Photoemission of Holes from Silicon into Silicon Dioxide

ALVIN M. GOODMAN
RCA Laboratories, Princeton, New Jersey
(Received 25 July 1966)

Photoemission of holes from silicon into thermally grown silicon-dioxide layers has been observed. Measurements of the threshold energy for this effect are consistent with a value of about 4.92 eV for the energy difference between the conduction band edge in the silicon and the valence band edge in the oxide at the silicon–silicon-dioxide interface. The mean drift range (*Schubweg*) for holes in the oxide is much less than that for electrons. From measurements of the photocurrent versus electric field, it is inferred that for holes in the oxide valence band, the product of mobility and mean time before trapping is $\lesssim 10^{-14}$ m^2/V.

I. INTRODUCTION

THE photoemission of electrons from the valence band of silicon into the conduction band of silicon dioxide (at the Si-SiO_2 interface) and the subsequent transport of the electrons through the oxide have recently been studied.[1–3] Analysis of the spectral variation of the photocurrent yield (electrons per photon) was used to determine the threshold energy for the photoemission process and thus to determine the energy difference between the Si valence band and the SiO_2 conduction band at the Si-SiO_2 interface.

The photoemission of holes from the conduction band of a metal into the valence band of a semiconductor at their mutual interface has been observed by Williams[4] and by Spitzer and Mead.[5] It should be possible in a similar experiment to observe the photoemission of holes from the conduction band of Si into the valence band of SiO_2. The threshold energy for this process should be the energy difference between the Si conduction band edge (or the Fermi level in the case of n-type degenerate Si) and the SiO_2 valence band edge at the Si-SiO_2 interface. This experiment was carried out in the present work with the result that $E_{CS}-E_{VO}$ the energy difference between the conduction band edge in the Si and the valence band edge in the oxide is 4.92±0.10 eV. In addition, the variation of the photocurrent through the oxide was measured (at constant photon flux and energy) as a function of electric field in the oxide. The results indicate that $\mu_p\tau_p \lesssim 10^{-14}$ m^2/V where μ_p is the hole mobility in the oxide and τ_p is the mean time the hole spends in the oxide valence band before immobilization by deep trapping. A nontrivial part of the work involved the elimination of alternative explanations (e.g., electrons in the oxide conduction band) for the observed photocurrents.

The details of the sample preparation, measurements, and interpretation are presented in the following sections.

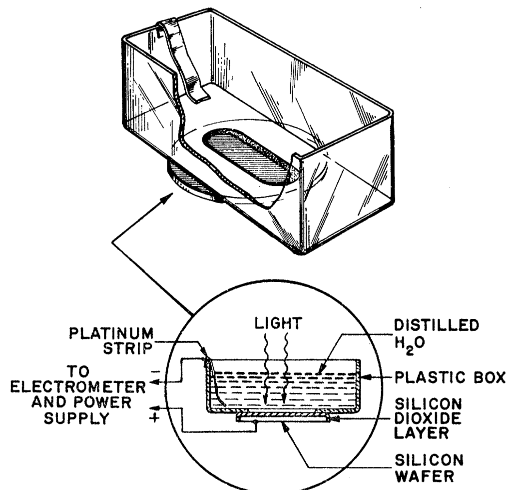

FIG. 1. Silicon–silicon-dioxide–water cell for photoelectric measurements.

II. MEASUREMENTS AND PRELIMINARY DISCUSSION

A. Sample Preparation

The silicon dioxide used in this work was in the form of layers or films thermally grown on the (111) faces of single crystal degenerate n-type (0.00088 or 0.002 Ω-cm) and p-type (0.0006 Ω-cm) silicon wafers. The growth was carried out in an air-steam atmosphere at 1100°C. In all, 12 oxide layers (on 12 separate wafers) were used. The layer thicknesses ranged from 0.84 to 6.4 μ. A low-resistance pressure contact to the back of each silicon wafer was obtained by sandblasting that surface to remove the oxide.

In *most* of the experiments to be described, the sample electrode configuration was that shown in Fig. 1; the one exception will be discussed in part E of this section. One contact to the SiO_2 layer is the Si on which it is grown. The counterelectrode (contact on the opposite side of the SiO_2 layer) as shown in Fig. 1 is distilled, de-ionized water. The water is contained in a Lucite box which has been fastened to the SiO_2 layer with Goodyear VPE200 cement. A slot which had previously been milled in the bottom of the box allows the water to contact the SiO_2. A strip of platinum foil is used to make contact with the water. The light passes through the water on its way to the sample.

