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Photoemission of Electrons from Silicon and Gold into Silicon Dioxide

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Photoemission of electrons from both silicon and gold into thermally grown silicon dioxide layers has been observed. In each case, the energy threshold for photoemission is found to vary with the electric field in the oxide. Within experimental error, this variation is consistent with the theoretical Schottky effect, assuming an effective value of image-force relative dielectric constant of about 2.15. The extrapolated zero-field threshold energies for silicon and gold are about 4.2 and 3.8 eV, respectively. From measurements of the photocurrent versus electric field, it is inferred that for electrons in the oxide conduction band, the product of mobility and mean time before immobilization by deep trapping is of the order of 10^{-13} m^2/V.

I. INTRODUCTION

PHOTOEMISSION of electrons from the valence band of silicon into the conduction band of silicon dioxide has been observed by Williams[1] in three-layer sandwich structures consisting of (1) a silicon wafer, (2) a thermally grown film of silicon dioxide, and (3) an evaporated partially transparent gold film. He determined a threshold value of photon energy for this process. He found that with a sufficiently large bias voltage across the oxide, most of the electrons passed completely through the oxide without being trapped.

In the present work, using similar structures, photoemission of electrons from both gold and silicon into silicon dioxide has been observed. The threshold values of photon energy are found to vary with the electric field in the oxide. Within experimental error, this variation is consistent with the theoretical Schottky lowering of the effective work function[2] assuming a value of image force relative dielectric constant in the oxide of about 2.15.

The variation of the photocurrent through the oxide (at constant photon flux and photon energy) has been measured as a function of the electric field in the oxide. After correction for "Schottky effect," the measurements are consistent with $\mu\tau$ values of the order of 10^{-13} m^2/V, where μ is the electron mobility and τ is the mean time the electron spends in the conduction band before immobilization by deep trapping.

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

II. EXPERIMENTAL DETAILS

A. Sample Preparation

The oxide films were grown on 111 faces of single-crystal degenerate n-type (0.002 Ω-cm) wafers. The growth was carried out in an air-steam atmosphere at 1100°C. In all, 4 oxide layers (on 4 separate wafers) were used; two were about 2.1 μ thick and two were about 5.3 μ thick. A (low-resistance) pressure contact to the back of each silicon wafer was obtained by sandblasting that surface to remove the oxide. Eight thin partially transparent gold electrodes (area$\sim$0.2 cm^2) were applied to the front face of each oxide layer. A heavier "dot" of gold $\sim$1 μ thick was also applied by evaporation on top of each electrode to facilitate connection by a pressure contact. The sample configuration, as is shown in Fig. 1, is effectively a "sandwich" of oxide between a slice of silicon on one side and a partially transparent gold layer on the other.

B. Measurements

Monochromatic light is focused on the thin gold electrode. Some of the light passes through the gold and the oxide layer and is absorbed in the silicon. If the photon energy is high enough, electrons in the silicon may be given sufficient energy to allow them to enter the conduction band of the oxide. If the gold layer is positively biased with respect to the silicon, the field in the oxide will cause the electrons to drift through the oxide toward the gold, and this electron drift can be measured as a current in the external circuit.

Some of the light is absorbed in passing through the gold. If the photon energy is high enough, electrons in the gold may be given sufficient energy to allow them to enter the conduction band of the oxide. If the gold layer is negatively biased with respect to the silicon, the field in the oxide will cause the electrons to drift toward the silicon, and this can be measured as a current in the external circuit.

It is also possible in principle for the current flow in the external circuit to be explained in terms of hole motion through the oxide. That this does not in fact seem to be the case has been shown by Williams.

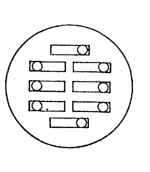

FIG. 1. Schematic construction drawing of a sample (not to scale).

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[1] R. Williams, Phys. Rev. **140**, A569 (1965).

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

The measurement circuit consisted of a stable power supply and an electrometer to measure the photocurrent. The output of the electrometer was connected to a recorder for current versus time measurements.

