

Photoemission of Electrons from Silicon into Silicon Dioxide

RICHARD WILLIAMS

RCA Laboratories, Princeton, New Jersey

(Received 25 May 1965)

Electron transport in thermally grown layers of SiO_2 has been studied. Electrons are introduced into the oxide by photoemission from the adjoining silicon crystal. Specimens consist of a silicon crystal covered with an SiO_2 layer about 2 microns thick and, over this, a semitransparent gold electrode. On illuminating, light passes through the gold electrode and the oxide and is absorbed by the silicon. With appropriate voltage applied between gold and silicon, there is a steady photocurrent for light of wavelengths shorter than 2900 Å. Various possible origins of the photocurrent were investigated, and it is concluded that the current is due to photoemission of electrons from the silicon into the SiO_2 conduction band. By analysis of the spectral response of the photocurrent a photoemission threshold of 4.25 eV is obtained, independent of whether the silicon is n -type or p -type. This is roughly 0.9 eV smaller than the threshold for photoemission from silicon into vacuum. Using the vacuum photoemission threshold and the known optical absorption edge for SiO_2 , a diagram of the energy relations at the Si- SiO_2 interface is constructed. It is found that deep electron traps are present in concentrations around $3 \times 10^{14}/\text{cm}^3$. Trapped electrons are stable against thermal ionization for hours at room temperature in the dark but may be ionized by visible light. From the spectral response for ionization of traps it is found that the trap levels lie 2 eV below the conduction-band edge. Measurements of the kinetics of trapping give a capture cross section of $1.3 \times 10^{-12} \text{ cm}^2$, indicating that the trap is a Coulomb attractive center with a positive charge. Comparison of the magnitude of the capture cross section with a current model for capture by a Coulomb attractive center gives an estimate for the microscopic mobility μ of electron in the SiO_2 conduction band. The estimated value of μ is either 34 or 17 cm^2/Vsec depending on whether the trapping center is singly or doubly charged.

INTRODUCTION

THE most important feature determining the electrical transport properties of an interface between two solid materials is the relative location, on the energy scale, of the energy bands for the two different materials. For metal-semiconductor systems this means the energy difference between the Fermi level in the metal and the edge of the conduction band or valence band in the semiconductor. This difference can be measured by studying photoemission of electrons or holes from the metal into the semiconductor.^{1,2} Data giving the quantum yield for photoemission as a function of the energy of the exciting light may be analyzed to give a threshold for photoemission which is the desired quantity. The analysis is the same as that used to obtain a photoelectric work function from experiments on photoemission of electrons into vacuum. Several metal-semiconductor systems have been studied in this way. Results have been given for the energy difference and, in some cases, for the rate of energy loss by excited electrons or holes.³⁻⁵

It is of considerable interest to have similar information for systems in which one member is a high-band-gap insulator. The photoemission experiments with semiconductors have been greatly facilitated by the fact that a Schottky barrier forms at the interface. This makes the effective thickness of the semiconductor

specimen about one micron since the effective thickness is that of the Schottky barrier. In a thin specimen, effects of electron trapping are minimized. In addition there is a high electric field in the semiconductor at the interface. This gives a high collection efficiency for photoemitted electrons. To obtain similar conditions in an insulator requires specimens having a total thickness of no more than a few microns, which is difficult to achieve with most crystalline insulators. However, thermally-grown deposits of SiO_2 on single-crystal silicon are readily obtained in micron thicknesses.⁶ Such deposits have excellent insulating properties and sustain applied electric fields above 10^6 V/cm without destruction.^{6,7} They are amorphous rather than crystalline.^{6,8} In this work we have observed photoemission of electrons from silicon into SiO_2 using thermally-grown deposits of SiO_2 on single crystal silicon. This has given the energy difference between the valence band of silicon and the conduction band of SiO_2 . Information about electron transport in the oxide has also been obtained, along with details about trapping processes.

EXPERIMENTAL DETAILS

The oxide films were thermally grown on the 110 faces of single-crystal silicon wafers. The growth was at 1050°C in an air atmosphere containing steam.⁹ Wafers from four different silicon crystals were used. Two were

¹ R. Williams and R. H. Bube, *J. Appl. Phys.* **31**, 968 (1960).

