Surface-field-induced feature in the quantum yield of silicon near 3.5 eV

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A broad feature near 3.5 eV was observed in the internal quantum-efficiency spectra of various silicon photodiodes. This appears to be the first time this feature has been reported. The feature was clearly resolved in spectra from photodiodes with strong surface fields at the oxide-silicon interface, but was small enough to preclude observation in a previously published spectrum of field-free silicon. The feature is attributed to a local maximum in the quantum yield for electron-hole pair production that is expected at direct transitions in the vicinity of the Γ point in the silicon Brillouin zone. Qualitative arguments suggest that the magnitude of the feature increases with increasing surface field due to field-assisted impact ionization, and in the case of depleted surfaces, also due to band-gap narrowing in the surface-depletion region.

INTRODUCTION

This paper reports measurements of the ultraviolet quantum yield of silicon in the presence of strong surface fields. These measurements show a broad peak near 3.5 eV that is not present, or at least is much smaller, in field-free silicon. This seems to be the first time this feature has been reported.

The quantum yield for electron-hole pair production in a semiconductor is the number of electron-hole pairs produced per absorbed photon. For photodiodes in which all photogenerated electron-hole pairs are collected without loss, the quantum yield is equal to the internal quantum efficiency, that is, the external quantum efficiency divided by one minus the reflectance. In photodiodes where recombination competes with collection by the junction, the quantum yield is equal to the ratio of the internal quantum efficiency to the collection of the diode junction.

Silicon is an indirect semiconductor whose indirect gap at room temperature is about 1.1 eV. This means that some of the electrons that are photogenerated at the threshold of the direct transition are energetic enough to create secondary electron-hole pairs through an impact-ionization process, and the quantum yield can exceed unity above this threshold. Moreover, the quantum yield has local maxima in regions where a significant contribution to the absorption coefficient comes from the neighborhood of a valence-band maximum or a conduction-band minimum. In this case one of the two photogenerated carriers has all of the excess energy and is much more likely to stimulate an impact ionization than when the energy is divided equally between the two carriers.[1] Since the threshold of the first direct transition in silicon, which occurs at ~ 3.5 eV, involves transitions from the $\Gamma_{25'}$ point at the top of the valence band to the Γ_{15} point in the conduction band, a local maximum in the quantum yield is a possibility at this photon energy.

Strong electric fields should increase the quantum yield by accelerating some of the energetic photogenerated carriers to even higher energies.[2] Moreover, surface fields accumulate, deplete, or invert the oxide-silicon interfaces. The high accumulation and inversion charge densities cause band-gap narrowing through many-body effects,[3] while the depletion-charge density causes band-gap narrowing due to the unscreened impurity ion potentials.[4] Any band-gap narrowing that reduces the energy needed to create a new electron-hole pair through impact ionization will increase the quantum yield accordingly.

Before we describe the internal quantum-efficiency measurements that we carried out on various types of photodiodes having strong surface fields, we will review the theory of the quantum yield for field-free silicon while generalizing it to the case of a nonzero field. Then, after describing the quantum-efficiency measurements and their results, we will interpret the latter in terms of the generalized theory of the quantum yield.

QUANTUM YIELD THEORY

The existence of a local maximum in the quantum yield can be explained in terms of (1) the process by which the absorbed photons distribute carriers over the silicon Brillouin zone (BZ),[1] and (2) the impact-ionization process by which energetic carriers lose energy to create new electron-hole pairs.[5]

We generalize the expression for the quantum yield for field-free silicon given in Ref. 1 to the case of an electric field as

$$\eta(\xi,h\nu)=1+\int dE\, P(h\nu,E)N(\xi,E)\ , \tag{1}$$

where $P(h\nu,E)$ is the joint distribution of photogenerated electrons and holes over the carrier kinetic energy E as a function of the energy $h\nu$ of the absorbed photon, and $N(\xi,E)$ is the average number of electron-hole pairs created by the impact ionization of a valence-band elec-

tron by a free carrier created with kinetic energy E in the presence of the electric field ξ.

Consider the function $P(h\nu,E)$. It describes the distribution of photogenerated carriers with respect to their kinetic energy E due to the absorption of a photon of energy $h\nu$. This function has a number of important properties. It is symmetric about $E=(h\nu-E_i)/2$, where E_i is the energy required to create an electron-hole pair across the indirect gap E_g. Notice that $E_i > E_g$ if the states near one of the band edges are occupied as is the case in heavily doped material. Also, notice that $P(h\nu,E)$ is zero for $E \leq 0$ and for $E \geq h\nu-E_i$ by conservation of energy, and its integral with respect to E is 2 (one electron plus one hole per pair).

