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RADIATION IONIZATION PROCESSES IN GERMANIUM AND SILICON CRYSTALS

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THE interaction of electromagnetic radiation and charged particles with crystals may involve ionization, i.e., the production of excess current carriers.* Experiments with single crystals of silicon have confirmed theoretical predictions on the effect of an externally-applied electric field on the process of photoionization. A study of photoionization in the inner portions of the fundamental optical absorption bands of germanium and silicon has shown that at sufficiently high photon energies the quantum yield rises to values considerably greater than unity. For photons of energies many times greater than the width of the forbidden band, the quantum yield is proportional to the energy of the photon. In ionization due to fast charged particles, the energy lost per electron-hole pair produced is independent of the particle energy.

1. INTRODUCTION

One of the types of action of photons and charged particles on crystals is ionization, i.e., the production of "free" current carriers, or electrons and holes. Phenomena such as photoconductivity, i.e., changes in the electrical conductivity of crystals due to light, γ rays, or charged particles, obey an equation having the following form for carriers of a particular type:

$$\Delta n = g\tau, \tag{1}$$

where Δn is the deviation of the concentration from the equilibrium value, g is the number of carriers produced per unit time per cm^3 due to absorption of radiation energy by the crystal, and τ is the mean lifetime of the carriers. As a rule, τ is a complicated function of the physical parameters of the crystal and of the temperature. In particular, it depends on the total carrier concentration. The theory of photoconductivity and analogous processes amounts to the analysis of the different cases of the general expression, Eq. (1).

One of the ways of studying the nature and quantitative characteristics of phenomena such as photoconductivity is to isolate and study the primary ionization process which determines the value of the generation rate g.

*B. M. Vul has suggested that the production of current carriers due to radiation energy (light, charged particles) should be termed radiation ionization. This designation permits us to distinguish these phenomena from thermal ionization and impact ionization in a strong electric field.

We shall limit ourselves below to those phenomena of photoionization and ionization due to charged particles which result from the liberation of valence electrons in semiconductor crystals. We shall not consider the ionization of impurity atoms or processes of thermal and impact ionization in a strong electric field.

2. THE EFFECT OF A STRONG ELECTRIC FIELD ON PHOTOIONIZATION

The spectral range of strong optical absorption in crystals exhibits a sharp limit on the long-wavelength side. From the viewpoint of the band theory, this corresponds to the minimum distance between bands. Quanta of frequency less than $\omega_0 = E_g/\hbar$ (where E_g is the width of the forbidden band) cannot be absorbed, since they do not have enough energy to eject a valence electron into the conduction band. The presence of an external electric field changes the picture considerably. Indeed, we cannot ascribe any definite energy to an electron with a given momentum in the external field. This is because the probabilities of finding it at all points in the crystal are identical, and its potential energy may take on all possible values. On the contrary, if we try to fix the potential energy precisely, i.e., localize the electron in a given unit cell of the crystal, its momentum may take on any value within the limits of the given band, and the energy again turns out to be indeterminate. If we wish to determine with maximum precision the bottom of the band in the vicinity of a given point x in space, we must form a packet of width Δx of wave functions of states near the edge of this band. This packet must contain only states of momenta differing by no more than Δp from the momentum at the bottom of the band. The parameters Δp and Δx must be defined such that the uncertainty in the energy

$$\Delta\varepsilon \sim \frac{(\Delta p)^2}{m^*} + qE\Delta x \tag{2}$$

is minimum (here m^* is the effective mass of the electron, q is the charge of the electron, and E is the electric field intensity). The condition of minimization of this function, taking into account the uncertainty relation $\Delta p \Delta x \gtrsim \hbar$, results in the fact that

$$\Delta\varepsilon_{\min} \sim \sqrt[3]{(qE)^2 \frac{\hbar^2}{m^*}} . \tag{3}$$

Hence, in an electric field the edge of the band is smeared out by an amount of the order of $\Delta\epsilon_{\min}$, and likewise the edge of the absorption band. In particular,

the absorption of quanta of energies less than E_g becomes possible. With certain limitations, this smearing out may be interpreted as a shift in the absorption "threshold" toward longer wavelengths.

A rigorous study of the problem of absorption of light by crystals in a homogeneous electric field has been carried out by L. V. Keldysh,[1] and has confirmed these qualitative ideas.* The general expression for the index of absorption α in the absence of an external field has the form

$$\alpha(\omega) = \frac{4\pi}{cn'\omega}\left(\frac{q}{m}\right)^2 \int |\mathbf{nM}(\mathbf{p})|^2 \,\delta\left[\varepsilon_e(\mathbf{p}) + \varepsilon_h(\mathbf{p}) - \hbar\omega\right] \frac{d^3p}{(2\pi\hbar)^3}, \quad (4)$$

where q and m are the charge and the mass of an electron, n' is the refractive index, $\epsilon_e(\mathbf{p})$ and $\epsilon_h(\mathbf{p})$ are the energies of an electron and of a hole in the crystal as functions of the momentum $\mathbf{p}$, $\mathbf{n}$ is the light-polarization vector, and $\mathbf{M}(\mathbf{p})$ is the so-called matrix element for the interaction of an electron with light. The presence of a δ-function in the integrand implies that the only processes contributing to the absorption are those in which the sum of the energies of the electron and hole generated precisely equals the energy of the absorbed quantum. In an electric field, the formula for $\alpha(\omega)$ remains practically the same, but the δ-function is replaced by the so-called Airy function $\mathrm{Ai}(x)$.[3]

