Photoemission of Electrons from *n*-Type Degenerate Silicon into Silicon Dioxide

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Photoemission of electrons from both the conduction and valence bands of *n*-type strongly degenerate silicon (10^{26} electrons/m^3) into thermally grown silicon dioxide layers has been observed. The threshold energies have been determined for the two processes and are used to obtain the following information about energies at the silicon–silicon dioxide interface. The energy difference between the conduction-band edge in the silicon and that in the oxide is ~3.29 eV. The energy difference between the valence-band edge in the silicon and the conduction-band edge in the oxide is ~4.22 eV. The difference between these values is less than the optical band gap usually attributed to lightly doped silicon.

I. INTRODUCTION

PHOTOEMISSION of electrons from silicon into silicon dioxide has recently been observed 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.[1–3] In Refs. 1 and 2, the photoemission was due to electrons in the valence band of the silicon undergoing optical transitions to higher energy states from which they could enter the conduction band of the oxide. The threshold energy for this process was about 4.2 eV.

In Ref. 3 it was shown that a profound change in the photoemission spectrum could be introduced by drifting positive ions through the oxide (at high temperature) to produce a layer of positive charge in the oxide very close (~10 Å) to the silicon–silicon-dioxide interface. This change was the introduction of a low-energy branch of the photoemission spectrum with a threshold at about 3.05 eV. The original response did not disappear or change drastically in character. The appearance of the new low-energy branch was attributed to one of two causes: (1) photoemission from the conduction band of a degenerate layer in the silicon which had been induced by the layer of positive charge in the adjacent oxide or (2) lowering of the barrier to photoemission by Schottky effect due to the high field ($\sim 1.1\times 10^7$ V/cm) caused by the positive-charge layer.

In either case, however, it appears worthwhile to report the observation of photoemission of electrons from highly degenerate *n*-type silicon into silicon dioxide. In this work, the photoemission from both the conduction and valence bands of silicon is unambiguous.[4]

II. EXPERIMENTAL DETAILS

The oxide films used in this work were grown on (111) faces of single-crystal degenerate *n*-type (0.00088 Ω cm) silicon wafers. The carrier density in these wafers is $\sim 10^{26}/m^3$. The growth was carried out at 1100°C. Three oxide layers (on three separate wafers) were used in the experiments; two were 6.4 μ thick and one was 3.5 μ thick. A (low resistance) pressure contact to the back of each wafer was obtained by sandblasting that surface to remove the oxide. Eight thin, partially transparent gold electrodes (area ~0.2 cm^2) were evaporated onto the front (free) surface of each oxide layer. The thickness of one of these sets of electrodes was measured during evaporation using a quartz crystal microbalance. This value (165 Å) was used later in the calculation of the spectral variation of the ratio of light incident on the sample to light absorbed in the silicon. A heavier "dot" of gold ~1 μ thick was also applied by evaporation at one end of each transparent electrode to facilitate connection by a pressure contact. The sample configuration, as is shown in Fig. 1 of Ref. 2, is effectively a "sandwich" of SiO_2 between a slice of highly degenerate *n*-type silicon on one side and a partially transparent gold layer on the other.

The measurement equipment and technique are identical to that described in Ref. 2. 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 may be measured as a current in the external circuit.

III. RESULTS AND DISCUSSION

The spectral distribution of the photocurrent was obtained by slowly sweeping the monochromator through the wavelength region of interest while recording the photocurrent. A typical result is shown in Fig. 1. The interferometric effect described previously[2] is almost entirely absent here because the thickness of the oxide (6.4 μ) requires the photocurrent undulations to be too close in energy to be resolved by the monochromator in the region $h\nu < 4.0$ eV.

[1] R. Williams, Phys. Rev. **140**, A569 (1965).
[2] A. M. Goodman, Phys. Rev. **144**, 588 (1966).
[3] R. Williams, J. Appl. Phys. **37**, 1491 (1966).
[4] To the author's knowledge, no clear case of photoemission of electrons from the conduction band of degenerate *n*-type silicon into vacuum has been reported.

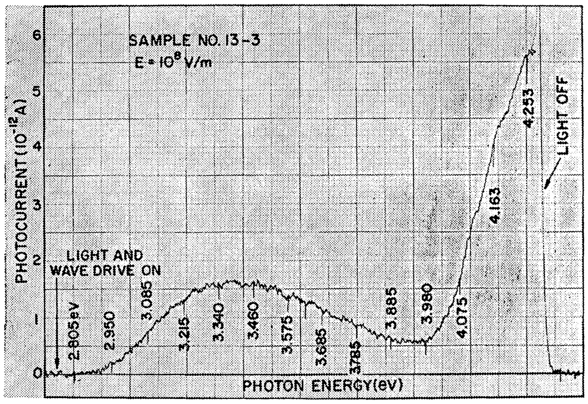

FIG. 1. Photocurrent versus photon energy for sample 13–3. The electric field in the oxide is 10^8 V/m directed toward the silicon.

