

Exoelectronic emission of semiconductors

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Usp. Fiz. Nauk **119**, 749-766 (August 1976)

PACS numbers: 79.75.+g

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1. INTRODUCTION. CONCEPT OF EXOELECTRONIC EMISSION. STRUCTURE SENSITIVITY OF THE EFFECT

Exoelectronic emission is a unique and highly sensitive surface effect. Its uniqueness and sensitivity determine the evolution of the views accompanying the development of the experimental research on exoelectronic emission. As noted by Scharmann, the cochairman of the 1970 International Symposium on Exoelectronic Emission, "at first the effect caused wonderment, later it was viewed as an undesirable disturbing factor, by now exoelectronic emission has developed as an independent branch of physics,"^[1]

Exoelectronic emission has been known since the early investigations of radioactivity. In 1897, Russell,^[2] repeating Becquerel's experiments on the action of radioactive substances on photographic plates, noted that mechanical working of a zinc foil leads to darkening of the emulsion. Curie^[3] observed in 1899 what he believed to be attenuating radioactivity of materials placed near radium salts. Tanaka,^[4] in a study of transformations in aluminum foil bombarded by 300-keV electrons, observed emission of low-energy electrons and ascertained that these electrons are not emitted by the atomic nuclei. An increased emission activity (dark background) was noted^[5,6] in Geiger-Mueller counters whose internal surface was worked by grinding.

The first systematic investigations of the phenomenon were carried out by Kramer,^[7,8] who also introduced the presently adopted terminology.

Exoelectronic emission (the Kramer effect) is the name given to low-temperature emission of electrons from the surface of a solid, resulting from various external actions: ionizing radiation, plastic deformation,

mechanical working and heat treatment, oxidation, adsorption, etc., which can be regarded as preliminary excitation of the emitter.

After the excitation has stopped, the emission is observed as a result of additional action-stimulation (electromagnetic and electric fields, temperature). What is usually registered is either thermostimulated exoelectronic emission (TSEE) or optically stimulated exoelectronic emission (OSEE).

A feature that distinguishes exoelectronic emission from "classical" types of electron emission is that the energy transfer in it is much smaller. Exoelectronic emission can be stimulated in practice with energy lower than threshold: thermostimulated exoelectronic emission is observed in the "sub-Richardson" temperature interval -150° – 500° C, while optical stimulation is produced by long-wave radiation which does not produce the normal photoeffect. The exoelectronic emission current is quite small (from 10^{-13} to 10^{-19} A), and in extreme cases it is possible to register individual electrons; the exoelectron energy as a rule does not exceed several electron volts.^[9,10] An appreciable contribution to exoelectronic emission is made by relaxation of the excited state of the emitter. This results also in a nonstationary behavior of exoelectronic emission in comparison with ordinary photoemission or thermionic emission. This circumstance makes it possible, in first approximation, to compare the kinetic laws governing exoelectronic emission with the kinetics of phosphorescence and thermoluminescence.^[11-13] A detailed formalized approach does not take into account the influence of the work function, exciton production, Tamm levels, and other excited states; in spite of this, however, it permits an approximate estimate of the parameters of thermostimulated exoelectronic emission.

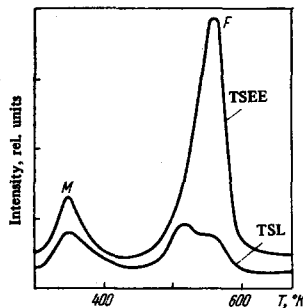


FIG. 1. Thermostimulated exoelectronic emission (1) and thermostimulated luminescence (2) of undeformed NaCl bombarded with x rays.^[14]

Exoelectronic emission accompanies various physical processes that occur in metals, semiconductors, and dielectrics. It reveals a high sensitivity to structure and, in particular, a connection with the defect content of the surface and near-surface layers of the material (the depth of the layer that emits exoelectrons is usually estimated at 10^3 – 10^4 Å).

A. Plastic deformation

The sensitivity of exoelectronic emission to structural changes that accompany plastic deformation can be illustrated by comparing the kinetics of thermostimulated luminescence (TSL) with that of thermostimulated exoelectronic emission from materials that exhibit both effects. Bohun^[14] has established that certain maxima of thermostimulated exoelectronic emission and thermostimulated luminescence have the same temperature positions in the case of an NaCl crystal exposed to x rays at room temperature and containing point lattice defects (*F* centers) (Fig. 1). In both thermostimulated exoelectronic emission and thermostimulated luminescence, plastic deformation induces dislocations and produced broad *R'* peaks that do not appear in undeformed crystals (Fig. 2). Plastic deformation leads to the appearance on the plot of the thermostimulated exoelectronic emission of a maximum not observed in thermostimulated luminescence, thus attesting to the high structure sensitivity of the thermostimulated exoelectronic emission.