² R. Williams, *Phys. Rev. Letters* **8**, 402 (1962).

³ W. G. Spitzer, C. R. Crowell, and M. M. Atalla, *Phys. Rev. Letters* **8**, 57 (1962); C. R. Crowell, W. G. Spitzer, L. E. Howarth, and E. E. LaBate, *Phys. Rev.* **127**, 2006 (1962).

⁴ A. Goodman, *Surface Sci.* **1**, 54 (1964).

⁵ W. G. Spitzer and C. A. Mead, *J. Appl. Phys.* **34**, 306 (1963).

⁶ M. M. Atalla, E. Tannenbaum, and E. J. Scheibner, *Bell System Tech. J.* **38**, 749 (1959).

⁷ S. R. Hofstein and F. P. Heiman, *Proc. IEEE* **51**, 1190 (1963).

⁸ J. J. Lander and J. Morrison, *Ann. N. Y. Acad. Sci.* **101**, 605 (1963).

⁹ The author is indebted to Dr. J. A. Amick for growing the oxides.

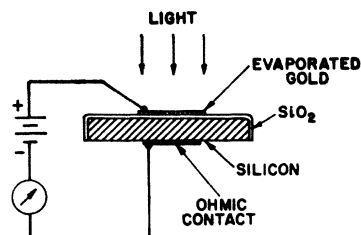


FIG. 1. Electrode geometry of the specimens used.

n-type with resistivities of 10 and 15 Ω -cm and two were *p*-type with resistivities of 18 and 20 Ω -cm. The oxide layers all had thicknesses in the range 1.4 to 1.9 μ . For each specimen several transparent gold electrodes were evaporated on top of the oxide. The area of each electrode was 0.225 cm². Gold was simultaneously evaporated on a quartz plate and the optical transmission measured over the appropriate wavelength region to correct measured photocurrents for light attenuation in the gold. An Ohmic contact to the back face of the silicon wafer was made at a point from which the oxide had been removed and a second connection was made to the evaporated gold electrode. The result was a thin specimen of SiO₂ with electrodes on opposite faces, one of gold and one of silicon. The electrode geometry and circuit connections are illustrated in Fig. 1. Light enters through the gold, passes through the oxide and is absorbed by the silicon. For light of sufficient energy, the excited electrons so produced may pass into the conduction band of the SiO₂. If a suitable bias voltage is applied across the oxide, they move through the layer and are measured as a current.

Two uv light sources were used. One was a medium high-pressure mercury arc (GE-H100 A-38 4T) giving lines on a strong underlying continuum. This lamp has a glass outer jacket which was removed. The other uv lamp was a low-pressure germicidal lamp giving only the 2537- \AA resonance line of mercury. During measurements specimens were mounted in a tight metal box fitted with a quartz window and containing a drying agent. For measurements with monochromatic light a Bausch and Lomb prism monochromator was used. uv-intensity calibrations were made, using both a sodium salicylate phosphor-photomultiplier method¹⁰ and direct measurements with a thermopile. Visible-intensity calibrations were made with a thermopile.

GENERAL RESULTS

The sample was biased to make the silicon negative and the gold electrode positive for all experiments except those where the effect of polarity was being studied. When light of any wavelength absorbed by silicon strikes the specimen there is a transient flow of current due to separation of hole-electron pairs in the silicon. This terminates as soon as enough charge is

¹⁰ K. Watanabe and E. C. Y. Inn, J. Opt. Soc. Am. 43, 32 (1953).

separated to counteract the field separating holes and electrons. This effect is a normal *p-n* junction photo-voltaic effect with the insulating oxide in series with the cell. It is easily distinguished from any of the photocurrents which will be discussed below.