[1] R. Williams, Phys. Rev. **140**, A569 (1965).
[2] A. M. Goodman, Phys. Rev. **144**, 588 (1966).
[3] R. Williams, J. Appl. Phys. **37**, 1491 (1966).
[4] R. Williams, Phys. Rev. Letters **8**, 402 (1962).
[5] W. G. Spitzer and C. A. Mead, J. Appl. Phys. **34**, 3061 (1963).

In *all* of the measurements, the Si was maintained at a positive potential with respect to the counterelectrode. This means that if holes are photoemitted into the SiO_2, they must come from the Si and, if electrons are photo-emitted into the oxide they must originate in the counterelectrode or at the interface between the counterelectrode and the SiO_2. Since the water is quite transparent in the ultraviolet region of the spectrum[6] for photon energies less than 6 eV, it seems reasonable to assume that energy cannot be transferred to the electrons in the water and that no electrons are photoemitted from the water.

In part E of this section an additional experiment is described in which a partially transparent *metal* counter electrode was used to deliberately photoemit electrons into the oxide. In this case, the electrode configuration was identical to that described in Ref. 2.

B. Preliminary Experiments

Light is focused on the Si-SiO_2 interface through the water and the slot in the plastic box. Some of the light is absorbed in the Si and some is reflected back through the SiO_2 and the water. The light absorption in the water[6] and the oxide[7] are negligibly small. The absorption of light in the Si transfers energy to electrons in the Si close to the Si-SiO_2 interface. If the photon energy is high enough, some electrons may be transferred to the conduction band from states deep in the valence band leaving "hot holes" with sufficient energy to enter the SiO_2 valence band. If the Si is positively biased with respect to the water electrode, the field in the oxide will cause the holes to drift through the oxide toward the water and this drift may be measured as a current in the external circuit.

The measurement circuit consisted of a stable power supply (Keithley Model 241) and an electrometer (Keithley Model 610A) to measure the photocurrent. The output of the electrometer was connected to a recorder for current versus time measurements. The photocurrent measurements were made using a "light-on–light-off" technique to eliminate error due to dark currents. The photocurrents measured were in the range 10^{-13} to 10^{-9} A, the lower limit being determined by the noise level which was usually about 10^{-13} A for the best measurements, but rose to 10^{-12} A or more for some samples with thinner oxide layers and in some cases even for thick oxide layers when the field exceeded $\sim 10^8$ V/m. The initial experiments were carried out using a General Electric H85A3/UV mercury arc lamp (with outer jacket removed) as a light source.

When the voltage was applied (sample in dark) between the Si and the water, a large charging current was observed. This current decayed with time (usually) to a steady state value of the order of magnitude of $\sim 10^{-12}$ A during a period of from $\frac{1}{2}$ to 20 h. The steady state current and the time required to reach it varied widely from sample to sample and with the applied voltage. Most of the photocurrent measurements were made using an applied voltage which was adjusted such that the electric field in the oxide was $\sim 10^8$ V/m.

After the dark current had settled down to its "steady-state" value, the light was turned on (i.e., the shutter was opened) and the photocurrent was recorded as a function of time. Initially, the photocurrent rose rapidly to a peak value and thereafter decayed with time, reaching a steady state value an hour or more later. The photocurrent rise time was less than the recorder rise time and was probably limited by the circuit time constant. The same qualitative behavior was observed for several samples. A typical curve of photocurrent versus time for initial exposure to uv light is shown in Fig. 2. When the light was turned off (i.e., the shutter was closed), the photocurrent returned rapidly to zero (i.e., the total current returned to the previous steady-state dark current value). Thereafter, the photocurrent was found to follow the light signal quite rapidly and the response time was generally limited by the time constant of the measuring circuit.

The steady-state photocurrent was found to be proportional to the light intensity.

