PHYSICAL REVIEW B VOLUME 12, NUMBER 8 15 OCTOBER 1975

Surface states from photoemission threshold measurements on a clean, cleaved, Si (111) surface

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(Received 3 December 1973; revised manuscript received 2 July 1974)

Very accurate measements of the photoemission yield have been performed on the (111) face of silicon as a function of photon energy in the threshold region down to the 10^{-10} range. Using a set of differently doped samples cleaved in ultrahigh vacuum, one can distinguish between surface- and bulk-state photoelectrons, and determine the approximate shape of the surface-state density (SSD) in the band gap. For the clean surface, the SSD increases from the Fermi level to the top of the valence band, approximately following a 3/2 power law and does not vanish when reaching the valence band. The effect of doping is computed and leads to an electron escape length of about 12 Å. The effect of steps is briefly mentioned.

I. INTRODUCTION

In the last few years, great attention has been given to the study, both experimental and theoretical, of electron surface states on clean semiconductors; silicon, in particular, has received most of the interest. Experimentally, many methods have demonstrated the existence of surface states on different clean faces of silicon. Up to now, the most fruitful results concerning their distribution have been obtained, through various techniques, from the optical or electronical excitations of transitions involving surface states. Optical absorption[1] and photoconductivity,[2] both recently applied to silicon,[3,4] show a competition between surface and localized bulk states so that information on surface-state distribution (SSD) can be obtained only by a difference between measurements before and after various surface treatments such as oxidation. The photovoltage method,[5] which has not been applied yet to silicon, can indicate the position of variations in the SSD but does not lead to its direct determination.

The exoemission of electrons excited by photons, electrons, or an electric field has also been used to obtain information on the SSD. First, indirectly, Allen and Gobeli[6] applied the photoemission technique in conjunction with contact-potential measurements in order to determine the absolute value of the band bending on differently doped silicon samples. In such experiments, the main problem is to get an accurate determination of the ionization energy from the photoemission threshold. More recently, a direct evidence of photoemitted electrons from surface states has been obtained from the difference between energy-distribution curves of the cleaved and oxidized (111) face of silicon[7,8]: in that case again, the results appear as a difference and the localization in energy cannot be better than about 0.1 eV, limit given by the electron-energy-distribution measurements. Furthermore, a similar uncertainty remains for the location of the Fermi level and of the top of the valence band at the surface.

Photoemission and electron-energy-loss spectroscopy have also been used to obtain information on the SSD of silicon for different surface conditions: the effect of the structural change on the (111) face, due to annealing and observed through low-energy electron diffraction (LEED) measurements by several authors, have been studied,[9–12] as well as the properties of (100) faces[10–12] and the effect of the degree of oxidation[12–14] of an initially clean surface.

Summarizing our knowledge from the present state of the literature on the clean, cleaved, (111) face of silicon, it appears that (i) the work function φ is constant for *n*- or *p*-type samples on a wide range of doping and equal to 4.85 ± 0.02 eV; (ii) the ionization energy Φ, sum of the work function and of the energy from the top of the valence band at the surface to the Fermi level, is independent of doping within 0.1 eV and has a value between 5.15 and 5.40 eV; (iii) the surface-state density becomes appreciable about 0.25 eV above the top of the valence band and reaches a maximum between 0 and 0.5 eV below the top of the valence band.

In this paper, we show that the accurate measurement of the photoemission yield in the threshold region, down to the 10^{-10} range, leads to the direct determination of the work function, with the same accuracy as from other methods, the ionization energy within 0.02 eV and the shape of SSD between the Fermi level and the top of the valence band.

II. EXPERIMENTAL

The silicon samples are *n* or *p* type with doping levels ranging from 10^{15} to 10^{20} carriers per cm^3.

They are cut in $5\times5\times20$ mm^3 parallelepipeds with the (111) plane along the square face and mounted in a chamber equipped with a MgF_2 window together with a cleaving device made of a tungsten carbide blade and a copper anvil. The chamber is evacuated by a turbomolecular pump and a titanium sublimation pump.