When the specimen was illuminated with the full light of the mercury arc a steady photocurrent was observed. Preliminary experiments with filters showed that the photocurrent was excited only by light with wavelengths shorter than 2900 \AA . Such a current could be produced by any of several mechanisms, in addition to that of photoemission of electrons from the silicon into the SiO₂. Chief among these are normal photoconductivity processes in the SiO₂ due to light weakly absorbed within the oxide itself, photoemission of holes from the gold electrode into the valence band of the oxide, and photoemission of electrons into air from any surface exposed to the light source and their subsequent collection at the anode. The last mechanism was ruled out by careful masking experiments showing that the photocurrent was produced only by light striking the gold electrode. (About one part in 10³ of the photocurrent appears to be due to this process, since it is difficult to avoid all scattered light. It is probably responsible for the upward curvature at the lowest voltages seen in the curves of Fig. 2.) Normal photoconductivity processes due to light absorbed in the oxide should give a current independent of the polarity of the applied voltage. There is every reason to believe that both the gold and silicon electrodes are blocking in the dark for the flow of both holes and electrons into the oxide. Free carriers produced in the oxide should move equally well for both polarities of applied voltage, and no carriers would enter from the electrodes. This would give a current independent of polarity. This is not what is observed. When the silicon electrode is negative and the gold positive, the photocurrent is from 30 to 1000 times larger than it is for the same illumination with reversed polarity. This argument assumes that light absorbed in the oxide would be weakly absorbed. This is certainly the case for the wavelengths used if the optical properties of the SiO₂ layers are similar to those of fused silica in the bulk. The photocurrent cannot be

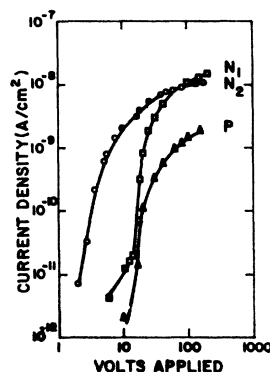


FIG. 2. Uv photocurrent as a function of applied voltage. The upper two curves are for oxides grown on two different *n*-type silicon wafers. The lower curve is for an oxide grown on *p*-type silicon.

due to photoemission of holes from the metal since it is unaltered when the gold electrode is replaced by an electrode of a different material. This will be discussed later. In addition it was found that at high applied voltage the photocurrent does not polarize and decrease with time even after periods of several hours. The only interpretation of the photocurrent consistent with all the data is that it is due to photoemission of electrons from the silicon into the conduction band of the oxide. They then move through the oxide by normal conductivity and out into the gold electrode. The silicon contact is highly blocking for electron flow in the dark. The dark current at the highest voltages used is of order 10^{-12} A/cm². This is much smaller than the photocurrents being measured.

Figure 2 shows the photocurrent as a function of applied voltage. The full unfiltered light of the mercury arc was used for this experiment. Data are shown for two different *n*-type crystals and one *p*-type crystal. The absolute values of the currents are not exactly comparable since the optical densities of the gold electrodes on different crystals were not identical, and we have corrected for this only in spectral response and quantum yield measurements. The curves are all similar in shape; there is no detectable photocurrent at the lowest voltages. This is followed by a steeply rising curve terminating at high voltages in a sublinear region which is almost a saturated current. The current is proportional to light intensity at all voltages. The curves are interpreted in the following way. At the lowest voltages electrons photoemitted into the oxide are trapped in deep traps and distortion of the applied potential due to the resulting space charge pinches off the current. At the beginning of the steeply rising part, most traps are filled, and the space charge no longer cancels the applied field. The behavior is then that of the traps-filled limit found in problems of space-charge-limited current.¹¹⁻¹³ In this case it is only photoexcited carriers which form the cathode reservoir from which carriers are injected into the crystal. Data giving the current as a function of time at various voltages support the idea that traps and space-charge polarization are important at low voltages. These are shown in Fig. 3 where the decay of current with time is plotted for various applied voltages. The same illumination was

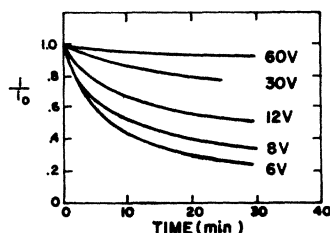


FIG. 3. Decay of photocurrent with time for several different applied voltages. I_0 is the current at zero time. Crystal N_2 , Fig. 2.