Corning glass color filters[8] were used in an attempt to establish an approximate threshold value of photon energy for the effect. Each of the three filters used has a high transmission in the uv region down to some "cutoff wavelength" and thereafter has very low transmission. The quotation marks are used because the cutoff is actually quite diffuse and extends over a wavelength region corresponding to a photon energy range of ~ 0.5 eV or more. For convenience, however, the cutoff may be arbitrarily defined as the 50% transmission point of the filter. In Table I, are listed the cutoff photon energies for each of the filters and the relative photocurrents for 3 samples when each filter is used. From

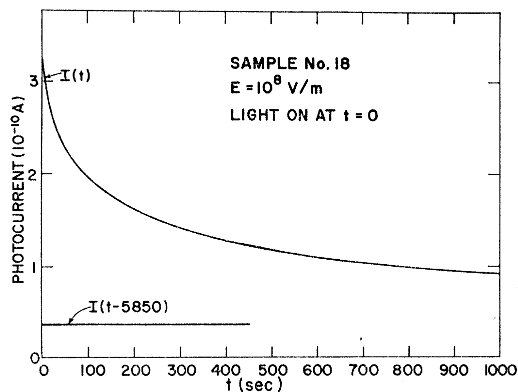

FIG. 2. Decay of photocurrent with time after initial exposure to uv light. Sample No. 18, $E = 10^8$ V/m.

[6] *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1929), 1st ed., Vol. V, p. 271.

[7] "Data File on Fused Quartz and Fused Silica," supplied by the Amersil Quartz Division of Engelhard Industries.

[8] Glass Color Filters, Brochure No. CF-3, Corning Glass Works, Corning, New York (unpublished).

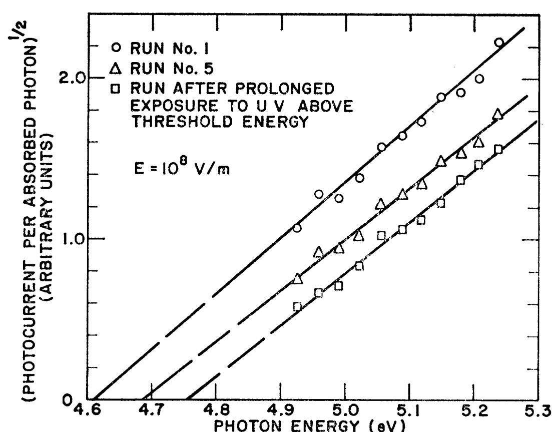

FIG. 3. Square root of photoelectric yield versus photon energy for three runs. Sample No. 16, $E=10^8$ V/m.

these results, it is reasonable to conclude that the threshold energy for the observed effect is greater than 4.0 eV, less than 5.2 eV, and probably close to 4.9 eV. Because of the diffuse character of the filter cutoff and the complex spectral variation of the light source intensity, it is virtually impossible to quantitatively estimate the probable error limits but a reasonable "educated guess" would be $\sim\pm 0.3$ eV.

The decay of the photocurrent with time after the initial exposure of the sample to light was interpreted as a trapping and polarization phenomenon in the oxide. Two experiments were then undertaken to determine whether the trapped carriers could be freed thermally or optically.

(1) Using unfiltered light, the sample photocurrent was allowed to reach a steady state after which the light was turned off. After 30 min the sample was reilluminated; the initial photocurrent was about 30% higher than the previous steady-state value. The photocurrent then decayed to the previous steady-state value within 6. min.

(2) The previous experiment was repeated with one change; viz., after the steady-state photocurrent was achieved with unfiltered light, a Corning No. 0-54 filter (see Table I) was placed in the light beam for 30 min instead of leaving the sample in darkness. No photocurrent was detectable during that time. After reillumination at the end of 30 min, the result was exactly

TABLE I. Steady-state photocurrent for three samples using filtered and unfiltered light from an H85A3/uv mercury arc lamp.

Filter	Filter cutoff energy (eV)	Photocurrent Sample No. 16	Sample No. 18	Sample No. 19
Unfiltered		$I_u=2.7\times10^{-12}$ A	$I_u=2.5\times10^{-10}$ A	$I_u=6.5\times10^{-11}$ A
0–54	4.0	···	···	···
7–54	4.9	$<0.01I_u$	$0.04I_u$	$0.023I_u$
9–54	5.2	$0.22I_u$	$0.18I_u$	$0.15I_u$

the same as in the previous experiment. Thus, light ($1.0\lesssim h\nu\lesssim 4.0$ eV) did not seem to be effective in freeing trapped carriers.