While under vacuum, the sample is illuminated with a monochromatic beam, a small fraction of which is permanently reflected by a quartz plate toward a reference photomultiplier. The reference signal $I_R(h\nu)$ and the photoemitted current $I_P(h\nu)$ are simultaneously recorded as a function of the photon energy $h\nu$ and the yield curves obtained by calculating I_P/I_R for about 50 values of $h\nu$. The effect of the optics and of the photomultiplier quantum response has been checked and shown to bring some distortion. However, the correcting term varies monotonically from 1 to about 3 over the whole energy range: this is quite small compared to the five orders of magnitude covered by a typical yield curve. The results given here are the uncorrected ones. Also, the reflectivity change of silicon, which is less than 10% over the whole energy range, has been neglected.

Monochromatic light from 4.5 to 6.2 eV is obtained through a double monochromator with quartz prisms, giving a resolution of 0.01 eV, illuminated by a 200-W Hg-Xe lamp. In the case of silicon, this lamp has the advantage that its emitted intensity is larger at photon energies where the photoemission yield is smaller. The double monochromator gives a stray light intensity in the 10^{-6} range, 10^3 times smaller than in a single monochromator, thus reducing the background current of photoelectrons to a negligible level. Though a double grating monochromator would also give a low level of stray light, the available intensity at the proper energy would be much smaller than with prisms.

The photoemitted current is detected through a channel electron multiplier. This detection has a very good sensitivity, since a current of one electron per second can be measured. However, great care must be taken to eliminate spurious currents coming from other sources. For this reason, ion pumps cannot be used and even the pressure gauge has to be switched off during measurements. The most important source of trouble comes from the fact that part of the photon beam illuminating the sample is reflected, extracting electrons from other surfaces: this effect is eliminated by a proper distribution of potentials within the cell and by focusing the electron beam from the sample into the entrance of the electron multiplier. Altogether, the true current emitted by the sample can be obtained within a few percent, even in the range of a few electrons per second. Since at the threshold energy the number per second of incoming photons is in the 10^{10} range, yield down to 10^{-10} can be accurately measured.

The recording conditions have to be specified, since the surface properties of silicon change at quite a fast rate, even at very low working pressures. In a typical experiment, the first recording starts about 2 min after cleavage and lasts 7 min. At a pressure of 5×10^{-10} Torr, a second recording between 10 and 17 min after cleavage shows a small but significant change compared to the first one (Fig. 1). At this pressure, the residual gas is essentially H_2; H_2O, N_2, and/or CO, and, at a lesser degree, CO_2 are also present. At a pressure of 5×10^{-11} Torr recordings are perfectly reproducible for more than 2 h, which gives ample time to obtain very precise measurements. In fact, the variation rate depends not only on the total pressure but also on the nature of the residual gases.

Altogether, the measurements give the quantum yield in arbitrary units with a resolution of 0.01 eV, imposed by the monochromator. The reproducibility on one sample is within a few per cent on the whole energy range. From one cleave to another, some differences appear; they will not be discussed here: only the common features of the results will be considered.

III. RESULTS

The main results are presented in Figs. 1 and 2. In Fig. 1, a typical evolution with time of the yield curves is shown for an *n*-type sample with 10^{15} carriers per cm^3 cleaved at a pressure of 3.6×10^{-10} Torr (similar results are obtained on samples with different impurity contents). Figure 2 shows the yield curves obtained within 1 h after cleavage at a pressure of about 5×10^{-11} Torr for a set of silicon samples of various types and doping levels. The changes with time which are observed in Fig. 1 occur over a few hours, and right after cleavage, the variation rate is small enough to allow a good determination of the yield curve for a clean surface without much distortion due to recording time. *A fortiori*, the curves of Fig. 2 are relevant of clean, cleaved surfaces.

