grain size, and the magnetic properties of these films will be investigated as well as the electrical properties.

ACKNOWLEDGMENTS

It is a pleasure at this time to acknowledge the assistance of D. D. Bacon in the preparation and of W. H. Haemmerle in the measurement of the thin films for this investigation. We are very grateful to H. Schreiber and J. E. Kessler for the x-ray fluorescence analysis of the V_3Ge films; to S. Trummer for the electron diffraction work; and to S. E. Koonce for the replicas. We would also like to acknowledge some helpful and illuminating discussions with R. D. Heidenreich and N. R. Werthamer.

PHYSICAL REVIEW VOLUME 134, NUMBER 1A 6 APRIL 1964

Quantum Efficiency of Silicon in the Vacuum Ultraviolet*

A. J. TUZZOLINO
Laboratories for Applied Sciences, University of Chicago, Chicago, Illinois
(Received 30 October 1963)

A measurement of the quantum efficiency of silicon has been carried out over the photon energy range from 4.9 to 21.2 eV by measuring the photoresponse of silicon surface-barrier photodiodes. The quantum efficiency increases from 2.0 at $h\nu=4.9$ eV to approximately 3 at $h\nu=6$ eV; between $h\nu=6$ eV and $h\nu\approx 10$ eV, the quantum efficiency is approximately constant and beginning at $h\nu\approx 10$ eV, increases strongly with increasing photon energy, attaining a value of 15 at 21.2 eV. This observed behavior is consistent with qualitative predictions based upon a model for secondary ionization effects in silicon proposed by Shockley and a simplifying assumption as to how the excess energy available following an ionization event is distributed between the original carrier and generated electron-hole pair.

1. INTRODUCTION

When a high-energy photon is absorbed in the bulk of a semiconductor, the photoelectron and photohole produced by the inner photoelectric effect may be of sufficiently high energy to interact, in turn, with valence-band electrons leading to the generation of new electron-hole pairs. This intrinsic impact ionization was first observed in the breakdown of silicon[1,2] and germanium[1,3] *p-n* junctions. The quantum efficiency, $\eta(\lambda)$, of the inner photoelectric effect, defined as the number of electron-hole pairs produced as a result of the absorption of one photon of wavelength λ, has been studied in several semiconductors, including germanium,[4,5] silicon,[6,7] indium antimonide,[4] and lead sulfide.[8]

In the case of silicon, the quantum efficiency has been studied for two photon energy ranges: the very-high-energy range in which many generations are involved, and the low-energy range in which the photocarriers just begin to generate additional pairs. A measurement of the quantum efficiency of silicon in the low-energy range (1–5 eV) has been reported by Vavilov,[6] who found that η has a value of unity from 1.5 to 3.4 eV, and beginning at 3.4 eV, η increases rapidly with increasing photon energy to a value of 2.1 at 4.9 eV. Vavilov attributed this increase in η above unity to impact ionization by photoelectrons and photoholes and interpreted the difference between the energy at which η begins to increase (3.4 eV) and the bandgap energy (1.1 eV) as the threshold energy E' for impact ionization in silicon. Assuming that the electron takes all of the excess energy of the photon, Vavilov's photon threshold of 3.4 eV gives $E'=3.4-1.1=2.3$ eV. Shockley[9] has presented a reinterpretation of the energy, 2.3 eV, in which he suggests that when a photoelectron and photohole are created, the residual kinetic energy is shared equally between the two, rather than being given entirely to the electron. As a result, at Vavilov's photon threshold of 3.4 eV, each carrier ends up with an energy of about 1.15 eV, which is taken to be the true threshold energy for pair production.

A determination of η in silicon for the very-high-energy range (γ-ray energies) has been reported,[7] where η was found to be proportional to the energy of the absorbed photon. A mean energy of 3.5 eV was found to be required to produce one electron-hole pair, which is equal to the mean energy required to produce one ion pair by a high-energy charged particle[7] (electron, proton, alpha particle).

---

* The research reported in this paper was supported by the National Aeronautics and Space Administration under NASA Grant NSG-179-61.

[1] K. G. McKay and K. B. McAfee, Phys. Rev. **91**, 1079 (1953).
[2] K. G. McKay, Phys. Rev. **94**, 877 (1954).
[3] S. L. Miller, Phys. Rev. **99**, 1234 (1955).
[4] J. Tauc, Phys. Chem. Solids **8**, 219 (1959).
[5] J. Drahokoupil, M. Malkovska, and J. Tauc, Czech. J. Phys. **7**, 57 (1957).
[6] V. S. Vavilov, Phys. Chem. Solids, **8**, 223 (1959).
[7] L. Koch, J. Messier, and J. Valin, IRE Trans. Nucl. Sci. **8**, 43 (1961).
[8] A. Smith and D. Dutton, Phys. Chem. Solids **22**, 351 (1961).
[9] W. Shockley, Czech. J. Phys. **11**, 81 (1961).

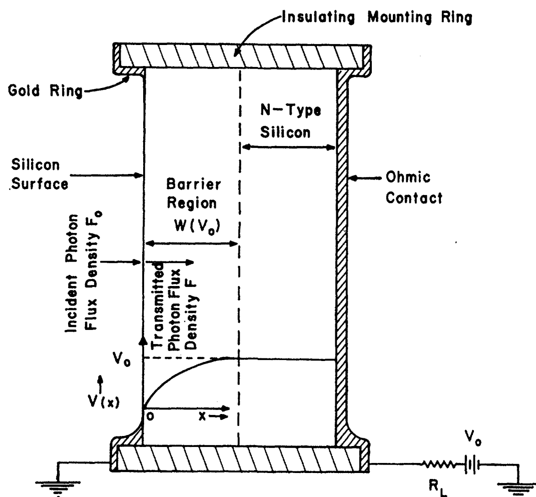

FIG. 1. Silicon surface-barrier photodiode (not to scale). Fringing effects near the periphery of the silicon wafer are ignored.