The light source was a high-pressure xenon arc (PEK Labs. X-200) which gives a strong continuum in the ultraviolet region of the spectrum. The arc was focused on the entrance slit of a Leiss double monochromator equipped with fused-quartz prisms. An electric-motor drive was connected to the monochromator wavelength dial for "spectral sweep" measurements. The monochromator output intensity was calibrated with a thermopile.

The photocurrent measurements were made using a "light on–light off" technique to eliminate error due to dark currents. All of the photocurrents measured were in the range 10^{-14} to 5×10^{-12} A, the lower limit being determined by the noise level which varied between 10^{-14} and 3×10^{-13} A depending on the sample and the applied electric field.

III. RESULTS AND DISCUSSION

A. Thickness and Threshold Determination

The spectral distribution of photocurrent was obtained by slowly sweeping the monochromator through the wavelength region of interest while recording the photocurrent. Typical results are shown in Fig. 2 for the gold polarity positive (a) and negative (b). The undulations in the photocurrent are due to the silicon-oxide-metal sandwich structure acting as an interferometer. It is easy to show that the thickness l of the oxide layer can be computed from the formula

$$l=Mhc/2n(E_{N+M}-E_N), \qquad (1)$$

where h is Planck's constant, c is the velocity of light in vacuum, n is the index of refraction of the oxide, and E_N is the photon energy corresponding to the photocurrent peak when the layer is N half-wavelengths thick.[3] The value of N need not be either integral or half-integral because the dielectric boundary surfaces (gold and silicon in the present case) are not perfectly reflecting. The value of M, however, *is* integral to a good approximation provided that the optical constants of the gold, silicon, and silicon dioxide do not change between E_N and E_{N+M}. Equation (1) was used to determine the thickness of each oxide layer using a value[4] for n corresponding to the energy $\frac{1}{2}(E_N+E_{N+M})$. The range of n in the wavelength region used for these measurements was 1.480 to 1.520. Computations of l for a given sample using values of M ranging from 1 to 8 gave results which were self-consistent within 1%. As expected, the computed thickness values were independent of sample polarity. On one sample the oxide thickness was also measured using the Tolansky technique.[5] The results of the two methods agreed within 3%.

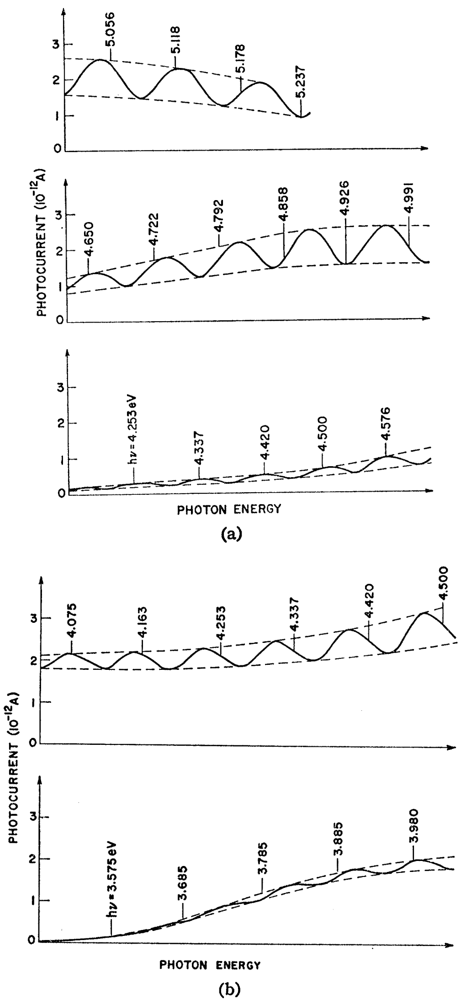

Fig. 2. Photocurrent versus photon energy for sample 7-2 with 400 V applied between the gold layer and the silicon wafer. (a) gold positive, (b) gold negative.