¹¹ R. W. Smith and A. Rose, Phys. Rev. **97**, 1531 (1955).

¹² A. Rose, Phys. Rev. **97**, 1538 (1955).

¹³ M. Lampert, Phys. Rev. **103**, 1648 (1956).

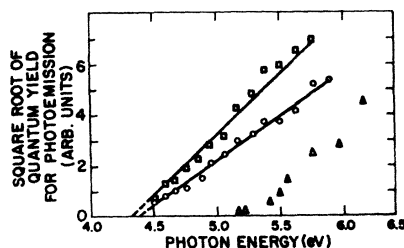


FIG. 4. Plot of the square root of the quantum yield versus photon energy. Squares and circles represent data obtained in this work for *p*- and *n*-type silicon specimens, respectively. The triangles are data taken from Ref. 15 for photoemission from silicon into vacuum, and are shown to permit comparison of the thresholds for photoemission into vacuum and photoemission into SiO₂.

used throughout. For the lower voltages the current decays to a small fraction of its initial value after 10 minutes. At 60 V it changes much less, and for voltages above 100 no change of the current with time is seen. At the higher voltages all traps are filled. With increasing voltage more and more electrons are pulled into the crystal and the limited supply of photoexcited electrons at the cathode begins to be exhausted. This leads to the approximate saturation of currents with voltage. At the highest voltage the operation is approaching that of a vacuum photocell in which all electrons photoemitted at the cathode are collected at the anode.

As mentioned above, the current is proportional to light intensity at all voltages. This seems at first to be inconsistent with the interpretation that there is a space-charge-limited current over part of the range. For a space-charge-limited current with Ohmic contacts there are always more than enough carriers supplied by the contacts. The value of the current is determined by the effect of the space charge on the potential in the bulk of the crystal. In the present case the cathode reservoir of electrons consists of photoexcited electrons whose density is proportional to the light intensity. Thus in the high-voltage saturation region, it is expected that the current should be proportional to light intensity. In the low-voltage region, however, where the current is limited by space charge, there should always be more than enough electrons in the cathode reservoir. The current is expected to be independent of light intensity as it normally is for a space-charge-limited current with Ohmic contacts.¹² An explanation of how a space-charge-limited current can depend on illumination has recently been proposed.^{14,15} If most of the electrons making up the space charge are trapped, light may free part of them so that they contribute to the current flow. The total space charge in the crystal is unchanged. The light changes only the ratio of free to trapped

¹⁴ J. Adolph, E. Baldinger, and I. Gränacher, Phys. Letters **8**, 224 (1964).

¹⁵ W. Helfrich, Phys. Status Solidi; **7**, 863 (1964); P. Jansen, W. Helfrich, and N. Riehl, Phys. Status Solidi **7**, 851 (1964).

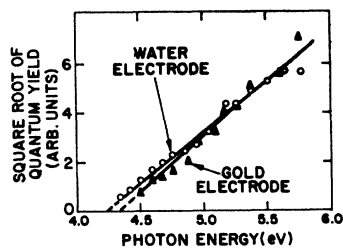


FIG. 5. Comparison of the thresholds obtained on the same oxide specimen with water and gold electrodes.

carriers and in this way enhances the current. The effect^{14,15} was demonstrated in anthracene. It appears that the same thing is happening here. The mercury arc used gives intense visible light, as well as ultraviolet. The visible light alone cannot produce a photocurrent through the SiO_2 , but it can enhance the photocurrent excited by the uv light. This explanation implies that the photocurrent involves both free and trapped carriers and that the trapped carriers may be freed by visible light. This is demonstrated below, and the nature of the trap is investigated.

SPECTRAL RESPONSE OF THE PHOTOCURRENT

The spectral response of the photocurrent was obtained using the mercury arc and a monochromator. Current per incident photon was measured over the range 2100 to 2850 Å. The square root of this current was then plotted against photon energy, as it is usually done with photoemission data. We have compared our data with those reported by Gobeli and Allen¹⁶ for photoemission from silicon into vacuum. This is shown in Fig. 4. From the present work data are given for one n -type crystal and one p -type crystal. These are compared with the vacuum photoemission results for a crystal having nearly the same resistivity. The threshold for photoemission from silicon into SiO_2 is roughly 0.9 V lower than that for photoemission into vacuum. There is no good theoretical justification for plotting the present data in this particular form since nothing is known of the band structure of the SiO_2 conduction band. As an empirical method for obtaining an approximate threshold in an objective manner, it appears to be satisfactory.