This paper reports the results of an experimental study of the quantum efficiency of silicon over the energy range from 4.9 to 21.2 eV. The aim of the present investigation was to extend Vavilov's earlier spectral response measurements in silicon to higher photon energies with the hope that such measurements might help to provide further insight into the phenomenon of across-the-gap impact ionization in this material. To determine η, it is convenient to make use of the high electric field which exists in the space-charge region of a reverse-biased silicon surface-barrier diode.[10] Any electron-hole pairs generated in the high-field region by a photon will be separated and will result in a photocurrent in an external circuit. If the incident photon flux, the photocurrent, and the reflectivity of the sensitive surface are measured, η may be determined, subject to certain assumptions which are discussed below.

2. PHOTODIODE

A silicon surface-barrier photodiode as used in this experiment is shown schematically in Fig. 1. The space-charge region extends from $x=0$ to $x=W(V_0)$, where V_0 is the applied bias voltage. The nature of the space-charge region and the operating characteristics of this type of photodiode in the visible and near-ultraviolet are discussed elsewhere.[10–13]

Three assumptions are made regarding the interaction of incident vacuum-ultraviolet photons with the silicon surfaces studied here and the subsequent motion of the optically generated carriers in the space-charge region. They are listed here and examined in Sec. 4 in the light of available experimental data: (a) Any photoemission arising from electrons in the valence band, in the conduction band, or in surface states may be neglected. (b) The presence of an oxide layer on the surface may be neglected. (c) There is no loss of optically produced carriers either at the sensitive surface or in the space-charge region because of recombination or trapping.

In view of the above, it is assumed that a photon transmitted at the surface, $x=0$ (Fig. 1), will interact with an electron initially occupying a state in a valence band, raising it to a high-energy state in a conduction band. If the excited electron and hole have enough excess energy, they may generate additional electron-hole pairs. The end result is that a number η of electron-hole pairs are generated as a result of the absorption of one photon. This process is illustrated in Fig. 2.

Referring to Fig. 1, let F be the steady-state flux density of photons of wavelength λ transmitted at $x=0$. Then the number of electron-hole pairs produced per unit time per cm^3, $g(x)$, at any x is

$$g(x)=\eta F\alpha e^{-\alpha x}, \tag{1}$$

in which α is the absorption coefficient for the photons. It can be shown[13] that as a result of this volume generation rate, the photocurrent in the photodiode is

$$I_{\mathrm{ph}}=-q\eta(1-R)N_0(e^{-\alpha W}-1), \tag{2}$$

in which q is the electronic charge, R is the reflectivity of the silicon surface, N_0 is the number of photons per unit time incident on the surface, and W is the depth of the barrier region. Since the optical absorption coefficient of silicon is very large ($>10^5$ cm^{-1}) in the wavelength interval considered here (2537–584 Å), and

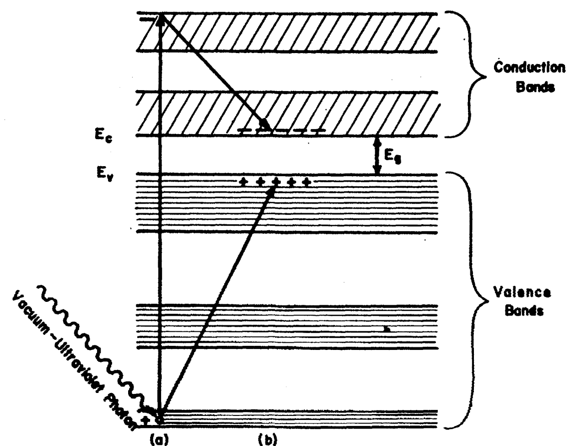

FIG. 2. (a) Production of an excited electron-hole pair in a semiconductor by the absorption of a vacuum-ultraviolet photon. (b) End result of the impact ionization process. A total number η of electron-hole pairs are generated as a result of the absorption of one photon.

[10] W. L. Brown, Natl. Acad. Sci.—Natl. Res. Council Publ. **871**, 9 (1961).
[11] H. Statz, Natl. Acad. Sci.—Natl. Res. Council Publ. **871**, 99 (1961).
[12] *Semiconductor Surface Physics*, edited by R. H. Kingston (The University of Pennsylvania Press, Philadelphia, Pennsylvania, 1957).
[13] A. J. Tuzzolino, E. L. Hubbard, M. A. Perkins, and C. Y. Fan, J. Appl. Phys. **33**, 148 (1962).

$W \approx 50\,\mu$ under operating conditions, the exponential term is negligible, and Eq. (2) reduces to

$$I_{\text{ph}} = q\eta(1-R)N_0. \qquad (3)$$

A measurement of I_{ph}, R, and N_0 allows η to be determined.

The photodiodes are operated in the reverse-bias mode, so that the total current in the diode is the sum of the "dark" current and the photocurrent given by Eq. (3).[13] Under experimental conditions, the diodes were operated at 6 V reverse bias, in which case the dark currents ranged from $\approx 5\times10^{-8}$ to $\approx 2\times10^{-7}$ A. The photocurrents were in the range $\approx 5\times10^{-10}$ to $\approx 10^{-11}$ A, making dc measurements of the photocurrents difficult in the presence of such large dark currents. To eliminate this difficulty, ac methods were used. The light incident on the photodiodes was chopped at 13 cps and the ac signal across a load resistor was amplified, rectified, and measured with a voltmeter.