This function declines exponentially for $x \gg 1$, and oscillates rapidly for large negative values of x. Hence, the fundamental contribution to the integral arises from the region defined by the condition $|\epsilon_e(\mathbf{p}) + \epsilon_h(\mathbf{p}) - \hbar\omega| \lesssim \hbar\Delta\omega_E$. That is, the application of the electric field leads to a smearing out of the δ-function over an energy range of width of the order of $\hbar\Delta\omega_E$. This fact may be very important for those frequencies in whose vicinity the refractive index varies greatly when the frequency is varied by an amount $\Delta\omega_E$. In particular, near an absorption edge, where this variation is especially sharp, it results in the absorption of frequencies less than ω_0, as has been noted. In the absence of a field, these frequencies are not absorbed at all. On the other hand, for frequencies greater than ω_0 but near enough to the edge, $\alpha(\omega)$ will be of the order of $\alpha_0(\omega + \Delta\omega_E)$. That is, there will be an effective shift in the absorption edge by an amount $\Delta\omega_E$ toward longer wavelengths.

For frequencies near ω_0, the expression for the absorption coefficient may be reduced to the form

$$\alpha(\omega, E) = \int_{-\infty}^{\infty} \alpha(\omega, 0)\, Ai\left(\frac{\omega - \omega'}{\Delta\omega_E}\right) \frac{d\omega'}{\Delta\omega_E}, \quad \Delta\omega_E = \frac{\Delta\varepsilon_{\min}}{\hbar}, \quad (5)$$

from which it follows that the absorptive index in an electric field may be determined by a particular type of averaging of the absorption coefficient observed in the absence of a field over the various frequencies (or as is equivalent, over the various possible positions of the absorption edge ω_0). The basic contribution to the average is given by the frequencies differing from ω by amounts of the order of $\Delta\omega_E$.

As shown in reference 3, this formula remains valid also for indirect transitions. However, in this case we must use the expression given in the theory of Hall, Blatt, and Bardeen[4] for $\alpha_0(\omega - \omega_0)$.

In fields of the order of 10^5 v/cm, the quantity $\hbar\Delta\omega_E$ may become as large as 10^{-2} ev. This is considerably greater than the value for any possible Stark effect, which might also lead to a shift in the absorption edge, as has been shown by F. F. Vol'kenshteĭn.[5]

We have conducted experiments jointly with K. I. Britsyn aimed at detecting the effect of a strong electric field on light absorption in single crystals of silicon.[6] Silicon shows a width of the forbidden band a little larger than 1 ev, and the effective mass of the carriers is considerably smaller than m. It was impossible to use in these experiments ordinary single crystals of silicon, as obtained by pulling from the melt or by zone melting, owing to their insufficiently high resistivity. In these experiments we used silicon which showed a resistivity of about 10^{11} ohm-cm at the temperature of the experiment ($T \simeq 100°$K). This silicon was prepared by irradiation in a reactor with a total fast neutron flux of about 10^{18} per cm^2. It was known from previous measurements[7,8] of the optical properties of silicon treated in this way that a new band with a maximum at about 1.8 μ appears near the absorption edge. This band, which is associated with defects, reduces somewhat the transmission in the immediate vicinity of the absorption edge. However, this change in the optical properties is due to local defects, rather than to a change in the band structure. Thus we may suppose that by using thin enough specimens we can perform measurements in the wavelength range where absorption involving interband transitions dominates.

A diagram of the experiment is shown in Fig. 1. The specimen in the form of a rectangular plate was placed between metal plates acting as electrodes. One of these metal plates was kept at liquid nitrogen temperature. Monochromatic light modulated at 500 cps was passed through the crystal, whose faces had been polished, and was collected by a refrigerated PbS photoresistor. The alternating voltage from the photoresistor was applied to a narrow-band amplifier, and the signal from the latter was applied to an indicating instrument. In the calculation of the absorption coefficients, we used data which we had previously published[9] on the reflectivity of silicon. Control measurements of the current through the specimen showed that the change in conductivity when the specimen was illuminated with light from a monochromator in the range $0.9 - 1\,\mu$ was insignificant. (The increase in current in a field of 5×10^4 v/cm upon illumination was not more than 5% of the value of the dark current.)