Investigations of the plastic deformation of metals^[15] have revealed a correlation between the emission curves and the dynamics of the defects in recovery and recrystallization. Data were obtained recently on the connection between the parameters of exoelectronic emission and the behavior of defects in superplastic flow of metals.^[16]

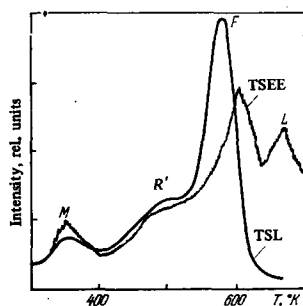


FIG. 2. Thermostimulated exoelectronic emission (1) and thermostimulated luminescence (2) of plastically deformed NaCl bombarded with x rays.^[14]

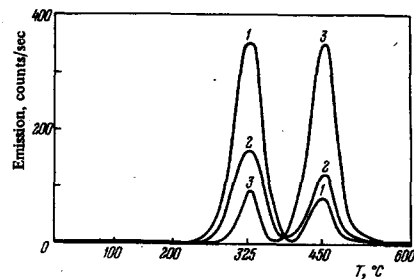


FIG. 3. γ sensitivity of thermostimulated exoelectronic emission characteristics of BeO as a function of the prior bombarding by deuterons with flux density^[30] (particles/cm²): 7×10^{11} (1), 1×10^{13} (2), and 2×10^{15} (3).

B. Phase transitions

The emission of electrons can accompany changes in the aggregate state of a substance, and also phase transitions in the solid state. This was first observed by Kramer in cooled Wood's alloy and in a study of the phase transitions of chromium and nickel. Indication of the structure state of a solid by the electron emission method was used to construct the lead-tin^[17] and aluminum-zinc^[18] phase diagrams. The appearance of exoelectrons was observed in^[19] in ferroelectrics and in^[20] in the case of phase transitions in uranium.

Second-order phase transitions were identified by the emission reaction when a nickel sample was heated.^[21] The maximum of the thermostimulated exoelectronic emission at 220–247 °C correlates with the transition of NiO from the antiferromagnetic to the paramagnetic state. The next thermostimulated exoelectronic emission maximum at 357 °C corresponds to the transition of the ferromagnetic state of nickel into the paramagnetic state (the Curie point).

C. Diffusion

Exoelectronic emission was used to observe diffusion migration of point defects (primarily vacancies) produced by quenching,^[22,23] plastic deformation,^[24,25] and ionizing radiation.^[26,27] In particular, it was shown in^[25] that the instant of emergence of vacancies to the sample surface is accompanied by the start of exoemission. In^[28] emission was initiated by dislocation motion excited by ultrasound.

D. Radiation damage

The sensitivity of exoelectronic emission to radiation damage was observed following various actions (bombardment by γ rays, electrons, particles, protons, etc.) in a wide range of radiation energies (from several keV to several dozen MeV^[29,30]). Most investigations were performed on ionic crystals, semiconductors, and dielectrics. Practically all cases reveal a dependence of the emission characteristics on the degree of structure damage in the surfaces of the investigated objects (Fig. 3). Good emission "memory" of certain materials, preserved for dozens of days after the bombardment, is reported in a number of papers.^[31,32]

E. Chemical and sorption processes

Electron emission accompanies changes produced in the surface state of a solid by chemical reactions and sorption processes. The characteristics of the emission depend on the oxidation, adsorption, and chemisorption conditions.^[33-36]

The structure sensitivity of exoelectronic emission under various conditions has stimulated a large number of experimental studies of this phenomenon. By now, four international symposia were held (Austria 1956, Czechoslovakia 1967, West Germany 1970, Czechoslovakia 1973), and a number of topical anthologies have been published.^[37-39]

2. INSTRUMENTS AND METHODS FOR REGISTERING THE PARAMETERS OF EXOELECTRONIC EMISSION

Two types of measurements of the exoelectronic emission intensity are in use at present: integral measurements of the emission current from the entire surface of the investigated object, and local measurements that yield, within the resolution limits, the distribution of the emission activity over the surface and its image in exoelectronic-emission contrast.

Both types of measurement can be carried out in vacuum, in air, and in other gas media. Their common feature is the need for measuring emission currents in a wide range of values from 10^{-11} to 10^{-18} A. Currents from 10^{-15} to 10^{-19} A cannot be reliably measured by ordinary radio-amplification methods, which are limited to 10^{-14} A in the case of direct current. Thus, in view of the value of the exoelectronic emission current, electrons must be detected by nuclear physics methods or by special electronic devices.

However, the methods of nuclear physics cannot be used to detect exoelectrons without additional measures, since these electrons, having in most cases a maximum energy from one to 100 eV, produce no ionization effect in the nuclear-radiation detector medium. This makes it necessary to use pulsed detector operation (involving counting individual electrons, low level of detector intrinsic noise, a sufficiently short dead time).

A. Registration with Geiger-Mueller counter

In nuclear physics, soft β particles are registered by placing the radioactive source, in the form of a thin layer on a side or end wall, inside the counter. This principle is used to detect exoelectronic emission with open Geiger-Mueller counters operating in air or in a special gas atmosphere. While having a sufficient gain for the registration of the exoelectronic electrons and simple to construct and to operate, open counters have a number of fundamental shortcomings. Foremost among them is the presence of feedback between the electron registration process (the gas discharge) and the action of this discharge on the surface of the investigated object, and also the dependence of the state of the surface and of the counter parameters on difficult-to-control ambient parameters such as pressure,

composition, humidity, etc. In spite of these shortcomings, open counters are widely used, and the experimental material accumulated to date on exoelectronic emission was obtained mainly by using these counters as exoelectron detectors. In the case of high electron emission intensity it is possible to use electrometers without ionization chambers as indicators for the emission current.