The low-frequency equivalent circuit of the photodiode is shown in Fig. 3. Quantities not affecting the performance of the photodiode as used here are not shown.[13] The current generator I_{ph} accounts for the ac photocurrent, R_B is the back-resistance of the photodiode, R_L is the load resistance, and R_A is the input impedance of the preamplifier. For the output signal to be proportional to the product $I_{\text{ph}}R_L$, R_L must be small compared to R_B and R_A. For a biased photodiode, R_B can be made orders of magnitude greater than R_L and if the applied bias voltage is greater than the product $I_{\text{ph}}R_L$, the photodiode remains biased and R_B remains very high. Under experimental conditions (applied bias of 6 V), the output signal was proportional to $I_{\text{ph}}R_L$ for all ranges of photocurrents and values of R_L up to one meg. The output signal was also measured as a function of the applied bias (6–22.5 V) and was found to be independent of the applied bias.

3. EXPERIMENTAL

3.1 Photodiode Fabrication

The general techniques used in the fabrication of the photodiodes were similar to those described in detail elsewhere.[14–17] Single-crystal *n*-type silicon was used as the starting material. The electrical resistivity ranged from 700 to 4000 ohm-cm and the minority carrier lifetime ranged from 400 to 2000 μsec.[18] Wafers approximately 500 μ thick were cut from single crystal rods and were mechanically polished. The areas of the wafers ranged from 0.56 to 2.75 cm^2. One face of the wafer was etched for from 3 to 5 min in CP-4 solution.[17] The wafer was then washed, mounted in an insulating ring, and allowed to age for two days to permit formation of a surface barrier on the chemically treated surface.[19]

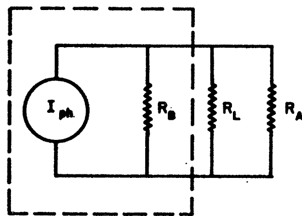

FIG. 3. Low-frequency equivalent circuit of a reverse-biased silicon photodiode. Quantities not affecting the low-frequency operation are not shown. I_{ph} is a current generator accounting for the ac photocurrent, R_L is the load resistance, R_B is the back resistance of the photodiode, and R_A is the input impedance of the preamplifier.

Electrical contact to the sensitive surface of the aged samples was made in three ways. In the first, a gold ring was evaporated over the periphery of the wafer and the mounting ring as shown in Fig. 1. In the second case, gold was evaporated over the periphery of the wafer, the mounting ring, and one-half of the sensitive surface. In the third case, gold was evaporated over the whole sensitive surface and mounting ring. In the last two cases, the thickness of the gold film on the sensitive surface was approximately 100 Å. Contact to the back of the samples was made by evaporating a thick (400 Å) film of gold onto the back of the wafer and mounting ring. Photodiodes with a gold film over the entire sensitive surface were used to measure reflectance or photon intensity, as described below.

3.2 Optical System

A Jarrell-Ash, vacuum monochromator, using the Seya-Namioka mounting, provided the dispersed radiation (8.0 Å per mm). The range of the grating motion was adjusted to permit scanning the wavelength region 500–4000 Å. The entrance and exit slits of the monochromator were fixed at 200 μ and a fixed slit 1×5 mm was placed behind the exit slit of the monochromator. The pumping system for the main chamber consisted of a mechanical pump and an oil diffusion pump. The vacuum obtainable in the grating chamber was 1×10^{-5} mm Hg.

The light source was a water-cooled discharge lamp with a quartz capillary similar to the lamp described by Hartman.[20] The discharge lamp was attached to the entrance head of the monochromator and the only pumping used on the lamp was that through the entrance slit from the main monochromator chamber.

[14] J. L. Blankenship and C. J. Borkowski, IRE Trans. Nucl. Sci. 7, 190 (1960).
[15] G. Dearnaley and A. B. Whitehead, Nucl. Instr. Methods **12**, 205 (1961).
[16] J. W. Mayer, J. Appl. Phys. **30**, 1937 (1959).
[17] G. Dearnaley and A. B. Whitehead, Natl. Acad. Sci.—Natl. Res. Council Publ. **871**, 265 (1961).
[18] The silicon used was obtained from Dow Corning Corporation, Hemlock, Michigan, and Merck and Company, Inc., Danville, Pennsylvania. The resistivity and lifetime values were specified by the suppliers.
[19] C. G. B. Garrett and W. H. Brattain, Phys. Rev. **99**, 376 (1955).
[20] P. L. Hartman, J. Opt. Soc. Am. **51**, 113 (1961).

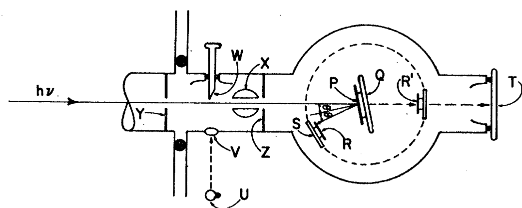

FIG. 4. Photodiode sample chamber. P: photodiode sample; Q: sample holder assembly; R: reflectance detector; S: reflectance detector assembly; T: calibrated photon detector; U: auxiliary light source; V: window; W: mirror; X: light chopper; Y: monochromator exit slit; Z: fixed external exit slit. The angle θ was 12°.

Hydrogen, helium, and neon were used in the lamp. The pressure in the discharge region ranged from about 200 μ to a few mm Hg, depending upon the gas. With the three gases used with the lamp, radiation between 584 and 2600 Å was obtained. Below 1000 Å, the lamp produced chiefly the resonance lines of helium (584 Å) and neon (744 Å). With hydrogen, usable intensities were obtained from 900 up to 2600 Å. The spectrum of hydrogen consists of the hydrogen molecular continuum, extending from 1700 Å to longer wavelengths and the many-lined spectrum of the hydrogen molecule from about 1650 to below 900 Å.[21,22] The atomic hydrogen resonance line at 1216 Å is also present with high intensity.