It can be seen from a comparison of Figs. 2(a) and 2(b) that the peaks of the photocurrent undulations occur at a different set of energies (wavelengths) for one polarity than for the other. Since a peak of photocurrent corresponds to a peak of light intensity at the photoemitting surface, it follows that the source of the carriers must be the silicon for one polarity and the gold for the other, provided that only *one* sign of carrier is involved for each polarity. It must then also be true

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[3] Equation (1) may be easily derived by (a) noting that the photocurrent peaks occur when $l=N\lambda_N/2$ and $l=(N+M)\lambda_{N+M}/2$ and (b) eliminating N between these expressions and writing the λ's in terms of the photon energies $\lambda_N=hc/nE_N$.

[4] The value of n was assumed to be equal to that for "Suprasil" fused silica given in a "Data File on Fused Quartz and Fused Silica" from the Amersil Quartz Division of Engelhard Industries Inc.

[5] A step was etched in the oxide layer with hydrofluoric acid. The step was contoured with a thin layer of evaporated silver and then measured using multiple-beam interferometry. For a general reference, see S. Tolansky, *Multiple Beam Interferometry of Surfaces and Films* (Clarendon Press, Oxford, 1948).

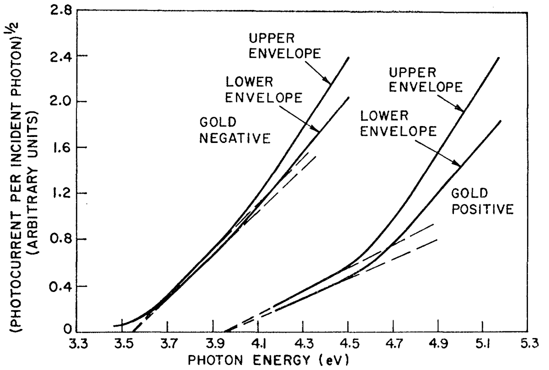

FIG. 3. Square root of the photocurrent per incident photon versus photon energy for sample 7-2. The data corresponds to the envelopes of Fig. 2.

that the sign of the carriers is the same for either polarity. Following Williams,[1] the photocurrent with the gold positive is ascribed to electrons emitted from the silicon. The photocurrent with the gold negative must then be due to electrons emitted from the gold.

The photocurrent was found to be proportional to the light intensity when the wavelength and sample voltage were held constant. This relationship was verified for both sample polarities and for several different wavelengths. It was thereafter assumed to be generally true, and the photocurrents were normalized accordingly.

In Fig. 3, the square root of the photocurrent per incident photon is plotted against photon energy for each of the envelopes in Fig. 2. The lowest straight line portion of each of these curves is extrapolated to obtain an intercept on the abscissa.

According to Fowler's theory[6,7] of photoemission of electrons from a metal, the extrapolated intercept value of a plot of [photocurrent per absorbed photon]$^{1/2}$ versus photon energy should be to a good approximation the threshold energy for escape of an electron in the metal at the Fermi level; i.e., the work function. In the present work, for the case where the gold is negative, the intercept should be the energy difference between the conduction band of the silicon dioxide and the Fermi level of the gold, if one assumes that the ratio of absorbed photons to incident photons is constant over the spectral range through which the straight line is drawn. That is, the intercept gives the effective work function of the gold relative to the conduction band of the oxide with which it is in contact, if it is assumed that the optical constants of the system do not change significantly over the photon energy range used to establish the intercept. This assumption seems reasonable since in this range: (1) the optical constants of gold[8,9] are not a strong function of wavelength, (2) silicon dioxide is transparent and its index of refraction varies but slightly,[4] and (3) the optical constants of silicon[10] do not change by more than about 20% as the photon energy varies from 3.5 to 4.0 eV. The fact that the upper and lower envelopes lead to the same intercept value is also encouraging.