In the spectral range corresponding to valence band-conduction band transitions involving phonons, we found

*W. Franz[2] has arrived independently at analogous conclusions.

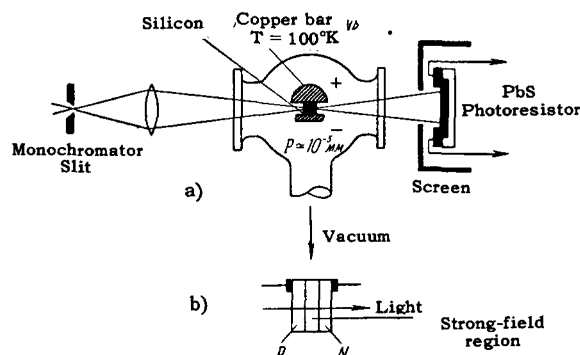

FIG. 1. Diagram of an experiment to observe the electrooptic effect in silicon.

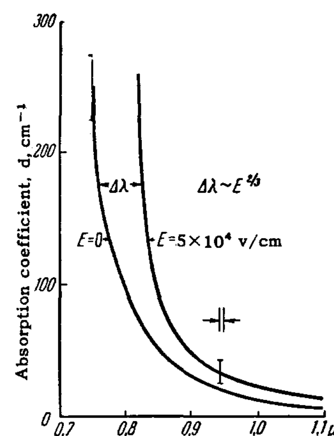

FIG. 2. The change in the absorption edge in silicon upon application of an electric field (the electrooptic effect in silicon).

an appreciable shift in the absorption edge, which became as much as 150 A for $E = 5 \times 10^4$ v/cm (Fig. 2). We see from the diagram that in the wavelength range $0.8 - 0.9\,\mu$, the application of the field brings about an abrupt increase in the absorption coefficient. The spectral range corresponding to direct transitions is to be studied separately with thinner crystals. The value of the observed shift $\Delta\lambda$ and its dependence on the electric field intensity in the specimen agreed with the theoretical predictions. The magnitude of the effect and the smallness of the change in conductivity due to the appearance of non-equilibrium carriers permit us to state that the observed phenomenon is a true "field effect," and is not associated with absorption by current carriers. The measurements were carried out under steady-state conditions (E = const.). However, the nature of the effect compels us to consider it to be lag-free. Thus, with the aid of a simple apparatus like that shown in Fig. 1, one could modulate light having a wavelength in the range $0.8 - 1\,\mu$ at very high frequencies.*

Besides continuing experiments on the effect of an electric field on optical absorption in homogeneous crystals, we can study the shift in the absorption edge upon passage of light through a region of high electric field in semiconductor crystals containing p-n junctions, that is, as in the diagram shown in Fig. 1b. In this case, the portion of the crystal outside the strong field will show no essential effect on the absorption in the spectral region into which the field shifts the absorption edge. Recently K. I. Britsyn has performed measurements of the optical transmission of silicon crystals to which a high-frequency field had been applied. He showed that the signal corresponding to the additional absorption in the crystal lagged behind the applied field E by no more than 2×10^{-8} sec. This upper limit is determined by the pulse rise time of the photomultiplier used to record the light intensity passing through the crystal.[10]

*M. N. Alentsev has called attention to the fact that by modulating the field in the crystal with a high (optical) frequency ω_m, we can in principle obtain a light beam emerging from the crystal, consisting of radiation of the fundamental frequency ω and the frequencies $\omega - \omega_m$ and $\omega + \omega_m$, i.e., a signal with a wavelength shorter than the original one.

3. PHOTOIONIZATION IN THE FUNDAMENTAL ABSORPTION BAND

a) The Quantum Yield of Photoionization and the Determination of the Quantum Yield in Crystals with p-n Junctions

The fundamental quantity characterizing the appearance of excess current carriers in a crystal is the quantum yield Q of photoionization, i.e., the number of electron-hole pairs produced by the absorption of one quantum. Absorption in the fundamental band near the absorption edge must be characterized by a quantum yield equal to unity, from the standpoint of the band theory. In the interior of the absorption band, the initial kinetic energy of the liberated photoelectrons or holes is large in comparison with the width of the forbidden band E_g. Here, the process of impact ionization must compete with the gradual transfer of this energy to the crystal structure.