In the results of Fig. 1, the band bending near the surface does not intervene, since the escape depth of electrons photoemitted from silicon is of 10 to 20 Å,[7] compared to a space-charge region depth of a few thousand angströms for the sample involved. The difference in behavior between the high- and low-energy parts of the yield curve must be pointed out: the high-energy part undergoes a mere translation toward lower energies as a function of time, while the low-energy part shows many changes in shape and energy. The high-energy behavior can be explained by bulk-state photo-

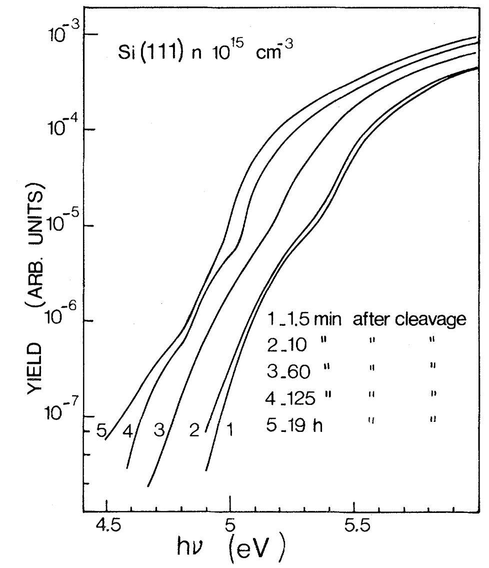

FIG. 1. Evolution of the yield curve (number of emitted electrons per incident photon) as a function of time for a cleaved, (111) face of n-type silicon with 10^{15} carriers/cm^3 at 3.6×10^{-10} Torr.

emission with a decreasing ionization energy. However, the structural changes which occur on the low-energy part of the yield can be attributed to an evolution of the surface-state density. In that picture, the high-energy part would be due essentially to bulk photoemission, whereas the low-energy part would be due to surface states.

The results obtained on differently doped samples (Fig. 2) bring an important confirmation of the above hypothesis. On the degenerate p-type sample, bulk electrons are present at the Fermi level so that the threshold coincides with the work function. As the doping changes towards nondegenerate p-type and n-type samples and because the work function of Si is practically doping independent,[6] the absolute threshold would shift towards higher energies if it were due to bulk-valence-electron photoemission, and a structure due to valence-band states would shift as well. However, the absolute threshold appears to be the same for all samples. Moreover, the structure observed on the low-energy side of the yield curves does not shift but becomes more and more pronounced as the band bending allows a better separation of the surface-state-electron emission. For the highly doped n-type Si, bulk electrons from the conduction band can be responsible for the slope changes close to absolute threshold. Thus, the absolute threshold is due to the surface states at and below the Fermi level and is independent of the bulk conditions. The low-energy part of the yield curves can be extrapolated to a unique value of 4.87 ± 0.02 eV, independent of the doping. This value is in very good agreement with that of 4.86 eV determined by Allen and Gobeli[6] and 4.83 eV by Erbudak and Fischer[9] from contact-potential measurements. This result also confirms that the Fermi-level position in the gap at the surface is practically independent of the doping level, if one assumes the ionization energy is not doping dependent.[15]

In order to dissociate the surface- and bulk-state contributions to the yield curves, the ionization energy and the shape of the valence-band contribution have to be determined. In Fig. 2, let us consider the yield curves of the slightly doped samples and of the most highly doped n-type sample. The lowering of the yield in the high-energy part of these curves compared to the low-energy behavior is most likely due to band bending, which, on these samples, acts only on bulk-state photoemission. This suggests that the influence of surface states can be neglected in that region of the curves, consistent with the conclusions drawn from Fig. 1. In the special case of the lightly doped samples where the bands are practically flat for the photoemission process, the high-energy part of the yield curve can be fitted with a $\frac{3}{2}$ power law. An excellent fit is obtained with a value of 5.35 ± 0.02 eV for the ionization energy. This implies that the photoemission yield, in the flat-band case, can be written