For the case where the gold is positive, the value of the energy threshold for photoemission of electrons from the silicon is somewhat less certain for two reasons. Firstly, the optical constants of silicon in the photon energy range (4 to 5 eV) used for the measurements change rapidly.[10] There is a peak of reflectance at about 4.5 eV and a peak of absorption coefficient at about 4.3 eV. Thus, the ratio of absorbed photons to incident photons in this range is a function of photon energy rather than a constant as has been assumed. It is difficult to determine accurately the effect on the apparent threshold; however, by considering points of equal reflectance and drawing straight lines through those points in Fig. 3, one is led to the conclusion that that the indicated threshold is probably low by not more than about 0.15 eV. The second reason is that Fowler's theory was developed for the Sommerfeld free-electron model of a metal and considered only intraband transitions. For a real semiconductor like silicon, the situation is quite complicated,[11–13] and the yield y (electrons per photon) may vary as the p power of energy above the threshold $(h\nu - h\nu_0)$, where p can theoretically[11] have the value 1, $\frac{3}{2}$, 2, or $\frac{5}{2}$ depending on the excitation and scattering mechanisms involved. More than one mechanism may be involved in the same energy range, complicating matters still further. In addition, measurements of photoemission from silicon into vacuum[12] have shown strong dependence upon doping and, in some cases, a range for which $p=3$. Empirically, however, the experimental results of the present work can be fitted well when p is between 2 and 3. As a practical expedient, it was decided to analyze all of the experimental data by assuming $p=2$, but it was observed that for a number of samples, when the same data was analyzed using $p=3$, an equally good fit was obtained which yielded an apparent threshold about 0.15 eV lower. Thus, to sum up, the absolute accuracy of the measurements of the threshold for photoemission of electrons from silicon into silicon dioxide is subject to an uncertainty of ±0.15 eV. Note, however, that this uncertainty will not apply to measurements of the threshold shift as a function of electric field (to be discussed in the next section) for a given sample since the error in the analysis procedure, if

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[6] R. H. Fowler, Phys. Rev. **38**, 45 (1931).

[7] A. L. Hughes and L. A. Du Bridge, *Photoelectric Phenomena* (McGraw-Hill Book Company, Inc., New York, 1932), p. 241.

[8] L. G. Schulz, J. Opt. Soc. Am. **44**, 357 (1954).

[9] *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1963), 2nd ed., p. 6–119.

[10] H. R. Philipp and E. A. Taft, Phys. Rev. **120**, 37 (1960).

[11] E. O. Kane, Phys. Rev. **127**, 131 (1962).

[12] G. W. Gobeli and F. G. Allen, Phys. Rev. **127**, 141 (1962).

[13] F. G. Allen and G. W. Gobeli, Phys. Rev. **127**, 150 (1962).

present, would be essentially the same for each threshold measurement.

Since the upper and lower envelopes were found to give essentially the same threshold values for several samples, all subsequent data analysis was performed on only the upper envelopes.

B. Schottky Effect

At an abrupt interface (contact) between a metal and an insulator, the photoelectric threshold (the effective work function of the metal with respect to the insulator conduction band) is a function of the voltage applied across the insulator because an electron in the insulator near the interface is acted upon by two forces, one due to the field in the insulator, and the other due to the image charge induced in the metal. The resultant lowering of the work function (Schottky Effect) according to simple electrostatic theory is (in mks units)

$$\Delta\phi = \tfrac{1}{2}(eE/\pi K\epsilon_0)^{1/2}, \tag{2}$$

where E is the electric field in the insulator (directed toward the emitting surface), e is the magnitude of the electronic charge, ϵ_0 is the permittivity of free space, and K is the effective image force relative "dielectric constant." The quotation marks are placed about dielectric constant because K may not actually be a constant as will be discussed later.

A similar description could be given for an abrupt interface between a semiconductor and an insulator, except that the appropriate photoelectric threshold value is not in general equal to the work function. Also, the simple metallic image charge description is valid for a highly conducting semiconductor, such as is used in the present work.

A measurement of the photoelectric threshold energy was made at 8 different electric-field values for each of three samples. The results were plotted against (electric field)$^{1/2}$, and a straight-line least-squares fit was used to obtain a zero-field value for the threshold energy for each sample. The decrease in the threshold energy from the zero-field value as a function of (electric field)$^{1/2}$ is shown in Fig. 4 for each sample. The theoretical Schottky effect is indicated by the three straight lines, each corresponding to a particular value of K. The value $K=1$ would be correct for emission into a vacuum and the value $K=3.8$ is the low frequency relative dielectric constant for silicon dioxide. The value $K=2.15$ corresponds to the average of the slopes for the straight-line fits for each sample.