A measurement was made of the absolute quantum yield ϕ for the photocurrent at 2300 Å (5.38 eV). The mean of two results, one for an n -type and one for a p -type specimen, was $\phi = (5 \pm 3) \times 10^{-5}$ electrons/quantum. ϕ is defined here as the number of electrons flowing through the oxide for each photon incident on the silicon. This may be compared with the quantum yield¹⁶ for photoemission from silicon into vacuum. For differently doped silicon crystals the values at 5.38 eV ranged from about 4×10^{-6} to 8×10^{-5} electrons per incident photon. Thus, the quantum yields found here

¹⁶ G. W. Gobeli and F. G. Allen, Phys. Rev. **127**, 141 (1962).

are comparable to those measured for vacuum photoemission at the same photon energy. It might be more appropriate to compare quantum yields, not at the same energy, but at energies lying an equal energy increment above the threshold. In this case the quantum yield for photoemission into SiO_2 is one order of magnitude smaller than that for photoemission into vacuum.

The possibility was mentioned earlier that the photocurrent might be due to photoemission of holes from the gold electrode into the valence band of the SiO_2 . This would, of course, require the same polarity of applied voltage as photoemission of electrons from the silicon into the conduction band. If the process were photoemission of holes, it should be very sensitive to changes in the outer electrode since it is there that the effective light would be absorbed. This possibility was examined by using two different outer electrode materials on the same area of SiO_2 . A spectral response measurement was made with a gold electrode, giving results similar to those shown in Fig. 4. Then the gold electrode was removed and replaced by an electrode of deionized water on the same area of oxide. The spectral response of the photocurrent was again measured for the same applied voltage. The result is shown in Fig. 5 where the spectral response curves for both materials are plotted together. Currents are in arbitrary units normalized to coincide at 4.95 eV. The threshold energies for the two different electrode materials differ by no more than 0.1 eV which is within the scatter of results obtained for different gold electrodes. More significant, the quantum yield of photocurrent for the water electrode was 5×10^{-5} electrons/quantum at 2300 Å. This is the same order of magnitude obtained for gold electrodes. Since the optical properties and the energy-band structures of gold and water are vastly different, the agreement in threshold energy and quantum yield for the two different electrode materials can only mean that the photocurrent does not originate in these electrodes but in the silicon electrode as we have assumed.

From the energy threshold measurements on seven different electrode areas (four different crystals in all)

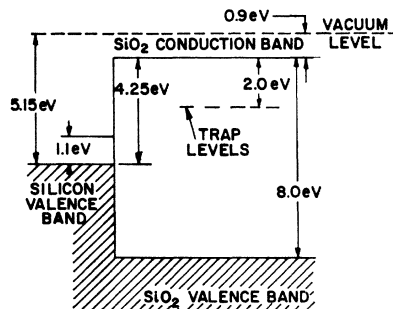


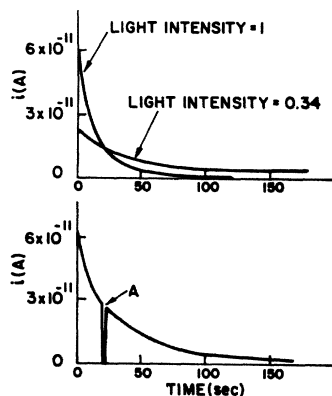
FIG. 6. Energy-band diagram for the interface between silicon and SiO_2 . Some bending of bands in the silicon usually occurs at the interface owing to charge in surface states. This varies widely from one specimen to another and is not indicated here.