Now consider the function $N(\xi,E)$ in Eq. (1). Its most important property is that it is a very steep function of the carrier kinetic energy E for small E.[5] Because it is so steep, $N(0,h\nu-E_i)$ gives the appearance of a hard threshold above 2.5 eV, but in fact, the true threshold, which is unobservable, occurs at $h\nu=2E_i \approx 2.2$ eV as determined by conservation of energy.[5]

Because $N(0,E)$ is a very steep function of E near the apparent threshold for impact ionization, the minimum value of $\eta(0,h\nu)$ for a given value of E_i is obtained when $P(h\nu,E)$ consists of a single δ function located at $E=(h\nu-E_i)/2$. Similarly, the maximum value of $\eta(0,h\nu)$ is obtained when $P(h\nu,E)$ consists of two δ functions, one at $E=0$ and the other at $E=h\nu-E_i$. In the region within a few tenths of an eV of the apparent threshold, the ratio of the maximum allowed quantum yield minus one to the minimum allowed quantum yield minus one is greater than 5×10^4. This shows how much greater the probability of impact ionization is if all the excess photon energy is given to either the electron or the hole rather than being divided equally between them. This is the reason that the quantum yield can have local maxima whenever the band edges are involved in the absorption process.

The dependence on surface field of the size and shape of the local maximum in the quantum yield can be qualitatively explained in terms of the acceleration to higher energy of the photogenerated carriers by the surface field,[2] and any band-gap narrowing[3,4] that occurs due to the charge imbalance caused by the surface field.

It does not appear possible to directly apply the results of the lucky-drift theory of impact ionization[2] in semiconductors to calculate $N(\xi,E)$ in terms of $N(0,E)$. The problem is that the lucky-drift theory is based on an approximately Maxwellian distribution of carriers over kinetic energy, while the distribution $P(h\nu,E)$ is markedly non-Maxwellian. Nevertheless, it is clear that $N(\xi,E)$ will increase with increasing electric field ξ. Besides this direct effect, the band-gap narrowing effects due to the charge imbalance associated with strong surface fields could cause a significant increase in $N(\xi,E)$ near the onset of the direct transition in silicon. A decrease of ΔE_i in E_i causes the apparent threshold of $N(\xi,E)$ to decrease by ΔE_i, and replaces $N(\xi,E)$ by $N(\xi,E+\Delta E_i)$. Because $N(\xi,E)$ is a very steep function of E near the threshold for impact ionization, $\eta(\xi,h\nu+\Delta E_i)-1$ can be significantly larger than $\eta(\xi,h\nu)-1$ for relatively small values of ΔE_i.

QUANTUM YIELD MEASUREMENTS

We measured the reflectance $\rho(h\nu)$ and the absolute spectral responsivity $R(h\nu)$ in A/W of front-irradiated photodiodes with inverted and depleted oxide-silicon interfaces as a function of photon energy $h\nu$ in the 3- to 4-eV spectral region. We calculated the internal quantum efficiency as

$$\eta(h\nu)=\frac{Kh\nu R(h\nu)}{1-\rho(h\nu)} , \tag{2}$$

where $K=1$ W A^{-1} eV^{-1}.

The relative spectral responsivity of the photodiodes was measured against a new version of a gold-black bolometer described previously.[6] The absolute responsivity was determined at the wavelength of 633 nm by reference to self-calibrated silicon photodiodes which had been directly compared to an electrical substitution radiometer.[7] An absolute, normal incidence reflectometer[8] was used to measure the specular component of reflectance of two of the photodiodes with dissimilar reflectance characteristics. These specular measurements were corrected to total reflectance on the basis of measurements of the ratio of diffuse to total reflectance by using an integrating sphere. The absolute reflectance values so obtained for these two photodiodes were then used to calibrate the reference port of an integrating sphere, used in turn to measure the reflectance of the remaining photodiodes. The internal quantum-efficiency data calculated from these results using Eq. (2) are estimated to be accurate to within $\pm0.4\%$.

All of the photodiodes that we measured had nominal 1 cm^2 active areas that were passivated with a thermal oxide, and all of them had strong surface fields due to positive charge trapped in the oxide. Since the absorption coefficient of silicon is very large in the ultraviolet, a substantial fraction of the incident irradiation was absorbed in the region of the surface field.

The internal quantum efficiencies of five Unite Detector Technology (UDT) inversion-layer photodiodes[9] and of three experimental inversion-layer photodiodes were measured. These types of photodiodes have induced junctions that are formed by inverting the front regions of p-type substrates with the positive charge that is trapped in a thermal oxide.[10] The major difference between the two types of inversion-layer photodiodes was that the experimental diodes had about five times as much positive charge trapped in their oxides as did the other type as indicated by an extended linearity range. There was a significant difference between the means of the quantum efficiencies of the two different types of inversion-layer photodiodes, as discussed later.