Although there is a great deal of scatter in the data, one can reasonably conclude that: (a) Schottky lowering of the photoelectric threshold is being observed, and (b) the effective value of K is neither the vacuum or low frequency value, but probably somewhere in between. Thus far, it has been assumed that K is a constant, and that some effective value does indeed exist. Although this is a reasonable first approximation, and will be used throughout this paper, it is important to recognize that K may actually be a function of the applied electric field, and a simple physical argument which suggests this possibility is presented in the appendix.

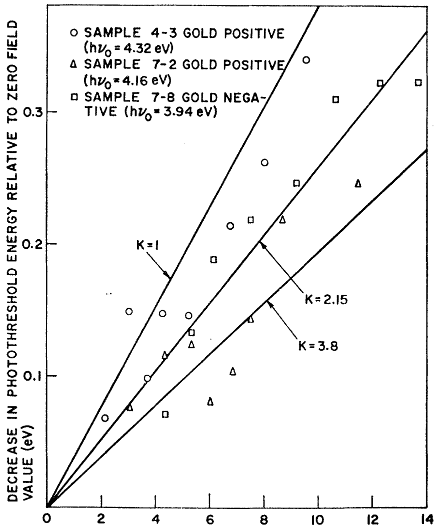

FIG. 4. Decrease in photoelectric threshold energy versus (electric field)$^{1/2}$ for three samples.

C. Measurement of the Electron Mean Range (Schubweg)

If for a given sample, the monochromator output is adjusted to a photon energy corresponding to a photocurrent peak (see Fig. 2), and the photocurrent is recorded as a function of increasing voltage across the sample, a curve is obtained which rises steeply at first, then bends toward the voltage axis but continues to rise at a decreasing rate. A typical set of data is shown in Fig. 5 (open circles). The current rises with increasing sample voltage for two reasons: (1) the increasing field lowers the energy threshold for photoemission (as discussed previously), and thus causes an increase in the electron current photoemitted into the oxide and (2) the mean range (or Schubweg) of electrons in the silicon dioxide increases directly with the electric field enhancing the photocurrent measured in the external circuit.[14] It is in principle possible to separate the two effects, if the theoretical form of at least one of them is known. In this work, the photocurrent values were "corrected" to eliminate the Schottky effect assuming that the yield is proportional to the square of the photon energy above the threshold value and an effective value for image force dielectric constant, $K=2.15$. This is shown in Fig. 5 as the filled circles. Also shown in Fig.

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

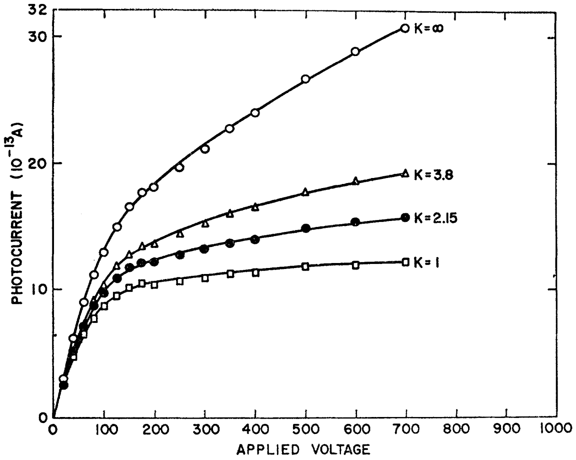

FIG. 5. Photocurrent versus applied voltage (Au positive) for Sample 7-2, Uncorrected: ○, Corrected: □ $K=1$, ● $K=2.15$, △ $K=3.8$, $h\nu_0=4.16$ eV, $h\nu=4.89$ eV.