The magnitude of the quantum yield of photoionization determines to a considerable degree the way in which one must solve the practically-important problems of recording and of direct transformation of the light energy into electrical energy. The simplest method of determining Q from data on the energy of the absorbed radiation flux and of the photoconductivity is often complicated by secondary factors which are difficult to take into account. In particular, this concerns the capture of the minority carriers. The possibility of using single crystals of germanium and silicon containing artificial n-p junctions permits the avoidance of errors involving capture phenomena. Also, it permits us quantitatively to take into account in the quantum-yield calculations the effect of the fundamental properties of the crystal being studied (the geometry, the absorption coefficient α, the bipolar diffusion constant D of the carriers, and the rates of volume and surface recombination). In the one-dimensional case, when the p-n junction is situated at a distance d beneath the illuminated plane surface

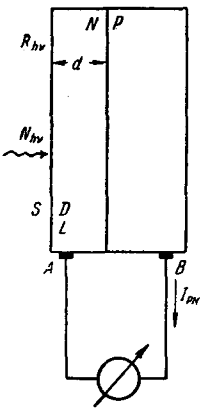

FIG. 3. Diagram of the determination of the quantum yield of photoionization from the photocurrent in a semiconductor crystal having a p–n junction. A and B are non-rectifying contacts.

of the crystal (Fig. 3), under the condition $1/\alpha \ll d$, the expression for Q takes the simple form:

$$Q = \frac{I_{PN}}{(1 - R_{h\nu})\, q N_{h\nu} \beta}, \tag{6}$$

where the "collection coefficient" β is defined in turn as

$$\beta = \frac{2}{\left(1 + \frac{SL}{D}\right) e^{\frac{d}{L}} + \left(1 - \frac{SL}{D}\right) e^{-\frac{d}{L}}}. \tag{7}$$

In these latter expressions I_{PN} is the short-circuit photocurrent, S is the rate of surface recombination, $L = \sqrt{D\tau}$ is the diffusion distance of the non-equilibrium carriers, $N_{h\nu}$ is the incident quantum flux, and $R_{h\nu}$ is the reflectivity of the crystal. This formula is a special case of the more complex expression for the collection coefficient to be used with arbitrary values of the absorption coefficient.[11]

In 1947, S. I. Vavilov pointed out that the quantum yield of photoluminescence may exceed unity in the range of sufficiently high photon energies.[12] The experiments of F. A. Butaeva and V. A. Fabrikant have confirmed this prediction.[13] We might expect that the increase in the quantum yield of photoionization might also show an effect on the number of current carriers due to the excess energy of the photon. This fact was found to be so in germanium crystals by S. Koc.[14]

The use of germanium and silicon crystals containing p-n junctions under simple experimental conditions allowing the use of the above formulas has permitted us to study the spectral dependence of the quantum yield of photoionization for photon energies up to 4.9 ev ($\lambda = 0.254\,\mu$). A schematic diagram of the apparatus used in these measurements is shown in Fig. 4. The basic components of the apparatus were a reflecting monochromator with an LiF prism, an incandescent lamp, a PRK-4 mercury lamp, and a SVDSh-500 lamp, which were used for the various spectral regions, and a cryostat in which the crystal being studied was placed. The intensity of the radiation incident on the surface of the crystal with the p-n junction was determined with the aid of a calibrated thermopile. The method of measurement is described in more detail in references 15 and 16.

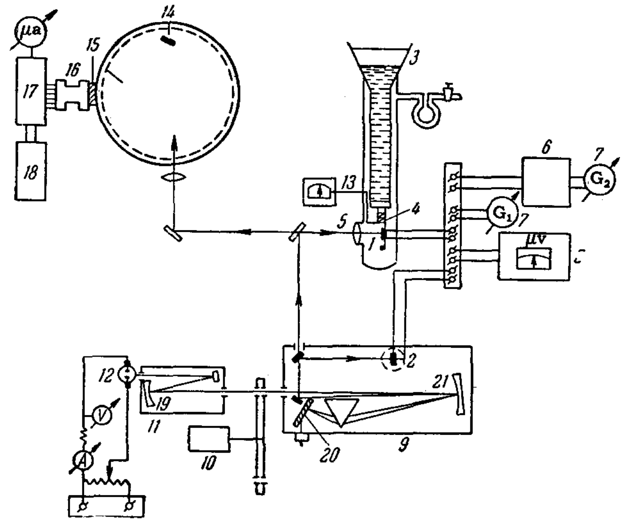

FIG. 4. Diagram of the experimental apparatus. 1 – specimen being studied of silicon containing a p–n-junction; 2 – thermopile; 3 – cryostat; 4 – electric heater; 5 – quartz lamp (f = 5 cm); 6 – potentiometer, type PPTN-1; 7 – G_1 and G_2 – low-resistance galvanometers, type M-21/4; 8 – narrow-band amplifier, type 28-I; 9 – reflecting monochromator; 10 – light chopper; 11 – reflecting condenser; 12 – light source; 13 – thermocouple and test instrument; 14 – fitting with MgO surface or with the specimen; 15 – plate containing a luminophor; 16-18 – photomultiplier with stabilized power supply (1500 v); 19-21 – aluminized spherical mirrors.

b) The Spectral Dependence of the Quantum Yield of Photoionization in Germanium Crystals

The measurements were performed on single-crystal plates of n-type germanium with a resistivity ρ of 10 – 20 ohm-cm, and an initial diffusion distance L of about 1.5 mm. The crystals were 0.3 – 0.6 mm thick. The p-n junction was created by fusing indium on the side opposite the illumination. A second, non-rectifying contact was made by fusing on tin at the same time.[17] The experiments with germanium were