A power supply for the lamp consisted of a regulated 0–150 V dc voltage supply and a current regulator. The lamp was usually operated at a current of about 2.5 A, although it was operated at times from 0.5 to 5 A. The operating voltage across the lamp usually ranged from 65 to 110 V, depending upon the particular gas and the pressure in the discharge region. Typical intensities (photons/sec) emerging from the 1-×5-mm final exit slit under operating conditions were 2×10^8 (584 Å), 2×10^8(744 Å), 2×10^{10}(1216 Å), and 2×10^{10} (1611 Å). When gas was flowing, the pressure in the main monochromator chamber was held below 1×10^{-3} mm Hg. A mercury "Pen-Ray Lamp"[23] was used to obtain line radiation at 2537 Å.

3.3 Sample Chamber

The sample chamber was mounted to the exit-slit chamber of the monochromator and contained the photodiode sample, a reflectance detector, and a calibrated photon detector. A schematic of the sample chamber is shown in Fig. 4. The photodiode sample P was mounted to a sample holder assembly Q, which could be rotated about its own axis or moved up and down, into or out of the path of the photon beam from the monochromator. The reflectance detector R was a silicon surface-barrier photodiode with 100 Å of gold on the sensitive surface.[13] This detector was mounted to a reflectance assembly S, which could be rotated about an axis coincident with the axis of rotation of the sample assembly.

To measure the reflectivity of the sample, the sample was pulled out of the beam and the reflectance detector adjusted to intercept the direct beam from the exit slit at position R′. The sample was then placed in the beam, rotated to the angle of incidence θ, and the reflectance detector was rotated to intercept the reflected beam at position R. The reflectance was determined from the ratio of the two reflectance detector signals. The minimum angle of incidence was limited by the position at which the reflectance detector assembly, when intercepting the beam reflected from the sample, began to obscure the incident beam. The minimum angle of incidence was 12°. Since the reflectance measurements were made at near normal incidence, the degree of polarization of the light diffracted by the grating was unimportant.[24] The sample chamber was maintained at a pressure of approximately 5×10^{-3} mm Hg by pumping on the sample chamber with a mechanical pump. The lower portion of the sample chamber could be isolated from the monochromator by a gate valve so that samples could be changed without breaking the vacuum in the monochromator.

The photoresponse of the photodiode was determined by placing the photodiode sample P in the chopped photon beam, noting the deflection on the voltmeter and the value of the load resistor. With the photon beam incident on the calibrated photon detector T, the photon flux was determined. The system was calibrated during the experiment by shining visible light from an auxiliary light source U, onto the sample detector or reflectance detector by means of the window V and the mirror W, measuring the resulting large dc photocurrent directly, and then noting the corresponding deflection on the voltmeter and the value of R_L when this beam was chopped. With this method, photoresponses as small as 5×10^{-12} A could be measured.

Photocurrents resulting from the auxiliary bulb source were read with a Keithley Model-410 dc micromicroammeter. For photocurrents interrupted at 13 cps, a Keithley Model-600 electrometer was used as the high-input-impedance preamplifier. From the preamplifier, the signal was passed to a Perkin-Elmer Model-081-0007 preamplifier and then to a Perkin Elmer Model-81 amplifier tuned to 13 cps. From the amplifier, the signal was passed to rectifying contacts on the chopper shaft X, where it was synchronously rectified. The signal was passed to a low-pass filter in the Model-81 amplifier and then to a Keithley Model-149 dc millimicrovoltmeter.

3.4 Photon Flux Calibration

Sodium salicylate is a convenient fluorescent material to use with a photomultiplier or photodiode to measure

[21] D. M. Packer and C. Lock, J. Opt. Soc. Am. 41, 699 (1951).
[22] F. S. Johnson, K. Watanabe, and R. Tousey, J. Opt. Soc. Am. 41, 701 (1951).
[23] C. B. Childs, Appl. Optics 1, 711 (1962).
[24] T. Sasaki and K. Ishiguro, Japan. J. Appl. Phys. 2, 289 (1963).

radiation in the vacuum ultraviolet because it does not sublime in vacuum and remains stable over many months. In addition, its relative quantum efficiency has been found to be constant from 850 to 3000 Å.[22,25] The efficiency appears to be 15% lower at 584 Å.[25] The photon detectors used here were of two types. The first system consisted of a silicon surface-barrier photodiode, with approximately 100 Å of gold on its sensitive surface, mounted directly behind a glass window onto which a layer of sodium salicylate was sprayed. This system was satisfactory for large photon fluxes ($N_0 > 5\times10^8$ photons/sec), but was unable to detect the lowest flux levels. The second system, which was used for most of the measurements, consisted of an RCA-6199 head-on-type photomultiplier tube with a coating of sodium salicylate on the end of the glass envelope. Both systems were calibrated by means of a calibrated nitric oxide chamber.[26,27]

When hydrogen was used with the discharge lamp, the stray light response of the sodium-salicylate photomultiplier system was taken as the response when the monochromator was set at 800 Å, assuming that the stray light intensity did not vary significantly with wavelength. Above 1700 Å, the second-order spectrum was removed by a 1-mm-thick plate of fused quartz which was placed behind the final exit slit. It the cases of He and Ne, the stray light intensity was negligible. The accuracy of the calibration of the sodium-salicylate photomultiplier combination was better than 10%. At high photon-flux levels, estimated uncertainties in the measured values of photocurrent, reflectance and photon flux were usually 3%, 3%, and 2% respectively. At the lowest flux levels, these values were 6%, 6%, and 5%. These values lead to an uncertainty in η as determined by Eq. (3) of approximately 8% at moderate to high flux levels and up to 17% at the lowest flux levels.