In addition, it was observed that allowing a previously illuminated sample to remain in the dark with no applied voltage for several days tended to restore it to nearly original condition (i.e., before illumination). The freeing of holes trapped in the oxide may therefore occur (a) thermally or (b) by tunneling between the trapping sites and normally filled states in the Si valence band. In (a) the thermal activation energy for the hole trap must be low ($E_{\mathrm{TH}}\lesssim 1$ eV). In (b) the traps may be deep but must also be very close (within $\sim$100 Å) of the Si-SiO_2 interface.

C. Spectral Measurements

In order to determine the threshold energy more accurately, a Leiss double monochromator with fused quartz prisms was used instead of the filters described in part B. However, the output of the monochromator was too low (using the same light source) to give a usable signal-to-noise ratio. In order to obtain a high light intensity in the photon energy region just above 4.9 eV, a number of different arc lamps were tested. The highest intensity in the 4.9 to 5.25 eV region was obtained using an OSRAM HBO 500 W high-pressure 500-W mercury arc lamp. This lamp was used as a source for the monochromator for all subsequent measurements. The monochromator output was calibrated using an Eppley thermopile. For "spectral sweep" measurements, an electric motor drive was connected to the monochromator wavelength dial.

The spectral distribution of the photocurrent was obtained by slowly sweeping the monochromator through the wavelength region of interest while recording the photocurrent. The sweep time was $\sim$5 min.

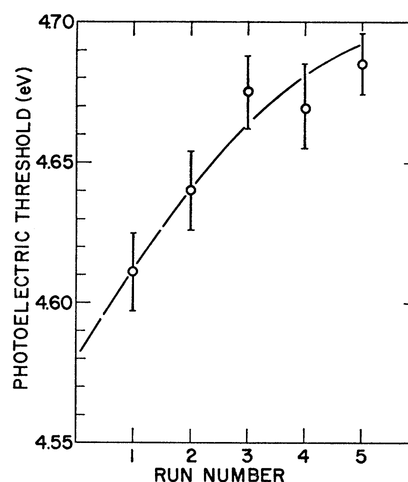

FIG. 4. Photoelectric threshold for 5 consecutive runs versus run number for Sample No. 16, $E=10^8$ V/m.

Subsequent sweeps showed qualitatively the same result; however, the photocurrent decreased slightly with each succeeding run. The photocurrent was normalized with respect to *absorbed* photon flux. The absorbed photon flux was assumed to be 1-r times the incident photon flux where r is the reflection coefficient at the Si-SiO_2 interface and is computed from published optical properties.[7,9] The reflections at the SiO_2-H_2O and the H_2O-air interface are small enough and vary so slightly over the wavelength region of interest that they may be neglected.

The *electron* photoemissive yield y (electrons per absorbed photon) for a semiconductor may vary as the p-power of energy above the threshold ($h\nu$-$h\nu_0$) where p can theoretically have the value, 1, $\frac{3}{2}$, 2, or $\frac{5}{2}$ depending on the excitation and scattering mechanisms involved.[10] More than one mechanism may be involved in the same energy range complicating matters still further. In addition, measurements of photoemission of electrons from silicon into vacuum[11] have shown strong dependence upon doping and, in some cases, a range for which $p=3$. For the case of photoemission of *holes* from Si into SiO_2, it is reasonable to expect the relationship between yield and energy to be no less complicated. Empirically, however, the experimental data seems to be fitted best with $\frac{3}{2}<p<\frac{5}{2}$. As a practical matter, all of the data were analyzed using the value $p=2$. If the value of $p=\frac{3}{2}$ or $p=\frac{5}{2}$ were used, the shift in the empirically determined energy threshold would be less than 0.1 eV. The square roots of photoelectric yield[12,13] v photon energy for three runs on one sample are shown in Fig. 3. Each of the straight lines is the minimum square error fit to the data points for that run. It is clear that the photoelectric threshold energy increases with increasing exposure to uv light above the threshold energy. In Fig. 4, the variation of the threshold energy is shown for 5 consecutive runs on one sample. Similar behavior was observed using other samples. This behavior is consistent with the trapping of holes very close to the Si-SiO_2 interface. The trapped holes raise the height of the maximum in the potential energy barrier for photoemitted holes. This is shown schematically in Fig. 5. In Fig. 5(a), no field is applied and the barrier has its "true" or "zero-field" value, ϕ_0. In Fig. 5(b), a field is applied which lowers the barrier by $\Delta\phi$ because of Schottky effect.[14] In Fig. 5(c), the barrier increases by $\phi_\oplus$ because of positive charge (holes) being trapped in the oxide.