B. Detection with secondary-emission instruments

Exoelectronic emission can be measured with relatively new types of slow-electron receivers, which constitute electron-optical systems with secondary-emission amplification of the electron flux. Among these types of instruments are the secondary electron multiplier, the semiconductor electron multiplier, and the channel electron multiplier. The advantages of detectors of this type over the ones considered above are the following:

- 1) High registration efficiency, reaching 60% because of the absence of absorption of electrons in the gap between the sample and the detector input;
- 2) The instruments are sensitive enough to register currents starting with 10^{-19} A against an intrinsic background of 0.1 electron/sec;
- 3) These detectors can operate only in high and ultra-high vacuum, which helps eliminate difficult-to-control ambient parameters;
- 4) As a rule, the secondary-emission properties of detectors are preserved in the atmosphere for a rather long time.

C. Local method of registering exoelectronic emission

Local methods of registration of exoelectronic emission, wherein the image of the surface is produced in exoelectronic contrast, are new means of studying the surface of a solid and establishing the nature of the emission centers. A sharp and magnified image of the distribution of the exoelectronic emission intensity as a function of the coordinates of the surface of the object was obtained by the authors of^[40-43]. The basis of the method of^[40-43] is scanning the surface of the investigated object by a focused light probe. The only detected emission signals come from those sections of the surface on which the probe spot is located at the particular instant. Synchronization of the motion of the beam in the cathode-ray tube of the indicated device with the motion of the scanning light probe, upon proper modulation by signals from the exoelectron detector, makes it possible to produce on the screen an image of the surface of the object in emission contrast, the distribution of the emission intensity over the surface. Visualization of exoelectronic emission by the method of^[40, 43] calls for exact synchronization of the motion of the scanning and reproducing rays, since the information is transmitted sequentially from point to point. The need for synchronization is completely obviated if a principally different method is used wherein the entire image is obtained simultaneously. This method is based on the operating principle of recently developed

channel electron-optical converters. The main unit of such a device is a block made up of parallel hollow channels, each of which is a channel electron multiplier.^[41] The output current of the channel excites a luminescent screen and serves as one element of the image.

D. Measurement of the electron energy

A most important characteristic of any type of radiation, besides the intensity, is the energy of the emitted particles. The energy parameters of exoelectrons contain information on the electronic phenomena that occur in the interaction between the solid and the ambient. There are sufficiently well developed methods for an energy analysis of electron fluxes which are large (usually 10^{-7} A) in comparison with the exoelectronic emission current. Electron energies up to hundreds of electron volts are measured with the electrostatic and electromagnetic analyzers described in^[44,45]. The direct outputs of these analyzing devices are the electron distributions in energy or velocity, respectively. Electrostatic and electromagnetic analyzers are used also to measure exoelectron energies at low flux densities.^[46] In this case the electrons passing through the analyzer systems are registered by the most suitable of the detectors considered above.

3. PHYSICAL NATURE OF EXOELECTRONIC EMISSION

When the nature of exoemission radiation is interpreted, principal attention is paid to identification of the surface emission centers and to reactions (in addition to external action) that can produce in the solids the conditions that contribute to electron emission.

A. Thermoactivation mechanism

Historically this was the first hypothesis advanced by Kramer to explain emission from the surface of mechanically worked metals and in phase transitions. Kramer believed that the electron escapes the solid as a result of the energy of exothermal transformations, which either causes the electron emission directly or is first converted into thermal energy. The term "exoelectronic emission" was introduced by Kramer precisely on the basis of this mechanism.

B. Model of electrically charged microgap

This model is based on the periodic variation of the work function of the electron as oxide layers build up on metallic surfaces.^[47] Deformation produces in the oxide layers cracks whose walls are electrically charged. The strongly damaged layer at the base of the crack acts as a source of the electron emission, since it has a lower work function.

C. Vacancy-diffusion mechanism of emission

This mechanism was proposed to explain the emission observed when metallic surfaces are deformed. Deformation of the object produces vacancies that can diffuse to the surface and annihilate with release of en-

ergy E_v . The combined energies of the vacancy and of the stimulating action become sufficient to overcome the work function:

$$E_v + h\nu > \Phi,$$

where $h\nu$ is the energy of the stimulating action and Φ is the work function of the electron.

The formation and diffusion of vacancies are assumed to be the principal processes during the course and after plastic deformation.

To describe in greater detail the emission mechanisms with allowance for the adsorption-oxidation processes, a compromise hypothesis was advanced, according to which the vacancies diffuse toward the surface and, after reaching it, turn into adsorption or oxidation centers. Another approach to the solution of the problem of the relation between the exoelectronic emission and deformation defects is given in^[48]. The deformation of the surface layers of metals leads to a change in the work function of the electron. In the time after the deformation, the crystal lattice of the metal becomes ordered. The work function returns to its previous level, a fact manifest in the attenuation of the emission.