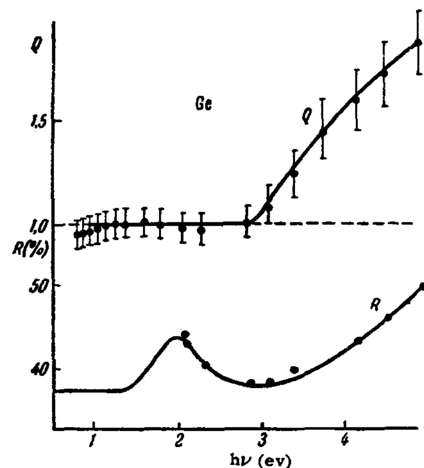

FIG. 5. The spectral dependence of the quantum yield Q of photoionization in germanium in the photon energy range up to 4.9 ev. Lower curve: reflectivity.

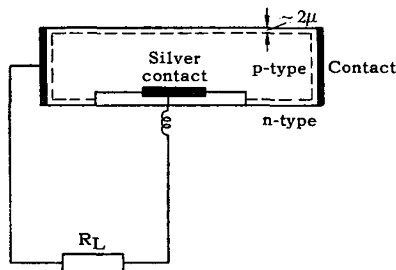

FIG. 6. Diagram of a silicon crystal with a p–n-junction and non-rectifying contacts.

conducted at room temperature. A typical curve of the spectral dependence of the quantum yield Q on the photon energy $h\nu$ is shown in Fig. 5, together with the spectral dependence of the reflectivity of the crystal surface, as used in the calculation of Q. The curve is distinctly divided into a region of constant Q equal to unity, occurring for photon energies no more than twice the width of the forbidden band, and a region in which the quantum yield increases with increasing $h\nu$. In the region where the quantum yield is constant, the data agree with Goucher's results.[18] A discussion and interpretation of the results obtained will be given below.

c) The Spectral Dependence of the Quantum Yield of Photoionization in Silicon Crystals

We have published experimental data on the spectral dependence of the quantum yield of photoionization in single crystals of silicon containing p-n junctions in 1958.[9] (See also references 15 and 19.) In these studies, we used silicon single crystals showing hole conduction in their initial state. The p-n junctions were made by thermal diffusion of phosphorus from the gas phase,[20] as is widely applied at present in preparing the silicon elements of "solar batteries." A diagram of a silicon crystal with a p-n junction and non-rectifying contacts is shown in Fig. 6.

From the data on the incident radiation flux, the reflectivity, and the photocurrent for all of the silicon crystals studied, we plotted curves of the relation of the product $Q\beta$ to the photon energy $h\nu$. Typical

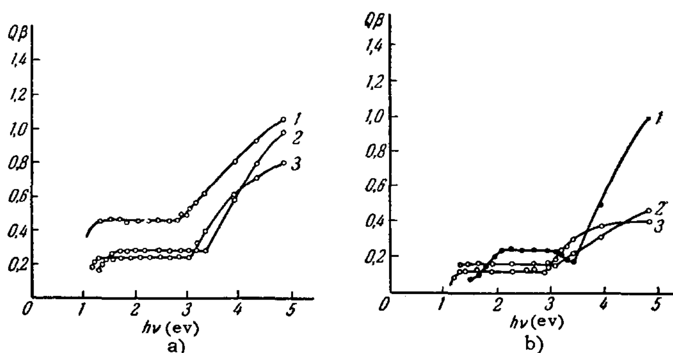

FIG. 7. (a) The spectral dependence $Q\beta = f(h\nu)$ for "shallow" p–n junctions. Curves of type I (1 – 400°K, 2 – 100°K, 3 – 300°K). (b) The effect of a "dead" surface layer on the function $Q\beta = f(h\nu)$. Curves of type II (1 – 100°K, 2 – 300°K, 3 – 400°K).

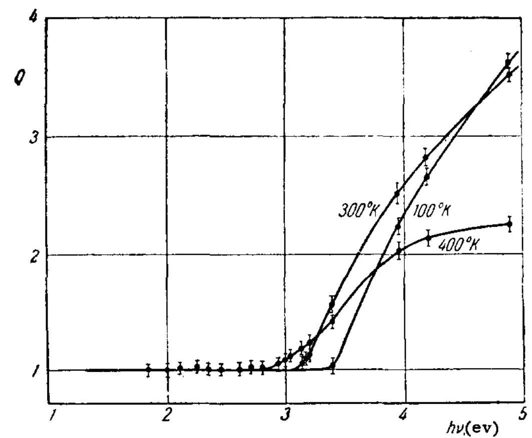

FIG. 8. Spectral dependence of the quantum yield in silicon at various temperatures.