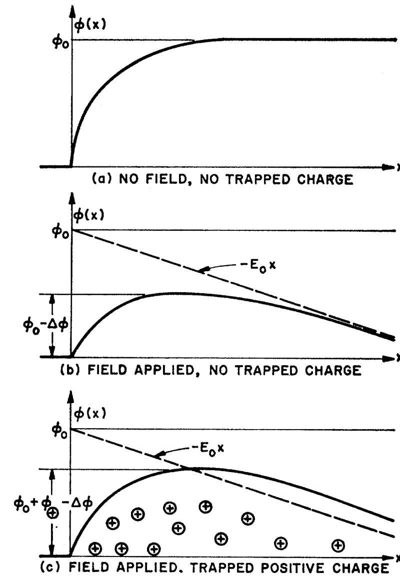

FIG. 5. Schematic representation of the energy barrier to hole emission from silicon into silicon dioxide. (a) No applied field, no trapped charge. (b) Applied electric field, no trapped charge. (c) Applied electric field, trapped positive charge.

A reasonable method for evaluating ϕ_0 is to use the value of the actual photothreshold ϕ_T from the first run on a previously unilluminated sample and set $\phi_0=\phi_T+\Delta\phi$. This assumes that $\phi_\oplus$ does not change significantly during the run. Since the run is made from low to high photon energy, an increasing $\phi_\oplus$ would tend to lower the photocurrent at the high-energy end of the sweep and the resulting intercept on a plot like that of Fig. 3 would give a misleadingly low value for ϕ_0. However, by considering the points at the high-energy end of the first run and the low-energy end of the second run (the equivalent of sweeping from high- to low-photon energy—which should produce an error in the opposite direction for the determination of ϕ_0), one can estimate that the maximum error involved in the original procedure is $\gtrsim$0.02 eV.

For p-type samples, ϕ_0 is $E_{CS}-E_{VO}$, the energy difference between the conduction band edge in the silicon and the valence band edge in the oxide. For degenerate n-type samples, $E_{CS}-E_{VO}=\phi_0-E_F$ where E_F is the Fermi-level position in the conduction band relative to the band edge.

For four previously unilluminated samples (two n type and two p type), the values of $E_{CS}-E_{VO}$ determined by the above procedure all fell in the range 4.92 ± 0.10 eV. The value of $\Delta\phi$ was assumed to be the same as that for electrons photoemitted into silicon dioxide.[2]

[9] H. R. Philipp and E. A. Taft, Phys. Rev. **120**, 37 (1960).
[10] E. O. Kane, Phys. Rev. **127**, 131 (1962).
[11] G. W. Gobeli and F. G. Allen, Phys. Rev. **127**, 141 (1962).
[12] Photoelectric yield is used here to mean electrons passing through the external measuring circuit per photon absorbed in the silicon. It is an *external* yield as compared with the *internal* yield which may be defined as photoemitted holes per absorbed photon. It is tacitly assumed that the ratio of external yield to internal yield is a constant equal to the mean range (*Schubweg*) for holes divided by the oxide thickness. This follows from the fact that the current measured in the external circuit is the charge (holes) photoemitted per second times the mean distance that it travels divided by the oxide thickness. See Ref. 13.
[13] W. Shockley, J. Appl. Phys. **9**, 635 (1938).

[14] H. K. Henisch. *Rectifying Semiconductor Contacts* (Oxford University Press, London, 1955), Chap. VII.

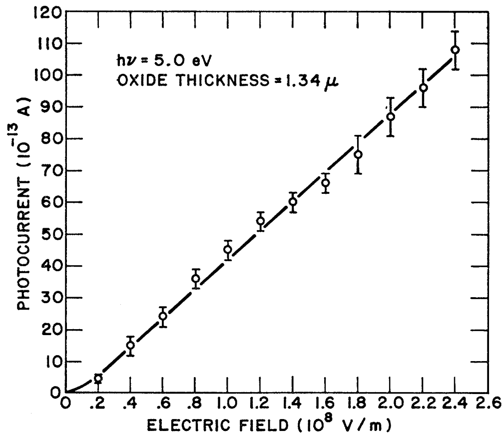

FIG. 6. Variation of photocurrent with photovoltage at constant photon flux and energy for sample No. 18.