D. Auger mechanism of the exoelectronic emission

According to the data of^[38,49,50] one of the mechanisms of thermostimulated exoelectronic emission and optically stimulated exoelectronic emission is the Auger process.

The "Auger electron" can take part in the exoelectronic emission if the following condition is satisfied^[49]:

$$E_{\text{kin}} = E_g - E_1 - E_2 - \chi > 0,$$

where E_g is the width of the forbidden band, χ is the electron affinity, and E_1 and E_2 are the energies of the recombining and emitted electrons.

The probability of nonradiative transition is proportional to $T^{-1/2}$ and R^{-6} (T is the absolute temperature and R is the distance between the nearest centers).

A theoretical explanation of the Auger mechanism of electron emission from semiconductors and dielectrics was given by Tolpygo and co-workers in^[49]. The hypothesis they advanced explains many features of exoelectronic emission.

E. Luminescence model of emission

This mechanism was developed on the basis of a certain similarity between luminescence and exoelectronic emission (Fig. 4). Both phenomena require preliminary activation and both attenuate in time. The processes can be stimulated by heating or by electromagnetic radiation in the optical band. At the present time doubts are being cast on the assumption that the trapping centers responsible for luminescence and exoelectronic emission are the same. Nonetheless, the

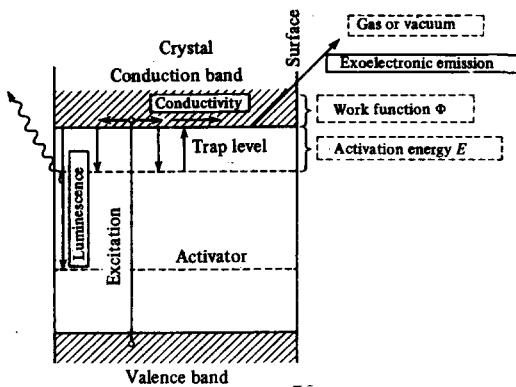


FIG. 4. Simplified band model of the processes of thermo-stimulated exoelectronic emission and thermostimulated luminescence under optical and thermal stimulation.^[29]

necessary condition for the excitation of exoelectronic emission is photochemical coloring of the crystals, for example with x rays or ultraviolet. In a number of studies it was established^[51-53] that the exoelectronic-emission centers in ionic crystals are volume color centers in the near-surface layers. Particular significance attaches therefore to F centers and to the dependence of their energy states on the dislocation concentration. With increasing dislocation density, the F -center concentration increases and, as a consequence, new exoemission maxima appear and their intensity increases. The peculiarities of the emission properties of crystals, due to the electric relief produced on the jogs where the dislocations emerge to the surface, have been determined from the shift of the thermostimulated exoelectronic emission spectra of LiF as a function of the edge or screw dislocations contained in it.^[52] In the case of an excess of edge dislocations (10^8 cm^{-2}), the spectrum shifts towards lower temperatures in comparison with the spectrum of a crystal containing an excess (10^7 cm^{-2}) of screw dislocations. A similar influence can be exerted on the emission properties by an atmosphere of charged vacancies.^[54]

F. "Field-emission" mechanism

This mechanism pertains primarily to thermostimulated exoelectronic emission from pyroelectric materials such as LiNbO_3 . A temperature-induced change of only 1% in the spontaneous polarization of this material gives rise to an electric field of intensity $8 \times 10^6 \text{ V/cm}$ perpendicular to the surface and sufficient for field emission.^[55] The energy of the electrons emitted in this case, which amounts to several kiloelectron volts, allows us to regard this mechanism as correct. The fact that electrons with energies up to 120 keV produced by mechanical working of LiF and NaF crystals have been registered can also be explained by invoking the model of surface charging of the crystal.^[56]

The high electron energies are explained as being due to bending of the bands and to electric fields on the surface of the emitting body. This situation can occur also when the surface of a dielectric is bombarded with charged particles, particularly electrons. If the bombardment regimes are maintained such that the sec-

ondary emission coefficient is $\sigma > 1$, then the surface of the dielectric is positively charged. The primary electrons lose all their energy at the end of their travel, are localized in trapping centers, and form negative space charge. Thus, a strong electric field is produced. The electrons excited into the conduction band become accelerated in the direction towards the surface. Since the acceleration can exceed considerably the slowing down by the scattering processes, the electrons are emitted with a relatively large kinetic energy unaffected by electron affinity. The model was corroborated by the fact that electrons of energy up to 90 eV were observed following electron bombardment of SiO_2 layers.^[57]

None of the advanced hypotheses and kinetic theories is capable at present to describe the numerous manifestations of the exoelectronic emission, but the concept of structure sensitivity is the basis for the development of further ideas concerning the physical nature of the effect. From this point of view, the experimental data on emission from elemental semiconductors and semiconductor compounds are likewise no exception.