we obtain for the threshold and the mean deviation of results: 4.25 ± 0.06 eV. This is the energy necessary to take an electron from the top of the valence band in silicon to the bottom of the conduction band in SiO_2 . To take an electron from the top of the valence band in silicon into vacuum requires an energy of 5.15 eV.¹⁶ Using the additional piece of information¹⁷ that the optical absorption edge for SiO_2 is around 8.0 eV an approximate diagram has been constructed to show the energy-level relations at the Si- SiO_2 interface. This is shown in Fig. 6. The conduction band in SiO_2 thus lies about 0.9 eV below the vacuum level. This is similar to the situation in alkali halides,¹⁸ so the gross features of the energy-level scheme in SiO_2 are similar to those of alkali halides. The trap level 2eV below the conduction band is an electron trap, normally empty, which can be filled by photoelectrons coming into the oxide from the silicon. Evidence for this is given in the next section.

ELECTRON TRAPPING

The form of the i - V characteristic and the polarization of photocurrent at low applied voltages were given as evidence that electrons are trapped in the oxide. To investigate this further the photocurrent was excited by monochromatic uv light with wavelength 2537 Å. The effects of shining visible light from a tungsten lamp on the specimen simultaneously were then observed. It was found that the photocurrent excited by the uv lamp was enhanced by visible light. When the visible light was turned on the current rose to a certain value well above that produced by the uv light alone. Then the current decreased with time to a value slightly above the original value due to the uv light. Apparently electrons accumulated in traps when only the uv light was present and were then freed by the visible light giving a transient additional current which then settled down to a steady-state value. This was

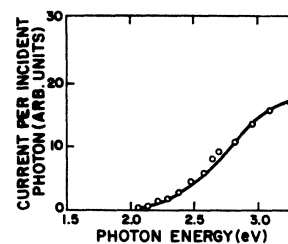
FIG. 7. Current due to the emptying of filled traps by visible light. The upper traces show the current for two different intensities of visible light. The lower trace shows the effect of interrupting the trace at point A by shutting off the light for 1 h, leaving the applied voltage on. After 1 h the light is again turned on and the measurement resumed.



¹⁷ W. Groth and H. v. Weyssenhof, *Z. Naturforsch.* **11a**, 165 (1956).

¹⁸ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1957), 2nd ed., pp. 69-74.

FIG. 8. Spectral response of the current due to emptying of traps by visible light. Each point represents the initial current produced by light of the given energy after all traps have previously been filled by uv light. *N*-type specimen.



confirmed by illuminating with only uv light for a period of time sufficient to accumulate trapped electrons and then illuminating with only visible light. The total current in this case was due only to trapped electrons freed by visible light. (It should be emphasized that, in the absence of previous uv illumination, visible light produces no photocurrent.) The transient photocurrents measured in this way are shown in Fig. 7. In the top curves the transient current is compared for two different intensities of visible light. In each case there was the same exposure to uv light. The initial value of the polarizing current is proportional to light intensity, and the areas under the two curves are equal, showing that the same total charge is carried in each case. This indicates that a fixed number of trapped electrons are freed by light into the conduction band of the oxide and removed by conduction in the applied field. The lower trace in Fig. 7 shows that the trapped electrons are at an energy well below that of the conduction band. This trace was made in the same way as the upper traces in Fig. 7 except that after the start of the trace, at the time indicated by A, the visible light was turned off and the sample was held in darkness for 1 h with the applied voltage left on. After this period, the visible light was turned on again and the trace continued. It is seen that the current-time trace follows exactly as if there had been no interruption. Thus, no observable fraction of the traps was emptied by thermal ionization at room temperature during this period. This indicates that the trap depth is well over 1 eV.

From the spectral response of the current which flows as the traps are emptied, it is possible to get an estimate of the optical depth of the trap. This was done by measuring the initial current values of transients, such as those in Fig. 7, excited by various wavelengths of visible light from a tungsten lamp and monochromator. Preliminary experiments with only a lamp and filters showed that no current was excited by wavelengths longer than 6000 Å. In Fig. 8 the current per incident photon is shown as a function of photon energy. For each point a previous standard exposure to uv was given, sufficient to fill all the traps. This may be interpreted either as absorption due to traps at a single level around 2.0 eV or as absorption due to traps distributed in energy, all lying below 2 eV. In the absence of information about the structure of the conduction band, no further interference can be made from the shape of the curve.

