvation layers, which affect the surface properties of solids when they are in contact with liquids. However, in studies of liquid boundary layers, the substrates used were predominantly amorphous or polycrystalline specimens with a certain averaged defect structure, which led to the formation of boundary layers of homogeneous or quasi-homogeneous (on the microscopic level) structure. At a level close to the elementary one, the structure of liquid boundary layers was not considered, which is evidently connected with great experimental difficulties. These difficulties are removed to a considerable extent in the study of solid boundary layers; moreover, the most complete structural information can be obtained from the example of boundary layers formed on the surface of single crystals with a sufficiently well studied real structure.

The real structure of the surface of a number of dielectric and semiconductor crystals (silicon, mica, quartz, NaCl, etc.) was investigated by electron-microscopic decoration methods. It was established ($^{3-6}$) that on the surface of crystals there are regions of different defectiveness and, correspondingly, of different electrical structure. A spectrum of active centers—point defects and their accumulations—was revealed on the surface of crystals. It is precisely at these active centers that heterogeneous reactions, and in particular oriented nucleation, proceed selectively. Selective surface reactions also proceed on the outer side of diffraction-amorphous solid boundary layers deposited on the surface of crystals. Various plastic films, as well as films of carbon, silicon monoxide, quartz, and others, with thicknesses up to 1000 Å, were used as solid boundary layers. Through these layers such heterogeneous reactions were carried out as oriented crystallization of gold, cadmium sulfide, lead sulfide, polyethylene, and a number of other substances. The density of oriented nuclei both directly on the surface of the crystals and on the outer side of the boundary layers is $10^{10}$–$10^{12}$ cm$^{-2}$, which corresponds to the density of point defects in crystals. The orientation and phase composition of the nuclei formed on the outer side of boundary layers are determined by the thickness of the layers. This can be explained by the fact that active centers, differing in electrical structure and symmetry, possess different ranges of action through boundary layers.

Of fundamental importance is the establishment of the mechanism by which structural information is transmitted through solid amorphous boundary layers, i.e., whether these layers are only an inert intermediate medium or whether they constitute a corresponding information network reflecting the structure of the surface of solids. It has been established that oriented crystallization of anthracene occurs on the contact side of polyvinyl chloride films separated from the surface of NaCl single crystals on which they had been obtained (7). The separated polyvinyl chloride films, possessing thermoelectret properties, as it were "remembered" the orienting properties of the surface of the substrate crystals. During the crystallization of silver chloride on positive and negative regions of the surface of a silicon single crystal, single-crystal and polycrystalline films are formed, respectively; this is due to the sensitivity of this crystallization reaction to the sign of the charge on the surface of the substrate crystal. A similar character of AgCl crystallization is observed on those regions of the contact side of carbon replica that were formed on positive and negative regions of the silicon surface (8, 9). Thus, structural information is preserved with sufficient stability in solid boundary layers without the necessity of obligatory contact of these layers with the surface of solids. It follows from these experiments that the transmission and "freezing-in" of information are most probably effected by an electret-type mechanism (10). In boundary layers, peculiar lines of connection are formed between active centers on the surface of solids and the surface of the boundary layers.

The role of the external polarizing field in inducing internal polarization in boundary layers is played by the electric fields of charged macroregions of the surface (for example, the fields of domains in ferroelectrics and of $p$–$n$ junctions in semiconductors) and by the local microfields of point defects. The occurrence of charged surfaces in dielectric crystals was considered in the works of Ya. I. Frenkel (11), K. Lehovec (12), and I. M. Lifshits and Ya. E. Geguzin (13). The latter showed the possibility of violation of the principle of local compensation of charge in crystals. In works (14–16) the existence was shown of charged regions on the surface of dielectric and semiconductor crystals, representing aggregates of charged vacancies and impurities of different sign. The field strengths of charged macroregions of the surface and of microfields of point defects at distances of atomic dimensions are very large, which ensures the emergence of an induced polarization structure in boundary layers. The existence of a spectrum of discrete active centers—point defects on the surface of solids—determines the emergence in boundary layers of a spectrum of discrete polarization structures—

carriers of information, propagating in these layers over different distances from the electrically active surface of the solid. A comparison of the properties of liquid and solid boundary layers shows that profound analogies exist between them, namely:

1. In solid boundary layers, under the influence of a spectrum of polarizing macro- and microfields, various polarization structures are induced. In liquid boundary layers, the existence has been established of polymorphic forms differing in their molecular and, consequently, electrical structure. The surfaces of both liquid and solid boundary layers at the atomic level must have a very complex form and a complex electrical structure.
2. A change in the composition of solid boundary layers and, correspondingly, of their electrical properties leads to a change in the spheres of long-range action of the surface of solids, effected through these layers. In liquid layers of different composition, there likewise occurs a change in the thickness of the boundary layer with special properties, as a consequence of different molecular structure.
3. The long-range influence of the surface of solids is manifested through nonpolar solid boundary layers. Nonpolar liquids also form boundary layers whose electrical properties differ from those of the bulk.
4. A change in the properties of liquid layers as a function of distance from the surface of solids has been demonstrated; moreover, a sharp transition to bulk properties often takes place. The long-range influence of solids does not manifest itself through solid intermediate layers of sufficiently large thickness. However, the copying of the electrical properties of the surface of a solid by the contact side of these layers proves a change in the structure of solid layers as a function of distance from the surface of the solid.
5. The emergence of a special structure of liquid boundary layers is explained by the initiating action of various functional groups (for example, hydroxyl groups) on the surface of the solid. The formation of a polarization structure in solid boundary layers is due mainly to point defects of the surface, the electrical properties of which in many cases are analogous to the properties of functional groups.
6. The formation, under certain conditions, of a quasicrystalline structure in liquid boundary layers may be compared with the epitaxial growth of solid layers on the surface of single crystals, when amorphous boundary layers become single-crystalline.

Thus, liquid and solid boundary layers may be considered from a unified point of view—that of the real structure of the solid on whose surface they have formed. In boundary layers there arises a complex polarization structure that regularly reflects the distribution of the electrical potential on the surface of real solids. On the elements of this polarization structure various heterogeneous reactions proceed without obligatory contact of the reacting molecules directly with the active surface of the solids. The emergence in boundary layers of a special polarization structure copying the electrical properties of the solid has decisive importance for many physicochemical and biological systems. In these systems, as a rule, there is a large number of membrane and disperse elements, i.e., a large number of diverse boundary layers, the induced polarization structure of which plays an important role in the formation of the properties of these systems and in the kinetics of the corresponding heterogeneous processes.

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Received
9 IX 1968

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