4. EXOELECTRONIC EMISSION OF ELEMENTAL SEMICONDUCTORS

A. General remarks

According to the classification given in Kyaémbre's review,^[58] all nonmetallic exoelectronic emitters can be divided into two groups. The first group contains substances with relatively broad forbidden band E_g and small electron affinity χ —principally ionic crystals such as alkali halides. Most investigations were performed on these crystals, and a parallelism has been noted between the thermostimulated exoelectronic emission and thermostimulated luminescence: the excitation produces in the volume or near the surface of the crystal definite local centers (of the color center type), the electron emission from which calls for much less energy than from the levels of the unexcited crystal. This gives grounds for comparing both processes, although the local emission centers and luminescence centers are not always identical. The most probable mechanism for the removal of the electron is the Auger process, but one cannot exclude the possibility of the electron falling into the conduction band as a result of thermoionization of the centers, followed by its emergence from the crystal as a result of thermal fluctuations, just as in ordinary emission.

From this point of view, the picture for the emitters of the second group, characterized by small values of E_g and large values of χ , is less clear. Typical representatives of this group are germanium and silicon, and the group includes the majority of semiconductor compounds. In these substances the conduction-electron density is high even at room temperature and their thermostimulated exoelectronic emission is hindered by the surface barrier. The high-temperature maxima of the thermostimulated exoelectronic emission should correspond to deep levels, either those which do not fit at all in the narrow conduction band, or else fall under the Fermi level and consequently are filled with-

out excitation.

Similar difficulties in the explanation of the effect within the framework of the band model were the reason why in many papers devoted to exoemission of semiconductors the principal attention is concentrated on allowance for the factors that lead to changes of the potential surface barrier by an external medium (sorption, oxidation). Since the sorption-oxidation processes are initiated to a considerable degree by structure defects of the surface, the emission mechanism should be determined by the actual conditions of excitation of the emitter from the point of view of generation and activation of the defect formations.

The foregoing features can be traced in the results of investigations of the exoelectronic emission of elemental semiconductors, in which the organization of the experiments contributes to the determination of the role of the structure defects of the surface, or else of the oxidation-sorption processes that develop on the surface.

Most studies have been devoted to emission under thermal stimulation.

B. Emission centers

In view of the complexity of the problem of determining the nature of emission activities of germanium and silicon, the most promising way of its solution is the use of relatively easily controlled types of emitter excitation, such as ionizing radiation.

The first investigations of the exoelectronic emission of germanium and silicon were made with excitation by x rays, and by electron, ion, or α -particle bombardment. Although the results of these studies, and incidentally of the succeeding ones, are very difficult to compare with one another because of the differences in the experimental conditions (for example, the electrons were detected with gas-filled counters and with secondary-electron multipliers), it can be stated that the dependence of the characteristics of exoelectronic emission on the type of excitation has been established. Bohun^[59] and Hanle and Gouge,^[60] by bombarding germanium samples with x rays, obtained maxima of thermostimulated exoelectronic emission near 300 °C. More complicated temperature emission spectra were observed by Seeger^[61] after bombarding *n*-type germanium with slow electrons; in this case emission appeared already at -150 °C.

The theoretical and experimental material obtained by studying the real surface of semiconductors gives grounds for concluding that a relation should exist between the volume and surface states when the surface is excited by radiation.

Radiation damage in germanium and silicon (even strong enough to make the surface of a single crystal amorphous^[62]) can be produced both by radiation and by ion bombardment. According to the data of^[63] for silicon, regardless of the type of irradiation (neutrons, protons, electrons, x rays, ion bombardment), the radiation damage observed near the surface consists

only of point-type defects. This agrees with the ideas of Litovchenko^[64] and Distler^[65] concerning the structure of the surface of a semiconducting crystal, according to which point defects play the major role as active centers for the development of heterogeneous processes. Point defects are regarded as electrically active formations that determine the defect structure of the oxide layers. The development of the oxidation seems in turn to generate in the semiconductor defects similar to those produced by irradiation.

Thus, excitation of a germanium or silicon surface by radiation produces on the surface of the semiconductor and in the oxide film an interrelated system of point defects corresponding to different electron trapping centers. The emission process is aided by the formation of positive charge in the oxide, concentrated within 20 Å near the Si-SiO₂ boundary.^[66] In Scharmann's opinion,^[1] the influence of oxygen on the emission activity of silicon is not excluded even by the fact that thermostimulated exoelectronic emission is registered after electron bombardment in a vacuum of 10⁻⁹ Torr.

The role of the charge phenomena was emphasized in^[57,67], where measurements were made of the exoelectron energies. In the case of excitation of thermostimulated exoelectron emission from the surface of oxidized silicon by slow electrons (0.5-1.75 eV), the energy of exoelectrons range from 15 to 85 eV, with the maximum of the distribution near 40 eV. In the authors' opinion, the trapping levels are formed on account of structure defects in the oxide. The decisive role is played here by the accelerating field that is produced in the direction of the vacuum by the electron bombardment in the dielectric SiO₂ layer.

It can be assumed that the excited states responsible for the thermostimulated exoelectron emission are localized in many cases not so much in the oxide as on the boundary between the semiconductor and the oxide phase. This is evidenced by data^[68] on thermostimulated exoelectronic emission of *p*-type silicon heat-treated at 900 °C in various gases (hydrogen, argon, oxygen, treatment time 30 min). It turns out that heat treatment leads to thermostimulated exoelectronic emission regardless of the composition of the medium, and the emission activity increases on going from hydrogen to oxygen, the largest intensity being noted after the removal of the SiO₂ film produced in the oxidizing medium. As a result of the heat treatment, the number of defects on the silicon surface is increased by formation of thermal dislocations and point defects of the vacancy-trivalent silicon type.^[69] If the oxide film is thick (more than 20 Å) it is difficult for the electron to emerge to the vacuum, whereas uncovering (by etching) the region where the space charge is concentrated increases abruptly the number of emitted electrons.