curves of $Q\beta$ versus $h\nu$ for temperatures of the irradiated crystal from 100° to 400° K are shown in Fig. 7. Depending on the state of the crystal surface and the depth at which the p-n junction is situated, these curves may be divided into two types. Curves of type I (Fig. 7a), corresponding to small thicknesses of the n-type layer and "pure" (etched) crystal surfaces exhibit a plateau or region of constant $Q\beta$ in the region of small $h\nu$ (up to about 3.2 ev). This region adjoins a region in which the product $Q\beta$ increases with increasing $h\nu$. Curves of this type may be directly interpreted by using Eqs. (6) and (7). In fact, in the case of sufficiently high absorption, i.e., under the condition $1/\alpha \ll d$, the value of β does not depend on the absorption coefficient α, as we can see from Eq. (7). According to the results of direct determination of values of α in the fundamental absorption band of silicon,[8] as well as from estimates of α which we have made from reflectivity data,[15] $1/\alpha < 10^{-5}$ cm even for photon energies above 2.5 ev, while for $h\nu = 4.9$ ev, $1/\alpha < 10^{-6}$ cm. Thus the condition of independence of β on $h\nu$ is fulfilled for $d \cong 10^{-4}$ cm even in the visible, and even to a greater degree in the ultraviolet.

However, for real crystals, β can be independent of $h\nu$ only when there is no "dead layer" near the surface. Within such a layer, the inactive absorption of photons may occur without the generation of current carriers; such an absorption is not taken into account in the derivation of expressions such as Eq. (7).

In our opinion, curves of $Q\beta = f(h\nu)$ of type II (Fig. 7b), characterized by a decline to the right of the plateau or by a highly non-linear increase of $Q\beta$ with $h\nu$, indicated the existence of a "dead layer" on the surface of the specimens. This is also evidenced by the spectral characteristics of the ordinarily-used silicon solar batteries,[20] as well as by the results of an experimental study of ionization in silicon upon bombardment by fast electrons.[19,21]

An analysis of spectral characteristics of type II, together with an independent determination of the rate

of surface recombination, may give some information on the "dead layer." This is of independent interest with regard to the problems of improving the efficiency of photoelements and the recording and counting efficiency of silicon detectors for charged particles having short path lengths.

From the standpoint of studying the primary process of photoionization, the most important spectral characteristic curves were those of the silicon crystals in which the region of constant $Q\beta$ was well marked, and was joined to the region of increasing $Q\beta$ without a decline. Of course, the influence of "dead layers" is not excluded even in this case. However, in practice they can have an effect only in the region where $Q\beta$ increases with $h\nu$. There, they will lead to a decrease in the product $Q\beta$, since the presence of a "dead layer" can only decrease the size of the photocurrent.

On the basis of the commonly-accepted ideas on pair generation by absorption of a photon, we must assume that the quantum yield is unity in the energy range $E_g < h\nu < 2E_g$, as is confirmed by the existence of a plateau. By extrapolating the constant value of β into the region where the product $Q\beta$ increases, we may arrive at the curves for $Q = f(h\nu)$, i.e., the spectral dependence of the absolute value of Q. Such curves are given in Fig. 8 for three temperatures: 100°, 300°, and 400°K.

d) Discussion of Results

As we stated at the beginning of this section, the increase in the quantum yield, which supersedes the constancy of yield as the photon energy is increased, may be explained most naturally by the process of impact ionization, i.e., the formation of secondary pairs of carriers, etc., as a result of the excess kinetic energy of the photoelectron or the hole. It is quite obvious that this secondary ionization results from the interaction of the photoelectrons with the valence electrons of the atoms of the fundamental substance of the crystal, rather than with impurity atoms. This is indicated both by the absolute values of Q observed experimentally and by the fact that the increase in Q takes place at room temperature, when the atoms of the ordinary donor or acceptor impurities in Ge and Si are almost fully ionized. Besides, the increase in Q with increasing $h\nu$ takes place only for values of $h\nu$ appreciably greater than the width of the forbidden band. According to the theory of McKay[22] and Wolff,[23] which they used in interpreting data on impact ionization in Ge and Si in a strong electric field, if the kinetic energy of a current carrier in a band exceeds a certain threshold value E_i, the probability of collision ionization must exceed the probability of energy loss by any other process. From McKay's data, $E_i \sim 2.3$ ev for silicon. Thus, according to this interpretation, the quantum yield must in-

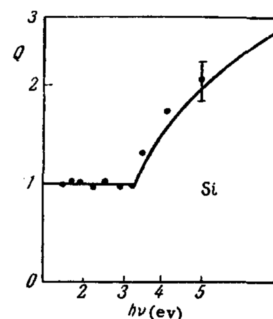

FIG. 9. A comparison of the data from Shockley's theory[24] on the quantum yield in silicon with experiment. The points are data from reference 19. $E_i = E_g = 1.1$ ev, $E_2 = 1.1$ ev, $n = nE_r/E_2 = 17.5$.

crease rather sharply to a value of two, beginning at the point $h\nu \gtrsim E_g + E_i$. This does not agree with the experimental data. On the other hand, according to this theory, Q cannot increase above a value of two without the generation of another pair. This must correspond to another break in the curve $Q = f(h\nu)$, which has been observed neither in silicon nor germanium.