5, for comparison are, "corrected" curves corresponding to $K=1$ (vacuum value) and $K=3.8$ (low-frequency value).

The electron mean range or Schubweg w is the average distance an electron *drifts* in the electric field before it is captured (i.e., immobilized due to trapping or recombination). Thus,

$$w=\mu E\tau=\mu V\tau/l, \tag{3}$$

where μ is the electron mobility, V is the applied voltage, l is the oxide thickness, and τ is the mean time an electron spends in the oxide conduction band before it is immobilized by deep trapping. If V_0 is defined as the value of V at which $w=l$, then, for the sample geometry employed in the present work, the theoretical form of the (corrected) photocurrent I versus applied voltage should be[14]

$$(I/I_0)=(V/V_0)(1-e^{-V_0/V}), \tag{4}$$

where

$$V_0=l^2/\mu\tau, \tag{5}$$

and I_0 is the photoemitted current in the absence of Schottky effect. If the experimental data for a sample of known thickness are fitted to the theoretical curve, the $\mu\tau$ product can be evaluated. This has been done for 6 samples; for the sake of clarity only three of these are shown in Fig. 6. The fit is quite good. When photocurrent data "corrected" using $K=1$ and $K=3.8$ were tried, no reasonable fit could be obtained.

IV. FURTHER DISCUSSION AND SUMMARY

In addition to the results reported in Sec. III, other threshold measurements were made and corrected for Schottky effect assuming $K=2.15$.

For the two wafers with 5.3-μ layers, the corrected threshold values for photoemission from the silicon, for four electrode areas, were in the range 4.19±0.04 eV. The corrected threshold values for photoemission from the gold, for four electrode areas, were in the range 3.81±0.14 eV.

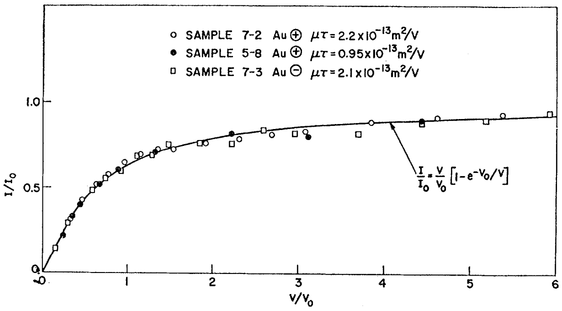

FIG. 6. Normalized photocurrent versus normalized voltage.

For the two wafers with 2.1-μ layers, the corrected threshold values for photoemission from the silicon, for three electrode areas, were in the range 4.31±0.04 eV. The signal-to-noise ratio of the measurements of photoemission from gold on these films was rather low; only one measurement was obtained, and the corresponding corrected threshold value was 4.06 eV.

The differences between the threshold energies found for the oxide layers of different thickness are probably not significant. The threshold values for the thicker layers are based on data in which the photocurrent undulations are closer together giving a more detailed picture of the spectral variation of the photocurrent envelopes. Thus, the threshold energies determined for the 5.3-μ layers are likely to be slightly more accurate.

The results of the measurements of the $\mu\tau$ product may be stated as follows: For three-electrode areas on two 5.3-μ oxide layers, the $\mu\tau$ values were in the range $(2.0\pm0.3)\times10^{-13}$ m^2/V. For three electrode areas on two 2.1-μ oxide layers, the $\mu\tau$ values were in the range $(0.7\pm0.3)\times10^{-13}$ m^2/V.

In summary, photoemission of electrons from both silicon and gold into silicon dioxide has been observed. Schottky lowering of the energy threshold for each of these processes has also been observed, and is consistent (within experimental error) with an effective K value of 2.15. The extrapolated zero-field threshold energies for photoemission from the silicon and gold are about 4.2 eV and 3.8 eV, respectively. The value of the product of the electron mobility in the silicon dioxide conduction band and the mean time before immobilization by deep trapping is of the order of 10^{-13} m^2/V.

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Teutsch for his critical reading of the first draft of this paper.

APPENDIX

It is possible to give a simple physical argument for expecting the effective K value to be non-constant as the applied electric field is varied over the region covered in the experiments in this paper.