Besides radiation treatment, one of the effective methods of emitter excitation is plastic deformation.

Thermostimulated exoelectronic emission of *n*-type silicon previously subjected to high-temperature (900 °C) plastic deformation in a vacuum of 10⁻⁵ Torr was investigated in^[70]. The temperature at which the

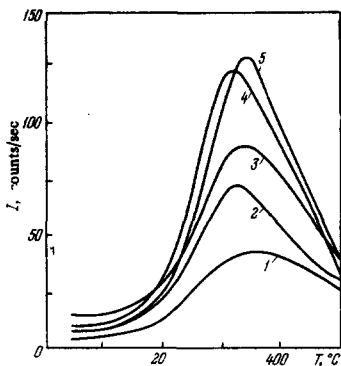


FIG. 5. Exoelectronic emission from Si deformed by dilatation.^[70] Relative strain ϵ (%): 0 (1, initial), 0.1 (2), 0.21 (3), 0.4 (4), and 1.14 (5).

thermostimulated exoelectronic emission is a maximum remains practically the same for different relative strains (Fig. 5), indicating that the emission centers are of the same type. These centers can be the points of emergence of the dislocations that produce the local trapping levels. This is confirmed by the obtained dependence of the number emitted electrons on the relative strain, which agrees with the analogous dependence of the dislocation density. The conclusion of^[70] agrees with data on the effective dislocations on the emission properties of silicon, obtained by measuring the work function.^[71] The dislocation structures of the silicon deformed in vacuum and of the oxide on its surface are apparently identical, since the dislocations generated on the boundary between the oxide and the crystal can "pierce through" oxide films up to 2000 Å thick.^[72]

The foregoing data allow us to conclude that the surface structure defects of germanium and silicon are the decisive factor in the generation of exoemission centers, the actual features of which are governed both by the type of excitation and by the influence of the ambient.

C. Emission kinetics

The general laws governing the variation of the emission current with time (the fall-off curves for optically stimulated exoelectronic emission with fixed frequency

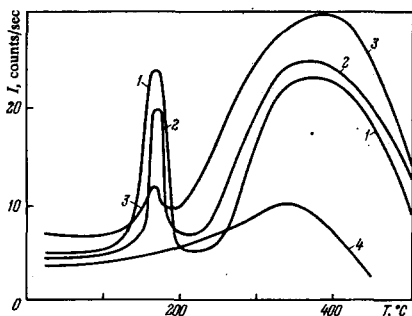


FIG. 6. Exoelectronic emission from the surface of Si after the first (1), second (2), and third (3) irradiation-annealing cycles.^[75] 4—Heating of sample after one irradiation-annealing cycle. Irradiation with 600-keV protons, flux density 10^{13} $\text{cm}^{-2} \text{sec}^{-1}$.

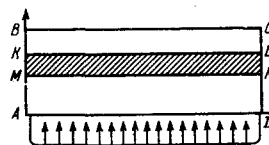


FIG. 7. Diagram of experiment performed to establish the connection between the exoelectronic emission and diffusion processes.^[75] ABCD—silicon sample, AD—plane bombarded with protons; BC—plane from which the emission is registered; KLMN—radiation damage zone; AB—sample thickness (400 μ); AM—distance between the damage zone and the bombarded plane (326 μ); BM—distance between the damage zone and the exoelectronic emission measurement (74 μ); KM—width of radiation-damage zone (1 μ).

of the light flux and the "glove curves" in thermostimulated exoelectronic emission) for germanium and silicon seem to remain the same as in the case of the well-investigated alkali halides. It is shown in^[61,73] that in optically stimulated exoelectronic emission from Si and Ge the fall-off curves can be formally described by using Nassenstein's formulas,^[74] which are analogous to the phosphorescence equations. Nassenstein has considered four cases: 1) individual discrete local levels, 2) uniform distribution of the local levels, 3) exponential distribution of the local levels, and 4) localization of the levels in a narrow energy interval. Despite the fact that the experimental results are most satisfactorily described by the equation for the third case, the limited amount of data does not permit unambiguous conclusions to be drawn concerning the mechanism of the emission of the exoelectrons.

The thermostimulated-emission curves of germanium and silicon are usually reduced with the aid of the known equations of the formal thermoluminescence kinetics. The shape of the "glove curves" makes it possible in principle to determine the molecularity of the process provided that the emission peaks can be distinctly separated. In most cases the emission peaks correspond to monomolecular processes, the activation energy E calculated from the kinetic equations being connected with the depth of localization of the exoelectron trapping center. The latter seems to be sufficiently well justified only for low-temperature thermostimulated exoelectronic emission peaks due to surface trapping levels. Values of E close to 0.6–1.1 eV can attest to the fact that the elementary act of electron emission from levels corresponding to structure damage goes through a diffusion stage wherein point defects migrate to the surface. Such a conclusion is drawn, in particular, in^[75], since the temperature regions of the emission coincide with the stages of annealing the disorder produced by proton bombardment (Fig. 6).