4. RESULTS AND DISCUSSION

The reflectivity R and the quantum efficiency η were measured for seven photodiode samples. The average reflectivity and quantum efficiency are shown in Fig. 5. The vertical lines indicate the maximum deviation in the value of R or η for any sample from the average value. Initially, measurement of photosensitivity spectra proved very difficult. Attempts were made to measure the photoresponse on photodiode samples which had been aged for three or four days ("new" samples). Not only were these new samples unstable in the environment of the sample chamber (this instability was usually evident as a varying or negligible photoresponse and at times, a very high noise level), but also exhibited irradiation fatigue effects at the 1216 Å hydrogen resonance line. These fatigue effects were observed after a time of irradiation varying from 10 sec to 1 min, depending upon the sample, and were observed as a sudden decrease in photosignal. After this sudden decrease, the photosignal decreased more slowly with time, dropping to a negligible value after a total time of a few minutes. These measurements were taken when the new samples were exposed to the full intensity at 1216 Å available from the optical system ($\approx 2\times10^{10}$ photons/sec). These fatigue effects were not observed at other wavelengths, possibly because of the lower intensities at other wavelengths and insufficient observation times.

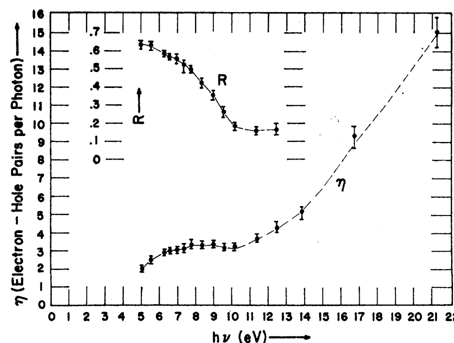

FIG. 5. Average reflectivity and quantum efficiency for seven silicon photodiode samples. The value of η at 21.2 eV has been corrected for the apparent decrease in the quantum efficiency of sodium salicylate at this photon energy.

After a sample had shown this fatigue effect, the original photosignal could be restored by moving the sample so that the collimated photon beam was incident on a previously unexposed portion of the sensitive surface. This showed that the loss of photosensitivity under irradiation occurred only over that portion of the sensitive surface illuminated by photons. In this manner, environmental instabilities could be separated from the effects of irradiation fatigue.

Fortunately, it was found that if the photodiodes were allowed to age for at least one week, they were stable under the vacuum conditions in the sample chamber, although they were still subject to fatigue effects at 1216 Å when exposed to the full intensity available from the optical system. However, by reducing the intensity at 1216 Å, it was possible to measure the photoresponse of the aged samples over the whole spectral range without any evidence of environmental instabilities or irradiation fatigue effects. Repeated determinations of the photoresponse of any of the aged samples agreed within experimental error.

The effects discussed above were similar to those observed by Smith and Dutton during their measurements of the photoresponse of PbS.[8] Possible reasons for the effects observed here are suggested by a brief consideration of the nature of a silicon surface prepared as described in Sec. 3.1. Much more detailed discussions

[25] K. Watanabe and E. Inn, J. Opt. Soc. Am. **43**, 32 (1953).

[26] The nitric oxide chamber was calibrated by J. Siomkajlo, U. S. Naval Research Laboratory, Washington, D. C. The accuracy of the calibration of this chamber was better than 5%.

[27] L. Dunkelman, J. Quant. Spec. and Radiative Transfer **2**, 533 (1962).

are given in the literature.[12,28,29] Located at the surface of a semiconductor is a space-charge double layer which may arise in several ways, such as preferential adsorption of ions of one sign, alignment of adsorbed atoms or molecules having an electrical dipole moment, or presence of electrons or holes bound at the surface in "surface states."[19] Surface states may be due to the termination of the lattice or to the presence of impurities such as an oxide layer or adsorbed gases or ions on the surface. In the case of silicon, an oxide layer $\approx$25–50 Å thick and adsorbed impurities are normally present on the surface. Operationally, two types of surface states are found: states which are assumed to be situated on the interface of the crystal and the oxide, and states which are believed to be predominantly situated on the outer surface of the oxide layer and arise from adsorbed gas molecules. For base material of n-type silicon, the net result of this surface condition is that electrons are trapped in the surface states. This negative surface charge is balanced by a positive space-charge region extending from the surface into the material to a depth of several microns, depending upon the resistivity of the silicon. The electric field resulting from the space charge gives rise to a "built-in" voltage drop, V_B, between the surface and the interior of the silicon. Application of a reverse bias, V_0, will extend the space charge region deeper into the bulk material.[10] For a "Schottky[30]"-type barrier region, the width of the space-charge region is proportional to the square root of (V_0+V_B). The variation of potential in the barrier region for this type of barrier is illustrated in Fig. 1. The exact variation of potential throughout the space-charge region of the photodiode samples used in this experiment is not important as long as the existing electric field is sufficiently strong to separate any electron-hole pairs generated by the absorption of a photon.

One possible explanation for the instability of new samples under vacuum and the fatigue effects exhibited eventually by all samples is that the surface states necessary for the existence of the barrier region can be altered significantly by conditions of moderate vacuum, by high-energy photon irradiation, and possibly by hydrogen ions from the discharge tube. Sufficient alteration or loss of such surface states would result in destruction of the barrier region and consequently, in a loss in photosensitivity. If these surface states result from the oxide layer or adsorbed species on this layer, it is reasonable to assume that these impurities are not tightly bound to the surface and may be altered or removed from the surface fairly easily by vacuum or bombardment, particularly when the surface is new. In most cases, the photoresponse of samples which had shown fatigue effects or instability was restored by removing the samples from the chamber and allowing them to age again for several days, supporting the above view. More detailed experimental studies of these effects and a better understanding of the nature of such surfaces are needed to arrive at a more quantitative explanation than that proposed here. The curves shown in Fig. 5 are for photodiode samples on which measurements were made after a period of from ten days to seven months from the time of their fabrication.