From our viewpoint, if we take into account the relatively small difference in the effective masses of the electron and hole in silicon, we must assume that when the initial pair of carriers is generated, the excess kinetic energy is divided approximately equally between them.[24] Hence we may expect a considerable increase in the quantum yield beginning at $h\nu \gtrsim 3E_g$. This occurs at about 3.3 ev in silicon at room temperature, in agreement with experiment.

Analogous ideas have been recently expressed in a more detailed form by W. Shockley.[25] He assumed the equal distribution of the energy between the initial current carriers arising from the absorption of a photon, and stated that the minimum energy necessary for impact ionization is equal to E_g. On this basis, Shockley studied quantitatively the relation between the probabilities of the competing processes of secondary ionization and of emission of a phonon of maximum energy E_r. By using the current very reliable data on the energy of phonons in silicon and germanium, as determined by the measurement of the energy of neutrons scattered by these crystals, Shockley constructed theoretical curves of the spectral dependence of the quantum yield. These curves agreed well with experiment

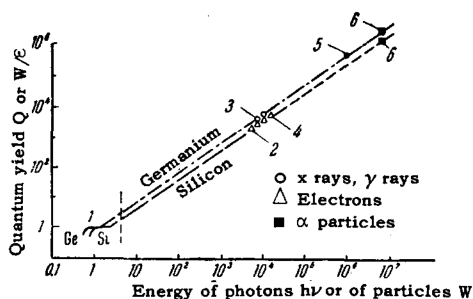

FIG. 10. Experimental data on ionization in germanium and silicon under the action of photons and charged particles. 1 – from references 9, 19; 2 – 29; 3 – 27; 4 – 21; 5 – 30; 6 – 28.

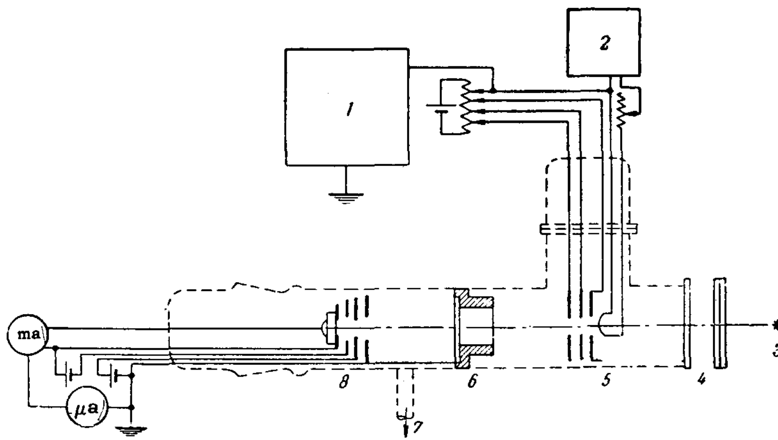

FIG. 11. Diagram of apparatus for studying ionization in semiconductors under the action of fast electrons. 1 – high-voltage power supply; 2 – storage battery; 3 – light source; 4 – filters; 5 – cathode; 6 – anode; 7 – vacuum; 8 – crystal with a p–n junction.

for silicon (Fig. 9), and satisfactorily for germanium. Here the only parameter whose value was selected was the average number of phonons n generated by the photoelectron up to the time it gives rise to the secondary pair. It turned out that for silicon at 300°K, n = 17.5. In addition to the theoretical papers already cited, the problem of impact ionization has been discussed by Antoncik,[26] who gave a qualitative explanation of the experimental data for Ge and Si without taking into account the distribution of the energy between the photoelectron and the hole.

In connection with the fact that the value of the quantum yield, in the region where it is considerably greater than unity, is determined by the interaction of "hot" electrons or holes with the crystal, it was of interest to get data on the photoionization process at widely varying temperatures. According to our results for silicon, the increase in $Q\beta$ and Q with increasing $h\nu$ is considerably temperature-dependent (see Figs. 7 and 8). We see from the typical curves presented here that at a high temperature (400° K), the increase in the quantum yield occurs at a considerably lower photon energy (2.95 ev), as compared with 3.4 ev at 100° K. This shift is partially explained by the narrowing of the forbidden band with increasing temperature. At 100° K, E_g for silicon is 1.17 ev, while at 400° K it is 1.04 ev. In view of the fact that an energy $E \geq E_g$ is expended in each act of production of the primary and secondary carrier pairs, we may thus explain a shift of $2(1.17 - 1.04) = 0.26$ ev. The remaining shift not yet accounted for, of the order of 0.2 ev, is greater than the experimental error, and cannot be explained by the theory. We may assume that this shift involves an increase in the relative probability of "indirect" electronic transitions involving phonons.