One of the experimental proofs of the role of vacancy diffusion as the limiting stage of the exoelectronic emission kinetics is provided by data on bombardment of n -Si samples by 6.3-MeV protons. The registered exoelectronic emission came from that plane of the sample (sample thickness 400 μ) which was opposite to the bombarded surface (Fig. 7), under isothermal conditions. The results of the experiments (Fig. 8) sug-

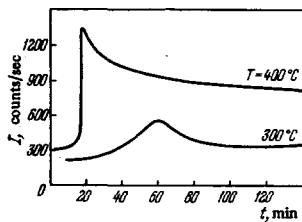


FIG. 8. Intensity of exoelectronic emission from *n*-Si bombarded with protons (63 MeV, 10^{11} particles/cm²) under isothermal conditions at 400 and 300°C.^[75]

gest that the change of the emission intensity is due to diffusion and annihilation of the defects from the zone where the radiation damage is concentrated, which is located 74μ from the investigated surface. The obtained values of the activation energy turned out to be equal to the vacancy diffusion activation energy.

At the same time, data on the kinetics of thermostimulated exoelectronic emission of silicon and germanium leave open the question of developing an adequate model for the mechanism whereby the energy needed to overcome the barrier is transferred directly to the electron.

5. EXOELECTRONIC EMISSION OF SEMICONDUCTOR COMPOUNDS

Exoemission measurements of the surfaces of compounds that can be regarded as semiconducting within the framework of the band model were carried out for a rather limited number of materials.

One of the first seems to be the study by Müller,^[76] who investigated the x-ray-induced thermostimulated exoelectronic emission of cuprous oxide samples obtained by oxidizing copper samples, and also of a layer of Cu₂O detached from the metal by rapid cooling. The emission maxima (150 and 280 °C), which were the same for different samples, were attributed to annealing of the damaged crystal lattice, as confirmed by x-ray structure analysis.

Photostimulated exoelectronic emission and thermostimulated exoelectronic emission of sulfides of arsenic, bismuth, and antimony were investigated in^[77,78]. These investigations have determined the dependence of the intensity and of the character of the thermostimulated exoelectronic emission on the type and dose of the irradiation, as well as the correlation between the thermostimulated exoelectronic emission and the electric conductivity of the crystals. In the authors' opinion there are two trapping centers responsible for the emission process—volume centers, produced by lattice defects of the basic material, and surface defects generated by oxygen adsorption. Release of electrons from levels of the first type leads to an increase of the thermostimulated conductivity and causes the appearance of certain peaks on the thermostimulated exoelectronic emission curves, whereas thermal ionization of the levels of the second type causes only electron emission without influencing the conductivity. The authors of^[77,78] believe that the parameters of the photostimulated exoelectronic emission and thermostimu-

lated exoelectronic emission are determined by the same centers.

The converse was deduced by Gross and Glaefke^[79] from a study of thermostimulated exoelectronic emission and photostimulated exoelectronic emission of polycrystal cadmium films bombarded with slow electrons (1.7 keV). The character of the attenuation of the photostimulated exoelectronic emission was independent of the sample heating, and the peaks of the thermostimulated exoelectronic emission were not altered by the illumination. On the other hand, simultaneous illumination and heating resulted in additive superposition of the photostimulated and thermostimulated exoelectronic emission curves.

The treatment of the emission mechanism in^[76-78] is on the whole analogous to the description of emission for ionic crystals.

The sensitivity of thermostimulated exoelectronic emission of sulfur compounds to low-energy action was observed also in^[80] in which polycrystalline CdS films were bombarded with electrons of energy 0.2–6.0 keV. The data of^[80] give grounds for assuming that the thermostimulated exoelectronic emission curves reflect the ability to generate structure defects under the influence of low-energy radiation. The appearance of the defects, such as cation and anion vacancies, is apparently due to the ionization mechanism. Heating the samples after the electron bombardment (Fig. 9) makes possible radiation-stimulated diffusion of the products of the destruction of CdS towards the surface,^[81] and the diffusion stage can be decisive in the kinetics of the thermostimulated exoelectronic emission (the activation energies for all the maxima of the thermostimulated exoelectronic emission are equal to 0.9 eV). An x-ray microprobe analysis has confirmed that in the forms not subjected to electron bombardment the cadmium is uniformly distributed over the surface, but after the bombardment regions appeared with noticeable chemical inhomogeneity of the components, the