The generally lower value of reflectivity, particularly at the shorter wavelengths, given in Fig. 5 compared with published values for silicon[24,31] is expected, since the magnitude and spectral detail of the reflectivity of a semiconductor are strongly dependent upon the surface quality, particularly at shorter wavelengths.[24,32,33] The surface quality depends upon the mechanical and chemical techniques used to prepare the surface and on the length of time during which the sample is exposed to the atmosphere before measurements of reflectivity are made. One measurement of reflectivity was made at 1216 Å on a silicon sample immediately after etching and a value of 0.42 was found, compared with a value of 0.19 which was obtained several weeks later. A similar measurement by Sasaki[34] on germanium showed a decrease in reflectivity of 10% at 1216 Å after the sample was exposed to air for 20 hours. Since the published values of the reflectivity of silicon were obtained on fresh surfaces,[24,31] the lower value of the reflectivity for the surfaces studied here is attributed to the age of the surfaces. The values of R given in Fig. 5 are considered to be adequate for the purposes of this paper.

The low values of the reflectivity below 1000 Å and the low intensities available at these wavelengths made it impossible to measure the reflectivity with the apparatus used and the reflectivity was taken as zero in calculating η from Eq. (3) below 1000 Å. This is believed to be justified since the reflectivity for fresh surfaces is less than 0.3 at 1000 Å and decreases rapidly with decreasing wavelength,[31] so that the values for the old surfaces studied here are probably much less than 0.1 below 1000 Å. No attempt was made to correct the data for the effect of any oxide layer on the crystal surfaces.[35,36]

Before discussing the values obtained for η, the assumptions introduced in Sec. 2 will be considered. In the case of the first assumption, any photoemission from a semiconductor such as silicon may be either a surface effect or a volume effect. In general, surface states on a semiconductor will absorb very little of the incident light. Absorption of about 10% is probably the upper limit.[37] For most materials studied to any

[28] A. Many, Phys. Chem. Solids **8**, 87 (1959).
[29] J. T. Law, in *Semiconductors*, edited by N. B. Hannay (Reinhold Publishing Corporation, New York, 1959), p. 676.
[30] W. Schottky, Z. Physik **118**, 539 (1942).
[31] H. R. Philipp and H. Ehrenreich, Phys. Rev. **129**, 1550 (1962).
[32] R. E. Morrison, Phys. Rev. **124**, 1314 (1961).
[33] H. R. Philipp and E. A. Taft, Phys. Rev. **120**, 37 (1960).
[34] T. Sasaki, J. Phys. Soc. Japan **18**, 701 (1963).
[35] R. J. Archer, J. Electrochem. Soc. **104**, 619 (1957).
[36] J. R. Booker and C. E. Benjamin, J. Electrochem. Soc. **109**, 1206 (1962).
[37] H. Frohlick and R. A. Sack, Proc. Phys. Soc. (London) **59**, 30 (1947).

extent, the photoemission has been found to be a volume effect.[38]

A study of photoelectric emission from silicon has been carried out over the energy range 4.9–6.3 eV by Gobeli and Allen.[39] Over this energy range the photoemission yield Y is less than 10^{-3} electrons/photon, with n-type samples giving a lower yield than p-type. The yield observed is interpreted as being due to a volume excitation effect and their data indicates that any photoemission from surface states is negligible. Unfortunately, no data are available over the photon energy range considered here. Although the yield Y may increase at higher photon energies, it seems unlikely that it would exceed ≈ 0.20, which appears to be, roughly, the upper limit for the yield observed for materials studied to date.[40] Assuming the yield does attain a value of ≈ 0.20, the corrected values for η would be, at most, 20% higher than the values given in Fig. 5. Such a correction is not large enough to affect the general dependence of η on $h\nu$ shown in Fig. 5 or any qualitative conclusions related to the impact ionization process based on this dependence.

The justification for the assumption of negligible loss of generated carriers in the barrier region follows from the fact that the carrier lifetimes ($>400\,\mu$sec) were much longer than the carrier transit time across the barrier region ($\approx 10^{-9}$ sec).[41,42] The assumption of negligible loss of photocarriers at the surface is supported by the data of Fig. 5. As already mentioned, measurements of η were made on seven samples. During the measurements, the surfaces were exposed to different conditions of vacuum and different atmospheres. In addition, the photoresponse was measured at several applied bias voltages, which gave rise to different magnitudes of the electric field at the surface of the samples. From these facts, it seems reasonable to assume that the photodiode samples had significantly different surface recombination characteristics.[43] Since the same value of η was obtained for all samples, within experimental error, any effects of recombination at the surface were small. In addition, for photon energies greater than 6 eV, the importance of surface effects should decrease, since the absorption coefficient of silicon decreases with increasing energy above 6 eV.[24]