The internal quantum efficiency of a Hamamatsu[11] type-1337 photodiode was measured as representative of a photodiode having a depleted oxide-silicon interface. This type of photodiode has a thermal oxide about 35 nm thick over a shallow p^+ (about 5×10^{18} cm^{-3}) front region in a lightly doped (about 5×10^{12} cm^{-3}) n-type substrate. We refer to this type of diode as a depletion-layer

photodiode throughout the remainder of this paper, even when its front surface is so strongly depleted that it is inverted. Notice that inversion of the front surface of this type of photodiode does not create an inversion-layer photodiode. The inversion and/or depletion layer in a depletion-layer photodiode competes with the metallurgical junction for minority carriers, whereas the inversion layer in the inversion-layer photodiode is an extension of the junction depletion layer and contributes to the collection of minority carriers.

The internal quantum efficiency of a new type of photodiode described recently[12,13] was measured as representative of photodiodes with accumulated oxide-silicon interfaces. There was no significant difference between the spectrum for this photodiode and for the experimental inversion-layer photodiodes and the results for this photodiode will not be discussed further.

Since the surface field in the inversion-layer photodiodes drives the photogenerated minority carriers away from the oxide-silicon interface and its high concentration of intraband states, these diodes usually have 100% collection efficiency.[13,14] On the other hand, the surface field in depletion-layer photodiodes drives the minority carriers toward the interface where they can recombine.[15] As a result, this type of photodiode usually has less than unit collection efficiency, as explained in a little more detail in the next section.

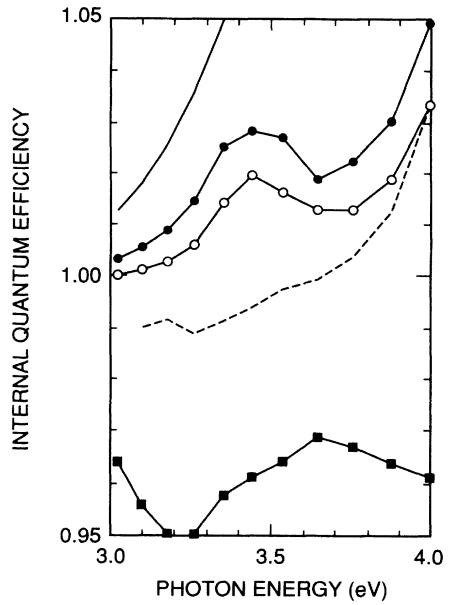

FIG. 1. The internal quantum-efficiency spectra of different types of silicon photodiodes between 3 and 4 eV. The greater than unity quantum efficiency and the local maxima both result from the fact that the quantum yield of silicon (average number of electron-hole pairs created per absorbed proton) is greater than unity in this spectral region due to the impact ionization of valence-band electrons by some of the most energetic photogenerated carriers. The spectra shown are typical of the following photodiode structures: (1) oxide/p^+nn^+ with depleted oxide-silicon interface (solid squares), (2) commercial inversion layer (solid circles), (3) experimental inversion layer (open circles), and (4) oxide/p^+nn^+ with flatband interface (dashed line). The upper limit for the quantum yield of field-free silicon is also shown as the continuous curve at the upper left of the figure.

EXPERIMENTAL RESULTS

The results of the internal quantum-efficiency measurements described above are shown in Fig. 1. Average spectra for the different types of photodiodes are shown as follows: Open circles for the experimental inversion-layer photodiodes, solid circles for the UDT inversion-layer photodiodes, and solid squares for the depletion photodiodes. The solid curve at the upper left of the figure is the upper limit for the quantum yield of field-free silicon. The dashed line applies to field-free silicon as discussed in the next section.

The spectrum for the depletion-layer photodiode has a large, broad peak superimposed upon an internal quantum efficiency that decreases with increasing photon energy. This reflects the interaction of the competition for photogenerated minority carriers between recombination at the oxide-silicon interface and collection by the diode junction, and the increase in the silicon absorption coefficient with increasing photon energy in this spectral range.

The field associated with the depletion layer attracts the photogenerated minority carriers toward the interface where recombination centers are localized. Photons of different energy create these carriers at a different average distance from the interface depending upon the absorption coefficient. However, above about 3.6 eV, the average absorption depth is less than the minority carrier diffusion length, so it does not matter where the photons are absorbed. But below 3.6 eV, the average absorption depth, which decreases with increasing photon energy, determines the fraction of the photogenerated minority carriers that will recombine at the oxide-silicon interface instead of being collected by the diode junction, and thereby determine the spectral dependence of the internal quantum efficiency.[15]

The spectra for the different types of inversion-layer photodiodes have peaks similar to, but less broad than, that observed for the depletion-layer photodiode. There is no recombination loss at the oxide-silicon interface for these photodiodes because the field associated with the inversion[14] and accumulation layers[12,13] repels the photogenerated minority carriers away from the recombination centers localized at the interface.