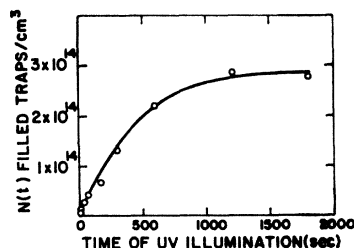


FIG. 9. Total number of traps filled by exposure to uv light as a function of the length of the exposure. N -type specimen.

Further information about the trap concentration and the kinetics of trapping was obtained by measuring the total numbers of traps filled by uv exposures of various lengths. The transient current in Fig. 7 falls to zero, indicating that all traps are emptied. The integral under the curve gives the total number of traps which were filled at the beginning of the measurement. Thus, all traps can be emptied and the number, $N(t)$, filled by a uv exposure of length t can be measured. In Fig. 9, $N(t)$ is shown as a function of t . The points are experimental values. The solid line is a theoretical-curve fit to the data and based on a model for the kinetics of trapping which will be developed below. After about 1000 sec of uv illumination the traps are filled completely and further illumination does not fill any more traps. The total trap concentration N_0 is $2.9 \times 10^{14}/\text{cm}^3$. This may be compared with an independent estimate of N_0 for the same specimen obtained from the i - V curve (Fig. 2). We assume the steeply rising portion of the curve to be following the voltage at which all traps are filled and obtain an approximate value for the traps-filled limit voltage. The value of N_0 obtained in this way is $6 \times 10^{14}/\text{cm}^3$. This may be considered satisfactory agreement between the trap concentrations measured by the two different methods, and it is assumed that the same traps are measured by these two different experiments. It may be noted that there is often a discrepancy of many orders of magnitude when two different methods are used to measure trap concentrations in the same crystal.^{19,20}

By analysis of the trapping kinetics, one obtains from the data an estimate of the capture cross section S of the trap involved. We consider the case where the electron moves in a straight line in the direction of the applied field. This applies where the electron drift velocity is equal to or greater than the thermal velocity. We show in the Appendix that for the special case of large capture cross section this result also holds for drift velocities smaller than the thermal velocity. We consider a unit area of oxide with a thickness y . When the current density is j , the number of electrons passing through the oxide per unit time is j/e . The rate of capture by traps is given by the product of j/e , the concentration of traps still empty, their capture cross

section, and the thickness of the oxide. Thus

$$y dN(t)/dt = (j/e)[N_0 - N(t)]yS.$$

The solution is

$$N(t) = N_0(1 - e^{-\alpha t}), \quad (1)$$

where $\alpha = jS/e$; N_0 , $N(t)$ are numbers of traps/cm³ filled at times 0 and t , respectively.

The function in Eq. (1) was plotted to give the solid line in Fig. 9, choosing N_0 and α to give the closest fit to the experimental points. From α it is possible to obtain S , since j is a measured quantity. For the data shown, the value of S is $1.3 \times 10^{-12} \text{ cm}^2$. A capture cross section of this magnitude is generally²¹ interpreted as being due to a positively charged coulomb attractive center. The simplest estimate for the expected cross section²¹ at room temperature gives the value $1.7 \times 10^{-12} \text{ cm}^2$ for a material with the appropriate dielectric constant. We conclude therefore that the trap is probably a positively charged center with a Coulomb capture cross section.

An idea of the extent of the trapping is given by the following. With 100 V applied, when all traps are empty and the trapping is strongest, one electron in every 12 passing through the layer is captured by a trap. Thus, the *Schubweg* is several times the layer thickness. The energy level of the trap is shown on the energy-band diagram of Fig. 6. This is meant only to indicate the general energy range where the traps lie and is not intended to exclude the possibility that the trap levels are spread over a range of energies below that shown.