4. IONIZATION BY ABSORPTION OF HIGH-ENERGY PHOTONS (X RAYS AND GAMMA RAYS)

The passage of x rays or γ rays through a crystal is accompanied by the appearance of fast electrons in the crystal due to the photoeffect or Compton scattering. We shall limit ourselves here to the energy range in which the formation of electron-positron pairs may be neglected in comparison with the two former processes.

Under ordinary experimental conditions, almost all of the fast electrons fail to emerge from the crystal, their energy being expended in the formation of a large number of excess current-carrier pairs and in the excitation of crystal vibrations.

In this case, the concept of the quantum yield of photoionization includes the complex chain of intermediate processes. The prevailing conceptions of these processes permit us to assume that the mean energy ϵ expended per pair of excess carriers must not depend on the energy $h\nu$ of the initial photon or the energy W of the fast electron. The photocurrents which appear in single crystals of germanium having p-n junctions under monochromatic x-irradiation with $h\nu \sim 10$ or 20 kev have been studied by the Czechoslovak physicists Drahokoupil, Malkovska, and Tauc.[27] M. V. Chukichev and the present author have studied ionization in germanium single crystals under irradiation by γ rays from Co^{60}. The values of ϵ determined in both studies coincided, being 2.5 ± 0.3 ev. Thus, in the region of high photon energies for germanium, $Q = h\nu/\epsilon$ (Fig. 10).

5. IONIZATION IN GERMANIUM AND SILICON CRYSTALS UNDER BOMBARDMENT BY HIGH-ENERGY CHARGED PARTICLES

The experimental study of ionization upon passage of fast charged particles through semiconductor crystals began about ten years ago. McKay performed experiments in 1953 to study ionization under bombardment by polonium α-particles in regions of strong electric field within p-n junctions. These junctions were created artificially by introducing impurities into single crystals of germanium.[28] Under these conditions the time of flight of the carriers, which is proportional to the field intensity, was very short, and recombination could be neglected. By measuring the amplitude of the voltage pulses at the electrodes on

the crystal, which served as a "solid ionization chamber," McKay determined the value of ϵ for ionization by α particles. The value of ϵ was 3 ev for germanium, and 3.6 ev for silicon. McKay's method is considerably harder to apply to particles subject to strong directional scattering, i.e., electrons and positrons. Hence, in determining the mean ionization energy ϵ for the action of fast electrons, we used a method analogous to the determination of the quantum yield of photoionization. Here, a current was created between the n-type and p-type regions of the crystal, owing to the carriers generated by ionization by the beam of fast electrons passing through the crystal.[29,21] These experiments were conducted by L. S. Smirnov, V. M. Patskevich, and the author. The experimental setup is shown in Fig. 11. We found that electron bombardment in vacuo leads to a rapid increase in the rate of surface recombination in n-type germanium. The change in the rate of surface recombination led to a steady decrease in the secondary current in the circuit between the p- and n-type regions in the crystal being bombarded. Hence it would be incorrect in the calculation of the "collection coefficient" to use the value of the rate S of surface recombination which the specimen exhibited prior to evacuation of the apparatus and bombardment. The error due to the change in the value of S could be eliminated by use of the following method. As is shown in the diagram, the crystal being studied could be directly illuminated by a beam of monochromatic light during the electron bombardment. The wavelength of the light was chosen in the region for which the quantum yield is unity. The distribution in depth from the surface of pair-generation processes was about the same for both light and electrons. The fact that the photocurrent due to the generation of carriers with Q = 1, and the current due to ionization by the fast electrons were measured simultaneously with a single instrument made it possible to obtain quite reliable quantitative results. The energy expended in the generation of carrier pairs by fast electrons in germanium was 3.7 ± 0.4 ev. Measurements at an electron energy of about 500 kev gave values of ϵ of 4.5 ± 1.5 ev.

An analogous method was used also in the determination of the mean ionization energy with fast electrons in silicon. The value of ϵ for silicon turned out to be 4.2 ± 0.6 ev. The values of the energy ϵ spent by α particles, fast electrons, and high-energy photons in the creation of a carrier pair in germanium and silicon is almost one order of magnitude smaller than the mean ionization energy in gases. This fact, together with the practical possibility of creating p-n junctions in semiconductor crystals and the use of such crystals as current generators, demands the thorough study of the possibilities of direct conversion of radiation energy (either light, or β particles, or γ rays) into electrical energy. On the other hand, the observed independence of the value of ϵ on the initial energy and type of the ionizing particles has served as a basis for the invention of semiconductor "proportional counters." The existing data for germanium and silicon are shown on a log-log plot in Fig. 10. Even at present, silicon and germanium counters greatly surpass gas counters in resolving power and counting rate. We may expect that in the next few years "solid counters" will become the fundamental type of detectors used in medium-energy nuclear physics, and will open new possibilities here for design of experiments which were previously impossible.

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