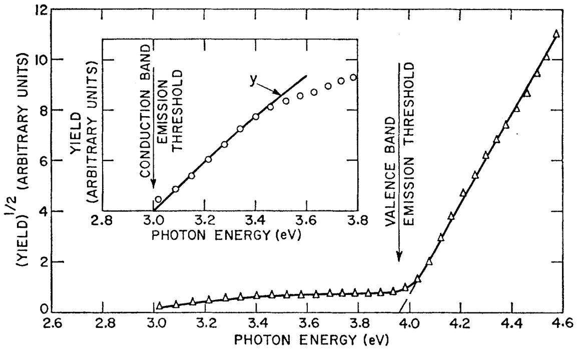

FIG. 2. Square root of yield versus photon energy for sample 13–3. The insert shows a linear plot of yield versus photon energy; the solid curve is a theoretical expression $y=C[1-(E_0/E)^{1/2}]$ fitted to the experimental points. See text and Appendix for explanation.

The published values of the optical properties of silicon,[5] silicon dioxide,[6] and thin evaporated gold films[7] were used to calculate the spectral variation of the ratio of light incident on the evaporated gold layer to light absorbed in the silicon for the one wafer for which the gold thickness was known. This information was in turn used to determine the yield (photocurrent per *absorbed* photon). A plot of $(\text{yield})^{1/2}$ versus photon energy is shown in Fig. 2. It is clear that there are two threshold energies corresponding to two different processes. The higher energy threshold corresponds closely (after correction for Schottky effect) to that found previously[1,2] for photoemission from the valence band of silicon (either nondegenerate or slightly degenerate) into the conduction band of silicon dioxide. The new threshold is lower by about 1 eV. The obvious explanation for the new lower energy threshold is the onset of photoemission from the conduction band of silicon into the conduction band of silicon dioxide.

The value determined for the low-energy threshold depends to some extent on the way in which the data are plotted. In the Appendix, a highly simplified model is used to derive a theoretical expression for the spectral variation of photoemission from a narrow band of filled levels at the bottom of the conduction band. This would seem to be the proper expression to which to fit the experimental data since the Fermi level in the silicon used in the present work is about 0.05 eV above the conduction-band edge (assuming that the bottom of the conduction band is still parabolic despite the heavy doping). In the inset of Fig. 2, the theoretical expression $y=C[1-(E_0/E)^{1/2}]$ is fitted to the experimental data to obtain a value for the low-energy threshold. It would also be possible to fit the experimental data almost as well using other assumed relationships between the yield and the energy above threshold; however, this would change the apparent threshold value. For example, if it were assumed that the yield should vary as the square of the energy above threshold, then the apparent threshold would be about 0.15 eV lower than that found using the expression for y.

Similar results were obtained using electrode areas on each of the three different wafers. From the plots of photocurrent (not normalized with respect to light intensity) versus photon energy it could be seen that the threshold values were approximately the same in each case. However, since the gold thickness was accurately known only for the electrodes on one wafer, only the data for those electrodes could be analyzed on a "per absorbed photon" basis. For three electrode areas on this wafer, the results may be stated as follows: (a) The energy difference between the conduction-band edge in the silicon and that in the oxide is 3.29 ± 0.02 eV; this number includes the correction[8] for Schottky effect and also takes into account (approximately) the position of the Fermi level in the silicon conduction band by assuming that the experimentally obtained threshold is the energy difference between the oxide conduction-band edge and the average energy of the filled levels at the bottom of the conduction band. (b) The energy difference between the valence-band edge in the silicon and the conduction-band edge in the oxide is 4.22 ± 0.02 eV (including the Schottky-effect correction) in good agreement with previous work.[1–3] These limits obviously do not include possible errors due to the method of data analysis.

The difference between these values is less than 1.05–1.15 eV, the range usually given[9] for the optical band gap of lightly doped silicon at room temperature. This would indicate that the band gap has decreased due

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

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

[7] J. E. Davey and T. Pankey, J. Appl. Phys. **36**, 2571 (1965).

[8] The experimentally determined threshold-energy values must be corrected for the Schottky lowering of the barrier (due to the electric field in the oxide) in order to obtain the "true" or zero-field threshold values. In all of the experiments described here the field was $E=10^8$ V/m and the corresponding Schottky correction (Ref. 2) is $\Delta\phi=0.26$ eV.