DISCUSSION

The experiments demonstrate that electrons may be photoexcited from the valence band of silicon into the conduction band of SiO₂. Effects of deep trapping do not seriously impede the flow of electrons through layers of micron thickness, except at the lowest voltages. The low concentration of traps is surprising since the layers are amorphous. A higher concentration of traps is often found in single crystals, even in materials where considerable effort has gone into producing crystals of high perfection. We have no information concerning the impurity or defect responsible for the trapping except that it appears to be a positively charged center. Certain color centers in fused quartz are produced by neutron irradiation.²² One of these shows an optical absorption lying in the same region of the spectrum as that of the trap studied here. No other information is available to extend this comparison any further.

Since no other information is available on electron transport in SiO₂, it is worth considering a rough estimate of the electron mobility which can be made from

¹⁹ R. H. Bube, J. Appl. Phys. **33**, 1733 (1962).

²⁰ J. Dresner and F. V. Shallcross, Solid State Electron. **5**, 205 (1962).

²¹ A. Rose, *Concepts in Photoconductivity and Allied Problems* (Interscience Publishers, Inc., New York, 1963), p. 121.

²² J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The Macmillan Company, New York, 1962), p. 291.

the present data. In a previous paragraph we cited a theoretical value for the capture cross section of a Coulomb attractive center. It is possible to derive the capture cross section in an alternative way which gives an expression containing the electron mobility.²³ According to this expression, the capture cross section is given by

$$S = 4\pi Ze\mu / Kv_{th}, \quad (2)$$

with μ the microscopic mobility, Ze the charge on the center, K the dielectric constant, and V_{th} the thermal velocity of the electron. To use this formula we assume that the electron mass is that of a free electron and solve for μ using the measured value of S . The value of Z is not known since we might be dealing with a singly charged center or a doubly ionized center. (Higher values of Z are rare.) With $Z=1$ we obtain for μ the value $34 \text{ cm}^2/\text{V sec}$ and with $Z=2$ we obtain for μ the value $17 \text{ cm}^2/\text{V sec}$. There is no alternative measurement with which to compare these estimates for the present work. In the case of the α center in KBr there is good agreement between mobilities calculated from Eq. (2) and measured mobilities.²³ There appears to be good reason, then, to believe that the electron mobility in SiO_2 has a value well above unity at room temperature.

Returning to Fig. 6, the high energy barrier against electron motion from silicon to SiO_2 is sufficient to account for the excellent blocking contact which is observed and the high fields which can be applied without breakdown. This is probably the most complete example available of experimental determination of the energy-band relations at an insulator-semiconductor interface.

ACKNOWLEDGMENTS

The author is indebted to R. Crandall, A. Goodman, M. Lampert, W. Merz, and A. Rose for valuable dis-

cussions during the course of this work and to R. Evans for help with the experiments.

APPENDIX

Equation (1) was derived on the assumption that the drift velocity of the electron is equal to or greater than the thermal velocity. For the applied fields used, this condition would be satisfied for any mobility greater than $20 \text{ cm}^2/\text{V sec}$, assuming an effective mass equal to the free electron mass. For smaller mobilities this no longer holds. For the smaller mobilities the mean free path for mobility scattering cannot be more than about 10 \AA . This is small compared to the radius of the scattering center encountered in these experiments, which is of the order 100 \AA . In moving through the oxide the electron thus sweeps out a volume consisting of the length of its path and a cylindrical cross section of 100 \AA diam. Any trap lying within this volume will capture the electron. On traveling through the layer of thickness y the electron will experience a total side-wise displacement Δ whose average value is related to the diffusion coefficient D and the transit time τ . For an applied voltage V , we have

$$\begin{aligned} \Delta^2 &= D\tau = \mu(kT/e)(y^2/\mu V), \\ \Delta^2/y^2 &= kT/eV. \end{aligned}$$

For an applied voltage of 100 V $\Delta/y = 1.6 \times 10^{-2}$. Thus, the over-all path is very nearly straight through the layer along the direction of the applied field. Since the mean free path for scattering is much smaller than the radius of the scattering center, the effective volume swept out by the electron as it moves through the oxide is a cylinder lying almost along the field direction with a slightly wrinkled surface due to the slight wandering of the electron. This means that the method used to obtain Eq. (1) is also a good approximation for any value of electron mobility below that required for the validity of the assumption used there.

²³ R. S. Crandall, Phys. Rev. **138**, 1242 (1965).