The distance from the emitting surface of the potential energy maximum for emitted electrons varies with the electric field in the oxide adjacent to the emitting surface. This distance x_m is given by the equation:

$$x_m=(16\pi K\epsilon_0 E/e)^{-1/2}. \tag{A1}$$

If it is assumed initially that there is a constant value of K, then x_m can be computed. By assuming that the electron velocity in traversing the distance x_m is about thermal velocity, the transit time can be obtained. The value of K should be comparable to that for electromagnetic radiation of roughly the same period as the transit time.[15] For 10^7 V/m$<E<1.5\times10^8$ V/m the corresponding wavelength range is in the near infrared region and $n=K^{1/2}$ for silicon dioxide in this region is not constant, violating the initial assumption.

Furthermore, at high fields ($E\gtrsim1.5\times10^8$ V/m), the value of x_m is at most only a few times the nearest-neighbor distance in silicon dioxide casting some doubt upon the use of the dielectric-constant concept based on polarization of a homogeneous medium.

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[15] Similar reasoning has been employed by S. M. Sze, C. R. Crowell, and D. Kahng, J. Appl. Phys. **35**, 2534 (1964).

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Transport Properties of LaF_3

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We report measurements of the lattice and bulk thermal expansion, fluorine nuclear magnetic resonance, and electrical conductivity of single-crystal LaF_3 in the temperature range 300–1000°K. In the lower portion of this temperature range, the measurements yield activation energies for the formation of Schottky defects of ~0.07 eV and for fluorine ion diffusion of ~0.45 eV. The activation energy for diffusion appears to decrease at higher temperatures. We propose a model for the crystal with low activation energy for the formation of neutral defects, and a higher energy for defect dissociation and diffusion. The apparent changes of activation energy are ascribed to the excitation of lattice vibrations near the Debye temperature.

I. INTRODUCTION

The temperature dependences of the electrical conductivity, thermal expansion and fluorine nuclear magnetic resonance of LaF_3 crystals have been measured. These experiments have produced a wealth of data with several unusual features. The data exhibit many interesting details but the principal characteristics are:

(1) Thermal expansion measurements have been made both with a dilatometer and with x-rays from 300–1000°K. The bulk of the crystal expands faster than the unit cell, which is indicative of Schottky defect formation. The measured activation energy (see Fig. 4) for the creation of Schottky defects is $E_S=0.069$ eV. This is an exceedingly low activation energy. It is especially surprising in view of the 1760°K melting point of LaF_3 crystals. Furthermore E_S increases linearly with increasing temperature, which is contrary to the behavior of most other crystals.

(2) The activation energy for diffusion below 360°K, as measured both by magnetic resonance and by conductivity, is 0.46 eV. Since the fluorine magnetic resonance line narrows,[1] the fluorine ions must be moving. Moreover, since the activation energy for diffusion is about the same for the magnetic resonance line narrowing and the conductivity, the fluorine ions apparently make the principal contribution to the ionic conduction.

(3) Above ~350°K the rate of increase of the conductivity with temperature (see Fig. 6) becomes smaller than the 0.46 eV measured below 350°K. The high-temperature data can be fitted by an activation energy of 0.082 eV, or by a T^{-9} temperature dependence entering into the conductivity. The bend over occurs at the effective Debye temperature of LaF_3.[2]

The model assumes that a large fraction of the Schottky defects are bound as neutral "molecular" holes. Mott and Gurney[3] point out that if the activation

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[1] K. Lee and A. Sher, Phys. Rev. Letters **14**, 1027 (1965).

[2] W. M. Yen, W. C. Scott and A. L. Schawlow, Phys. Rev. **136**, 271 (1964).

[3] The possibility of this phenomenon is mentioned in N. F. Mott and P. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), p. 41. The measured dielectric constant of LaF_3 is $\epsilon=14$. The Coulomb energy of a LaF_2^+ and an F^- separated by 2.3 Å, a La^{3+}-F^- distance, is 0.45 eV.