$$Y_{VB} \propto \int_{E_V}^{h\nu} (E - E_V)^{1/2} \, dE \, , \tag{1}$$

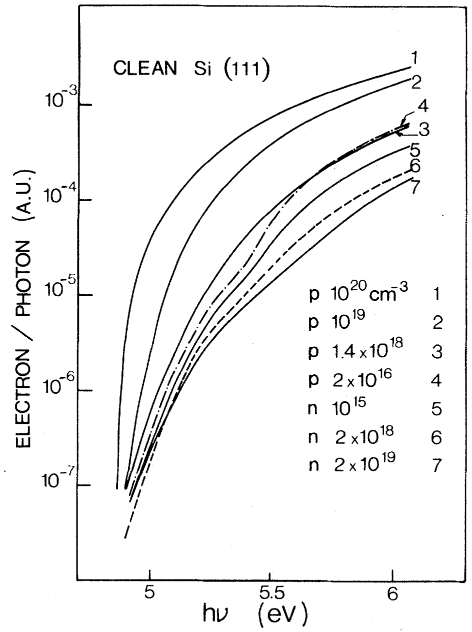

FIG. 2. Yield curves in arbitrary units obtained at 5×10^{-11} Torr within 1 h after cleavage along the (111) face of a set of silicon samples with different doping levels.

where E_V is the top of the valence band.

The bulk contribution to the yield curves has been checked by computing the valence-band contribution as a function of type and doping level of the samples. Comparison with the experimental curves should lead to a surface-state contribution arising from an SSD independent of the type and doping level of the different samples.

Since we simply want to account for the effect of band bending on the valence-band contribution to the yield curves, the calculation can be performed using simplified expressions if the band structure is considered independent of the distance x to the surface. (Up to now, the understanding of photoemission experiments did not need to take this effect into account, and it is shown that an electric field, even in the 10^6-V/cm range, does not appreciably change the band structure.) Then, if we use Spicer's three-step model,[16] and include the effect of light absorption and of the finite escape depth of the electrons, the yield can be written[17]

$$Y_{VB} \propto \int_{E=0}^{h\nu} \int_{x=0}^{\infty} n^*(E - E_V(x)) \times F(E) f_a(x) f_e(x) \tau(E)\, dE\, dx \ . \qquad (2)$$

$n^*(E - E_V(x))$ is a function of energy which accounts for initial- and final-state densities and transition probabilities; it depends on x only through $E_V(x)$, which locates the top of the valence band with respect to the vacuum level at depth x and thus accounts for band bending. This function can be called the effective density of states in the valence band, since it would be the actual density of states if both the transition matrix elements and the conduction-band density of states were constant. $F(E)$ is the Fermi-distribution function which we introduce to cover the cases where the Fermi level penetrates the valence band at high p-type doping levels. $f_a(x)$ is the number of photons still present at x; the photon absorption is assumed exponential with a constant characteristic length l_a, inverse of the absorption coefficient

$$f_a(x) \propto e^{-x/l_a} \ .$$

$f_e(x)$ is the escape function, i.e., the probability that an electron excited at x reaches the surface; it is taken as a simple exponential function

$$f_e(x) \propto e^{-x/l_e} \ ,$$

with an effective escape length l_e independent of energy[17] since the involved energy range is very small (about 0.65 eV from 5.35 to 6 eV). It appears that, in the case of silicon, l_a is about 10 times larger than l_e,[18] so that the photon absorption has negligible effect compared to the finite escape depth of the electrons. $\tau(E)$ is the threshold function,[17] i.e., the probability that an electron of energy E present at the surface does escape out of the crystal; it is assumed to be a step function independent of the surface-electric field due to band bending,

$$\tau(E) = \begin{cases} 0 & \text{for} \quad E < \varphi = \text{work function} \\ \text{const} & \text{for} \quad E > \varphi \ . \end{cases}$$

In the flat-band case, within the above assumptions, the variables of Eq. (2) separate, $F(E) \simeq 1$, and Eq. (2) must reduce to Eq. (1), which means

$$n^*(E - E_V(x)) = \begin{cases} [E - E_V(x)]^{1/2} = \left(E - E_{VB} - \dfrac{kT}{e}\, V(x)\right)^{1/2} & \text{for} \quad E > E_V(x) \\ 0 & \text{for} \quad E < E_V(x) \ , \end{cases}$$

where E_{VB} is the position of the valence band in the bulk, and $V(x)$ is the dimensionless value of the band bending.