Although the effects of the oxide film on the recombination of photocarriers at the surface appears to be small, the same is not necessarily true of the effect of the oxide film on the number of photocarriers produced. The values for η given in Fig. 5 were calculated from the experimental data under the assumption that the oxide film was nonabsorbing. At any wavelength at which there is appreciable absorption by the oxide film, the value of η given in Fig. 5 will be too small. From Archer's work,[35] the seven photodiode samples studied had oxide thicknesses lying in the range from ≈ 31 to 40 Å. No detailed information is available at present concerning the physical or optical properties of such films on a silicon surface[12,28,29] so that it is not possible to predict quantitatively the effect such films have on the measured values of η. However, we may estimate the amount of absorption by these films if it is assumed that the absorption coefficient of such an oxide film lies in the range 10^5–10^6 cm^{-1} for photon energies above that where fundamental absorption sets in. A comparison of the reflectivity given in Fig. 5 with published values[24,31] and other reflectivity measurements[33] indicate that absorption by the oxide film becomes important for $h\nu > 8$ eV. Assuming that fundamental absorption by the oxide film sets in for $h\nu > 8$ eV and choosing a value of 10^6 cm^{-1} for the absorption coefficient of the oxide film, the measured values of η would be too small by factors of 1.36 and 1.49 for the ten-day-old and seven-month-old samples, respectively, for $h\nu > 8$ eV (excluding additional reflection losses at the oxide-silicon interface). This indicates that over portions of the wavelength range studied, the measured values of η could be too small by perhaps a factor of ≈ 1.4. Hence, the assumption that the effect of the oxide film is negligible may not be valid, and the use of the data of Fig. 5 in any quantitative sense is questionable. If it were possible to measure the photoresponse at various wavelengths of a sample of known oxide thickness and a sample of minimum oxide thickness (≈ 12 Å),[35] a more quantitative estimate of the influence of the oxide film on the measured values of η could be made. Unfortunately, such a comparison was not possible since a minimum of two days was required for fabrication and aging[19] of the photodiodes and in addition, the instabilities already discussed did not disappear until the photodiodes had been aged for approximately ten days.

The apparent dip in the curve between 8.9 and 10.8 eV may result entirely from the presence of the oxide film and indicates that absorption by the film is becoming important for $h\nu \approx 10$ eV, which is consistent with what is observed in reflectivity measurements. Although the oxide film begins to affect the measured values of η for $h\nu > 8$ eV, and may affect the values of η strongly (correction factor of ≈ 1.4) for $h\nu > 10$ eV, the general features of the corrected η dependence on $h\nu$ should be similar to the measured dependence, i.e., the variation in η from 6 to ≈ 10 eV would be small compared with the increase in η above $h\nu \approx 10$ eV. Therefore, it is felt that the general dependence of η on $h\nu$ shown in Fig. 5 is characteristic of bulk silicon and that this data can be of use in a qualitative discussion of the impact ionization process in silicon.

The variation of η with photon energy shown in Fig. 5 resembles the variation of η with $h\nu$ found by

[38] W. E. Spicer and F. Wooten, Proc. IEEE **51**, 1119 (1962).
[39] G. W. Gobeli and F. G. Allen, Phys. Rev. **127**, 141 (1962).
[40] L. Dunkelman, W. B. Fowler, and H. Hennes, Appl. Optics **1**, 695 (1962).
[41] W. L. Brown, IRE Trans. Nucl. Sci. **8**, 2 (1961).
[42] J. W. Mayer, Natl. Acad. Sci.—Natl. Res. Council Publ. **871**, 1 (1961).
[43] T. M. Buck and F. S. McKim, J. Electrochem. Soc. **105**, 709 (1958).

Vavilov at low photon energies.[6] There is a region of photon energy (6–10 eV, in this case) in which η is roughly constant, and for higher photon energies, η increases very strongly. The most outstanding feature of the variation of η with $h\nu$ is the large increase in η as the photon energy increases above ≈ 10 eV, and the large value of 15 at 21.2 eV.

The problem of electron impact ionization in semiconductors has been treated by Antoncik[44] and Dexter.[45] In these treatments, only the ionizing action of electrons is considered, and the minimum energy $\bar{E}$ which an electron must have to be able to generate an electron-hole pair is determined from the conservation laws for energy and crystal momentum in the process 1 fast electron $\rightarrow$ 2 electrons+1 hole.

Assuming that the electron does not interact with the lattice, Antoncik obtained a value of 1.23 eV for the threshold energy $\bar{E}$ in Si. This value was obtained using a simplified model of the band structure for Si. Owing to the interaction of the fast electron with the lattice, the true threshold energy E' for pair generation should be greater than $\bar{E}$ by tenths of an eV.[44] It is interesting to note that Shockley's threshold of 1.15 eV (see Sec. 1) is in good agreement with Antoncik's value of 1.23 eV, which Antoncik derived on the basis of several simplifying assumptions regarding the band structure of Si and by assuming no electron interactions with the lattice. Antoncik also derives an expression for η for photon energies in the neighborhood of $\bar{E}$, assuming that a fast electron can ionize only once, and that the band structure for the energies considered may be described by the effective-mass approximation.[44,45]

The results of Antoncik's work cannot be applied to interpret the data of Fig. 5 for the following reasons: (a) For the photon energies considered here, the photocarriers have excess energies several times the bandgap energy and one would not expect the effective-mass approximation to be valid for energies so far from the band edges; (b) In principle, the same considerations which were applied to impact ionization by electrons should apply equally well to impact ionization by holes. The results of Vavilov[6] indicate that both the photoelectron and photohole are active in generating pairs even in the low-energy range.[9] Antoncik's treatment does not include impact ionization by holes; (c) If one wished to include the possibility of impact ionization by holes, the distribution of the photon energy between the photoelectron and photohole would have to be known. This is a problem which has not yet been solved.[44] In addition, for the high energies considered here, the original photoelectron and photohole may generate more than one pair, and a given generated pair may have enough excess energy to generate more pairs. To treat the effects of these multiple ionizations quantitatively, one would have to know the distribution of energy among the three carriers (original carrier and generated pair) subsequent to pair formation. This is a second problem not yet satisfactorily solved.[9] In view of the above, no attempt is made here to interpret quantitatively the dependence of η on $h\nu$ shown in Fig. 5.