D. Hole Range Experiments

An attempt was made in this work to determine a value for the product $\mu_p\tau_p$ where μ_p and τ_p, are respectively, the hole mobility in the oxide valence band and the mean time before immobilization by trapping. This was done by observing the variation of the "steady-state photocurrent" through the oxide (at constant photon flux and energy) as a function of applied electric field in the oxide. It is expected that the photocurrent will rise with increasing field for two reasons: (1) the increasing field lowers the energy threshold for photoemission (as discussed previously) and thus causes an increase in the hole current photoemitted into the oxide and (2) the mean range or *Schubweg* w of holes in the oxide increases directly with the electric field enhancing the photocurrent measured in the external circuit.[15] If the hole range reaches the thickness of the oxide, l, a definite saturation effect is expected. Such an effect has been seen for electrons photoemitted into silicon dioxide.[2] In only two cases was it possible to obtain a plot of hole photocurrent versus applied electric field for a large variation of electric field; the other samples either became noisy or broke down completely.

For the thinner of the two oxide layers, the plot is shown in Fig. 6. There is just a hint of a saturation effect near $E=1.2\times10^8$ V/m; at higher fields, the photocurrent increases again but this could be due to Schottky effect. It is not possible to account for the Schottky effect quantitatively in this region for two reasons: (1) At high fields ($E\gtrsim1.5\times10^8$ V/m), the distance of the potential maximum from the emitting surface is at most only a few times the nearest-neighbor distance in SiO_2, casting some doubt upon the assumptions employed in the usual Schottky effect derivation, and (2) it is difficult to account quantitatively for the trapped charge in the oxide. Nevertheless, one can conclude that $w=\mu_pE\tau_p\gtrsim l$ for $E=1.2\times10^8$ V/m and $l=1.34\times10^{-6}$ m. Thus, $\mu_p\tau_p\gtrsim10^{-14}$ m²/V.

The data for the thicker oxide showed no evidence of photocurrent saturation, leading to the conclusion that $\mu_p\tau_p<3\times10^{-14}$ m²/V in agreement with the result for the thinner oxide.

E. Elimination of Possible Alternative Explanations

It is important to explore the possibility of an alternative explanation for the results which have been described; viz, the possibility that electrons are being liberated by light from traps in the oxide or at the oxide-water interface and that the charge trapping effects are actually due to the trapping of electrons rather than holes. This possibility was obviated by using the *same* oxides (3 samples) with partially transparent gold counter electrodes to deliberately photoemit electrons into the oxides (see Fig. 1 of Ref. 2). In these experiments, the electrons were photoemitted from the gold and the observed photocurrents behaved quite differently from those previously ascribed to holes. In one case[2] it was shown that for electrons. $\mu_n\tau_n=2.1\times10^{-13}$ m²/V. For all three samples, it was shown that with $E=10^8$ V/m, steady electron photocurrents could be observed with negligible decay due to trapping. It follows that the charge carriers involved in the experiments described in parts B, C, and D of this section were not conduction band electrons. Thus, the possibility of an alternative explanation has been eliminated.

III. SUMMARY

The results of Sec. II may be summarized as follows:

(1) The photoemission of holes from silicon into silicon dioxide has been observed.

(2) Analysis of the spectral variation of the photoelectric yield for this process leads to the conclusion that $E_{CS}-E_{VO}$, the energy difference between the conduction band edge in the silicon and the valence band edge in the oxide is 4.92±0.10 eV.

(3) For a given electric field, the mean range for holes in silicon dioxide is much smaller than that for electrons; $\mu_p\tau_p\gtrsim10^{-14}$ m²/V where μ_p and τ_p are, respectively, the hole mobility and mean time before trapping.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge valuable discussions with R. Williams during the course of this work. I also wish to thank H. Parker for preparing the oxide layers and J. J. O'Neill, Jr., for assistance with sample preparation and some of the measurements.

[15] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948) 2nd ed., Chap. IV.