The shape of $V(x)$ in the space-charge region has been determined using standard expressions,[19] and the results are presented in Fig. 3 for the different samples. The energy difference between the Fermi level and the top of the valence band at the surface E_{VS} has been taken equal to 0.48 eV, independent of type and doping level since the ionization energy is assumed doping independent and the work function is found to be practically constant. The parameter l_e is adjusted for each sample to obtain the best fit with the experimental data in the high-energy region.

The results for Y_{VB} are summarized in Fig. 4, for which a common value of 12 Å has been obtained for the effective-escape length of excited electrons, in agreement with other authors.[6,7]

We can now compare the experimental results of Fig. 2 with the computed curves of Fig. 4. For the most highly doped p-type sample, the contribution of surface states to photoemission is masked by the valence-band contribution: the agreement between experimental and computed curves is very good. For the next two p-type samples, the surface-state contribution cannot be neglected any more, but its determination is not accurate since it is small and overlaps very much the contribution of valence-band states.

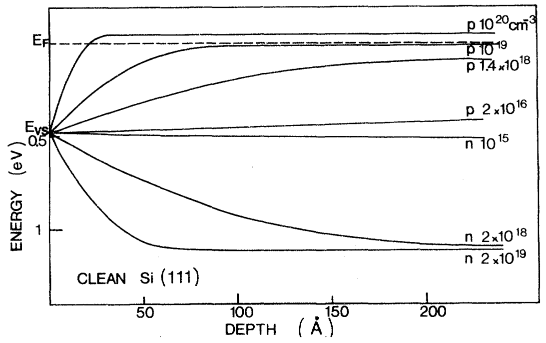

FIG. 3. Shape of the space-charge region for clean, cleaved, (111) face of silicon at various types and doping levels. Only the valence band is drawn.

The other four samples have experimental and computed yield curves which are markedly different, and a determination of the surface-state contribution to the photoemission yield is thus possible. In order to compare the relative values of this contribution from one sample to another, we have to recall that the experimental data are given in arbitrary units such that the absolute values at a given energy are not directly comparable. However, the computed results, which are proportional to the yield due to valence-band states, reflect the absolute change as a function of type and doping. Therefore, it is sufficient to adjust the high-energy part of the experimental curves with the corresponding computed one. Then, substracting the computed contribution of valence-band states from the adjusted experimental results, we obtain the surface-state contributions of the different samples. Let us remark that for these four samples, the contribution of the valence band is zero between the Fermi level and the top of the valence band at the surface. The results are shown in Fig. 5, curve 1. We note that, within about 10%, the contribution of surface states in the band gap to the photoemission yield is independent of the type and doping level of the sample.

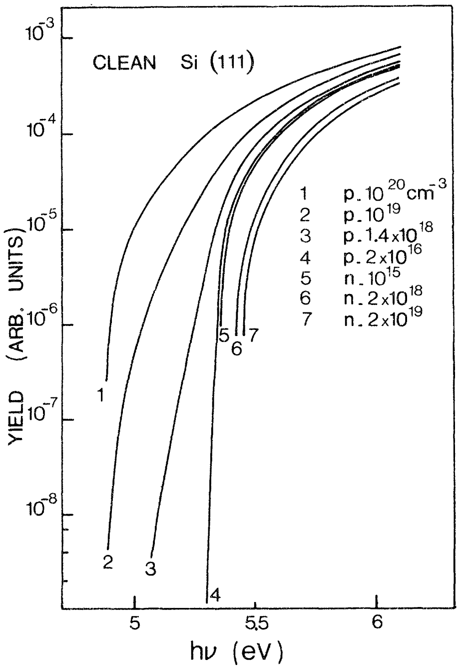

FIG. 4. Computed contribution of the valence-band electrons to the photoemission yield for samples of various types and doping levels.