A qualitative interpretation of some of the aspects of the observed dependence of η on $h\nu$ may be obtained by making use of a model proposed by Shockley to explain impact ionization effects in silicon.[9] Shockley emphasizes that his model is empirical rather than theoretical since band structure considerations are disregarded. The four parameters which characterize the model are: The threshold energy, measured from a band edge, for a carrier above which it may produce an electron-hole pair, E_i; the mean free path between scattering by phonons, L_R; the mean free path between ionizations for a carrier with energy greater than the threshold energy, L_i; and the energy of the phonons involved, E_R. All four parameters are taken as constants. Shockley assumes that when a low-energy photon of energy $h\nu$ is absorbed in silicon, the difference between the photon energy and the band-gap energy, E_g, is divided equally to give the photoelectron and photohole each an energy of $(h\nu-E_g)/2$. Each photocarrier may then ionize if this energy is greater than E_i. Shockley derives an expression for η over the range of $h\nu$ in which "third-generation" pairs can be neglected which is in excellent agreement with Vavilov's experimental results if E_i has the value 1.1 eV, and his model predicts a value for the mean energy required to generate one ion pair in silicon by a high-energy particle (MeV range) or a very-high-energy photon (keV range) of 3.5 eV, which is in very good agreement with values obtained experimentally.

Using Shockley's model, the approximately constant value for η in the range of $h\nu$ from roughly 6 to 10 eV and the strong increase in η for $h\nu>10$ eV may be explained. On the basis of Shockley's model, a 6-eV photon will give rise to a photoelectron and photohole each with an energy of 2.45 eV (measured from the band edges). Each of the photocarriers has a high probability of producing a pair so that η should be close to 3.[9] Actually, the probability that a carrier of energy E produce an ionization before slowing down from E to E_i should be explicitly considered, as well as the probability for the processes described below. No attempt is made here to introduce these refinements.

It will be assumed here that when a carrier (electron or hole) of energy E generates a pair, an amount of energy $(L_i/L_R)E_R$ is lost to phonons,[9] and an amount of energy E_g is lost in taking an electron across the band gap. The quantity L_i/L_R is the average number of phonons generated per ionization by a carrier with energy greater than E_i and is taken to have the value 17.5.[9] The phonon energy E_R has the value 0.063 eV,[9] so that the quantity $(L_i/L_R)E_R$ has the value 1.1 eV. It is further assumed that when a carrier generates a pair, the available energy remaining after the collision

[44] E. Antoncik, Czech. J. Phys. 7, 674 (1957); 8, 492 (1958).

[45] D. L. Dexter, U. S. Air Force Office of Scientific Research Report No. TN 60-99, 1960 (unpublished).

is equally shared between the original carrier and the pair, i.e., the original carrier ends up with $\frac{1}{2}$ the excess energy and the generated electron-hole pair each have $\frac{1}{4}$ of the excess energy. In view of these assumptions, the photocarriers each will have an energy of

$$\tfrac{1}{2}[(h\nu-E_g)/2-(L_i/L_R)E_R-E_g] \tag{4}$$

after each carrier generates the first pair. For $h\nu=6$ eV, Eq. (4) gives a value of 0.12 eV for the excess energy of the photoelectron and photohole after the first pairs are generated. This excess energy is less than E_i, so that no additional carriers can be generated and the excess energy is lost to the lattice. As $h\nu$ increases above 6 eV, the energy of the photocarriers after the first collisions also increases according to Eq. (4).

If η is to increase above 3, the photocarriers must have at least an energy E_i after the first collisions. This will not occur until $h\nu$ increases to 10 eV, at which point Eq. (4) gives a value of 1.12 eV for the energy of the photocarriers, so that each of the photocarriers may begin to generate a second ion pair, resulting in an increase in η above 3 as $h\nu$ increases above 10 eV. This predicted behavior is consistent with the observed variation of η with $h\nu$. Using the same arguments for $h\nu>10$ eV, where multiple ionizations by the photocarriers and ionizations by generated pairs must both be considered, this model predicts a monotonic increasing value for η over the photon range from 10 to 21 eV, although the values for η predicted by this model for $h\nu>10$ eV are much lower than those measured.

Obviously, assumptions other than those made above may be introduced, i.e., there is no justification for assuming that the energy $(h\nu-E_g)$ is equally shared between the photoelectron and photohole or that an original carrier ends up with one-half of the excess energy available after generating a pair. Many other possibilities exist for the manner in which the excess energy available after a collision may be shared among the carriers, although no other simple division of the excess energy among the carriers predicts the strong increase in η which is observed for $h\nu>10$ eV. Any detailed comparison of the observed behavior of η with predictions of a specific model would be premature in view of the uncertainty in the measured values of η resulting from the oxide film. Consequently, it does not seem worth while to discuss more general cases. The model discussed here was selected because of its simplicity and apparent consistency with the observed behavior of η.

5. CONCLUSIONS

The quantum efficiency of silicon over the photon energy range from 4.9 to 21.2 eV has been determined experimentally by measuring the photoresponse of silicon surface-barrier photodiodes. The principal finding is the relatively constant value for η over the photon energy range from roughly 6 to 10 eV and the strong increase in η with increasing $h\nu$ above 10 eV. A quantitative interpretation of the observed dependence of η on $h\nu$ was not possible in view of the lack of information as to the manner in which the energy of the absorbed photon is shared between the photocarriers and the lack of information as to how the excess energy available following an ionization event is shared between the original carrier and generated pair. Qualitative predictions based upon a model proposed by Shockley and a simplifying assumption regarding the manner in which excess energy is shared between carriers after an ionizing collison are consistent with the observed constancy of η from 6 to 10 eV and the observed increase in η beginning at ≈ 10 eV. Further experiments which should prove fruitful are a study of the quantum efficiency of silicon for photon energies greater than 21 eV and a study of photoemission in silicon for $h\nu>6$ eV.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. J. Kristoff and C. Vossler for their help with the apparatus and assistance in making measurements, to Dr. J. Burns, Dr. F. Rieke and Dr. C. Fan for many enlightening discussions, to J. Lamport and Dr. J. Simpson for their continued encouragement and helpful criticisms, and to Mrs. R. Allison for preparing the sodium salicylate films.