[9] T. S. Moss, *Optical Properties of Semiconductors* (Butterworths Scientific Publications Ltd., London, 1959).

to the heavy doping. Such an effect has previously been observed in studies of optical absorption in heavily doped germanium[10,11] and silicon.[12] In the latter case, however, no quantitative information about the decrease in band gap as a function of doping was obtained because of difficulties in analyzing the data.

IV. SUMMARY

The results of this work may be summarized as follows: (1) Photoemission of electrons from both the conduction and valence bands of n-type degenerate silicon into the conduction band of a thermally grown silicon dioxide layer has been observed. (2) The energy difference between the conduction-band edge in the silicon and that in the oxide is $\sim$3.29 eV. The energy difference between the valence-band edge in the silicon and the conduction-band edge in the oxide is $\sim$4.22 eV. (3) The difference between these values is less than the optical band gap usually attributed to lightly doped silicon.

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APPENDIX

In this section, a highly simplified model is used to derive an expression for the spectral variation of the photoemission of electrons from a narrow band of filled levels of density N at an energy E_0 below the "escape level." The narrow band of filled levels has a spread in energy ΔE which is much smaller than E_0 and may be conceptually regarded as a single level at the average energy of the filled levels. The escape level is either (a) the vacuum level in the case of photoemission into vacuum or (b) the energy of the conduction-band edge in the adjoining material in the case of "internal photoemission" across an interface. It is assumed that the filled levels are located at the bottom of an otherwise empty single parabolic band. Some of the electrons in the filled levels undergo optical transitions to higher states. The transition probability and the density of final states are assumed to vary insignificantly with energy. Scattering processes are not considered except for that of a "perfect escape surface" which can absorb only normal momentum. The hot electrons are assumed to be isotropically distributed in momentum space. This is indicated schematically in Fig. 3 where the hot electrons are uniformly distributed around the periphery of a sphere of radius p in momentum space. The intersection of this sphere with the "escape surface" (a plane p_0 from origin) defines a segment whose spherical surface contains those electrons which can escape. The fraction of all of the hot electrons which can escape is f_e and is given by

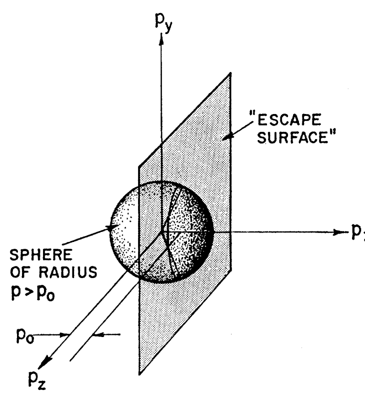

FIG. 3. The "hot electron sphere" in momentum space intersecting with the "escape surface." The intersection defines a segment whose spherical surface (darkly shaded) contains those electrons which can escape.

$$f_e = \frac{\text{spherical area of darkly shaded segment}}{\text{area of sphere}} = \frac{(p-p_0)}{2p}. \quad \text{(A1)}$$

In terms of the threshold energy E_0 and the photon energy E, this becomes

$$f_e = \frac{1}{2}\left[1-\left(\frac{E_0}{E}\right)^{1/2}\right] = \frac{1}{2}\left[\frac{(E/E_0)-1}{(E/E_0)+(E/E_0)^{1/2}}\right]. \quad \text{(A2)}$$

It can be seen from the last expression for f_e that the numerator varies linearly with photon energy above threshold while the denominator is a much more slowly varying function of E near the threshold. Thus, to a fair approximation, the escape factor should vary linearly with photon energy above the threshold value. If the electrons in the narrow filled band being considered are the only ones to undergo optical transitions or if other optical absorption processes are "spectrally flat," then the photo-electric yield y will be proportional to the calculated escape factor:

$$y = C[1-(E_0/E)^{1/2}]. \quad \text{(A3)}$$

Thus far, the effect of finite temperature has been ignored. Qualitatively, however, it can be seen that since the electronic energy levels at the bottom of the conduction band will actually be populated according to the Fermi-Dirac distribution function rather than the artificially simple way assumed at the outset, the yield should not be expected to cut off sharply at the threshold energy. Instead, the yield should be expected to "tail off" gradually over a photon energy range of the order of several kT wide about the threshold.

[10] C. Haas, Phys. Rev. **125**, 1965 (1962).
[11] A. B. Fowler, W. E. Howard, and G. E. Brock, Phys. Rev. **128**, 1664 (1962).
[12] V. K. Subashiev and G. B. Dubrovskii, Fiz. Tverd. Tela **6**, 1303 (1964) [English transl. Soviet Phys.—Solid State **6**, 1017 (1964)].