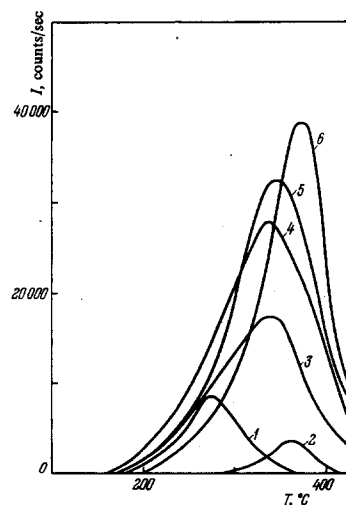


FIG. 9. Exoelectronic emission of cadmium sulfide bombarded with electrons of energy (keV): 2 (1), 0.8 (2), 4 (3), 4.5 (4), 3.5 (5), and 5 (6).^[75]

cadmium content exceeding the stoichiometric value by 6–12%. The extremal character of the dependence of the emission maxima on the electron-bombardment energy, obtained in^[80], can apparently be attributed to the presence of competing processes: on the one hand, the penetrating power and the ionization ability of the electrons increases with their energy, and on the other hand the depth of the excited layer is increased and the emergence of the electron to the surface of the sample is made more difficult. The optimal ratio of these processes is reached at 4 keV, making the depth of the emission-sensitive layer 1500 Å according to^[82].

The spectra of the thermostimulated exoelectronic emission from the surface of gallium arsenide exposed to a glow discharge in an argon atmosphere were obtained in^[83]. Here, too, notice is taken of the role of the crystal-lattice structure defects responsible for the high-temperature maximum (290–300 °C).

The high sensitivity of BeO to small doses and to low-energy radiation was demonstrated in a number of studies.^[29–32] The exoelectron trapping levels are connected in this case with vacancies on the oxide surface. In particular, the thermostimulated exoelectron emission activity increases sharply when silicon is impregnated in the surface. In the authors' opinion, the silicon ion can replace the Be²⁺ ion inside the emitting layer and act like an electron trap responsible for the thermostimulated exoelectronic emission maximum at 325 °C due to the additional charge of Si⁴⁺ relative to the usual position in the Be²⁺ lattice. The possibility of such a process is indicated by the relative proximity of the dimension of the beryllium ion (0.31 Å) and of the silicon ion (0.41 Å) and their geometric coordination. The fact that the emission properties of BeO could be controlled by introducing into the solid solution of the main substance activators in the form of ions with different charges (B³⁺, Al³⁺, Li¹⁺, P⁵⁺), chosen from the condition that the ion radii of the host and of the doping substances be equal (the ion radius for P⁵⁺, for example, is 0.34 Å), suggests that this mechanism is reliable. Activation of BeO by lithium, for example, has increased the thermostimulated exoelectronic emission maxima at 450 and 535 °C by 50 and 20 times, respectively.

Using ESR, it was found in^[84] that thermostimulated exoelectronic emission of irradiated beryllium oxide is connected with two types of activators, one of which determines the localization of the hole or electron traps, and the other ensures release of the electrons.

At the same time, Peterson *et al.*^[85] assume, on the basis of the exoelectron energy measured after x-ray excitation of BeO (1.5–10 eV), that the thermostimulated exoelectronic emission cannot be explained with the aid of the usual models, including the Auger process. The authors of^[85] connect the action of the radiation with formation of electrons in air near the surface of the sample. Penetrating into the sample, the electrons become thermalized in the layer, produce a region of negative space charge, and hence positive surface charge.

A connection between the emission characteristics of oxide systems and surface charge can be traced in the data of^[86]. Comparison of the thermostimulated exoelectronic emission of pyrocerams bombarded by α particles and 2.5-keV electrons with the results of decorating the surface by chemical precipitation of CdS shows that the concentration of the active electric centers of the surface increases abruptly after the irradiation in comparison with the initial sample. This effect can also be directly connected with the radiation damage produced in the near-surface layers that create the local sections of the non-equilibrium charge.

6. CONCLUSION

The use of the exoelectronic emission effect as a highly sensitive method of investigating surfaces of semiconducting materials raises a number of theoretical and experimental problems.

The interpretation of the physical nature of the exoelectronic emission, as a whole, has so far not gone beyond the phenomenological stage and calls urgently for more theoretical research in this field. The most important is the solution of the problem of the most obscure stage of exoelectronic emission, namely the mechanism whereby the electron leaves the crystal. Explanation of this mechanism should be aided by further development of experimental work, using a large number of semiconducting materials under strictly controlled excitation and ambient conditions.

The many factors involved in exoemission, and its dependence on the stimulation parameters, on the type of surface defects, and on the energy locally released near the surface both as a result of internal (structure) processes and as a result of chemical interaction with the ambient, raises also the problem of improving the experimental procedures. A functional approach to the investigation and practical utilization of exoelectronic emission is quite promising.

It is also necessary to compare exoemission and inertialess processes of electron emission from an excited emitter, particularly ion-electron emission.

The features of the exoelectronic emission method offer great possibilities of its applications to nondestructive control of semiconducting materials and articles.

For example, in^[87] thermostimulated exoelectronic emission was used to estimate the depth of the damaged layer of silicon subject to mechanical working, and in^[81] optically stimulated exoelectronic emission was used to monitor the state of the surface of silicon plates after technical and chemical working for the production of integrated circuits, while the feasibility of quality control of single crystals of germanium by exoemission was demonstrated in^[89].

There are interesting examples of the effective use of exoelectronic emission in dosimetry of ionizing radiation and neutrons,^[90] and in the examination of the surface state of lunar fragments.^[91–93]

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Translated by J. G. Adashko