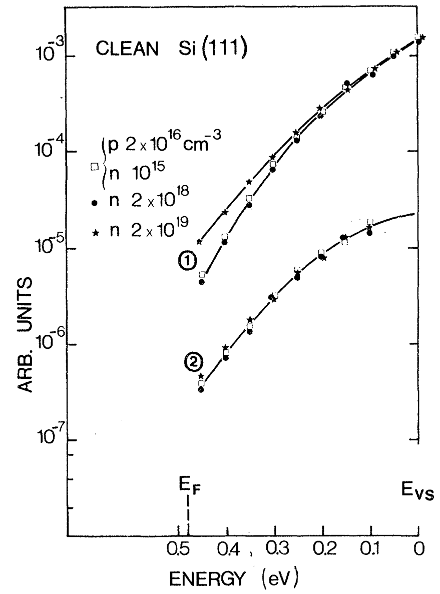

FIG. 5. Surface-state contributions to the photoemission yield for the different samples, referred to the top of the valence band (curve 1) and the corresponding first derivative showing the surface effective density of states (curve 2).

This result is very important and shows, in particular, (i) the pinning of the Fermi level in the band gap at about 0.48 eV, whatever type and doping level for the clean, cleaved, (111) face of silicon is demonstrated, except for a slight deviation at doping levels higher than 10^{19} cm^{-3} n type; (ii) that the 12 Å escape length of the electrons is confirmed.

In Fig. 5, curve 2 represents the first derivatives of curves 1, also in arbitrary units. It gives the shape of an effective SSD in the band gap below the Fermi level, in the same sense as $n^*(E - E_V(x))$ is an effective density of valence states for the bulk: curve 2 in Fig. 5 would be proportionnal to the actual SSD if both the transition matrix elements and the density of final states were constant and if the threshold function for surface states is a step function. From Fig. 5, we see that the effective

SSD increases from the Fermi level to the top of the valence band where it does not vanish, in agreement with the results of other authors.[7,8] A relatively good though approximate image of the shape of the effective SSD in the band gap is given by a $\frac{3}{2}$ power law. While independent of doping, the effective SSD is not identically reproducible from cleave to cleave; in fact, there is a dispersion in the region situated within 0.15 eV from the top of the valence band in the gap. This dispersion can be tentatively attributed to the effect of the step density at the surface.

IV. CONCLUSION

In this paper, we have shown that an accurate measurement of the total photoemitted current as a function of photon energy on a set of variously doped semiconducting samples with a resolution of 0.01 eV allows (i) the determination of the work function, ionization energy, and escape length of electrons and (ii) the separation of the bulk and gap surface-states contributions. This is quite general and can be applied to other semiconductors when reproducible surface conditions can be obtained.

In the case of the clean, cleaved, (111) face of silicon which has been studied here a work function of 4.87 ± 0.02 eV, an ionization energy of 5.35 ± 0.02 eV, and an escape length of 12 Å are obtained, independent of type and doping. The effect of band bending on the valence-state contribution to the photoemission yield can easily be calculated by simplifying assumptions and using the values of the last two parameters. The surface-state contribution leads to an effective SSD in the gap below the Fermi level, which can be very crudely represented by a $\frac{3}{2}$ power law. The present distribution is in over-all agreement with the steplike distribution starting at about 0.27 eV from the top of the valence band, which has been proposed earlier[20] to explain different experiments.

ACKNOWLEDGMENTS

The able technical assistance of D. Dagneaux and B. Hélie is gratefully acknowledged. The authors are indebted to Dr. F. Proix for numerous fruitful remarks.

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