COMPARISON WITH FIELD-FREE QUANTUM YIELD

A quantum yield spectrum for photodiodes with an oxide-silicon interface at the flatband condition was reported previously by Wilkinson, Framer, and Geist[16] (WFG). These authors measured the reflectance and relative spectral responsivity of three p^+nn^+ photodiodes in the 3.1- to 6-eV spectral region. They used a corona discharge[17] to store electrons on the thermal oxide of depletion-layer photodiodes to minimize the effects of recombination occurring at the oxide-silicon interface. Their goal was to apply enough charge to completely eliminate the effect of interface recombination, and there-

by isolate the effect of the quantum yield, under the assumption that the quantum yield was independent of electric field.

The criterion that WFG used to terminate the corona charging produced a nearly flat band condition at the interface.[18] Later attempts[19,20] to apply oxide bias with a corona discharge induced very large positive charge accumulation at the oxide-silicon interface, as indicated by a dramatic deterioration of the collection efficiency of the photodiodes upon removal of the charge.[18] The difficulty in controlling the corona discharge caused it to be abandoned as a means of applying oxide bias. However, the difference between the postcorona behavior of the photodiodes used by WFG and those used in Ref. 19 and 20 is important. It confirms that the measurements made by WFG were on photodiodes whose oxide-silicon interfaces were near the flatband condition. Therefore WFG actually measured the quantum yield for field-free silicon, and that fact is important for the interpretation of our data.

Except for the rise in quantum efficiency starting at about 3.3 eV, no feature as large as 1% is evident in the portion of the WFG spectrum shown in Fig. 1. The features smaller than 1% are not believed to be real, but to reflect small measurement errors. Perhaps the inflection point around 3.6 eV is the local maximum that is evident in the internal quantum-efficiency spectra of the photodiodes with the strong surface fields. However, this feature is too small, relative to other features that are believed to be measurement errors, to allow a firm conclusion. Below 3.7 eV the small average difference between the internal quantum efficiency and unity is caused by the competition between the recombination of photogenerated minority carriers at the oxide-silicon interface and the collection of these carriers by the junction as described in the preceding section in connection with the depletion-layer photodiodes.

INTERPRETATION OF DATA

In order to interpret the data in Fig. 1 in terms of the theory of the quantum yield, we define

$$L(h\nu)=[\eta(h\nu)-1]/N(0,h\nu-E_i)\ , \tag{3}$$

where $\eta(h\nu)$ is the measured quantum yield, and $N(0,h\nu-E_i)$ is the upper limit for the quantum yield in the absence of an electric field.

The function $L(h\nu)$ was calculated from the internal quantum-efficiency spectra shown in Fig. 1, and the results are plotted in Fig. 2. The internal quantum-efficiency spectra for the inversion-layer photodiodes were used without correction, but the spectra for the depletion and flatband photodiodes were divided by nominal collection efficiency data as described below.

The collection efficiency calculations were done with PC-1D,[9,21] which is a one-dimensional, solar cell modeling program that iteratively solves the drift-diffusion equations with realistic models of the transport properties. The surface charge at the oxide-silicon interface was set to zero for the flatband photodiode, and to $2\times10^{12}\ |e|\ \mathrm{cm}^{-2}$ for the depletion-layer photodiode, and the surface recombination velocity for each photodiode was adjusted to obtain a collection efficiency that caused $L(h\nu)$ to approach zero at 300 nm. The values so obtained were 1500 cm/s for the flatband photodiode and 3000 cm/s for the depletion-layer photodiode.

The value of $2\times10^{12}\ |e|\ \mathrm{cm}^{-2}$ is nominal, but the surface recombination velocity and surface charge are strongly correlated in determining the collection efficiency. In fact, setting the surface charge density to $2\times10^{11}\ |e|\ \mathrm{cm}^{-2}$ and the recombination velocity to 86 000 cm/s gives the same collection efficiency from 2.8 to 4.1 eV within 5 parts in 10^4. Therefore the error introduced by using the nominal surface charge density in the collection efficiency calculation is very small.

The values of $L(h\nu)$ calculated as described above are plotted in Fig. 2. Notice that any errors in the quantum-efficiency measurements or the collection efficiency calculation are magnified as the photon energy decreases due to the rapid decrease in $N(0,h\nu-E_i)$ with decreasing photon energy.

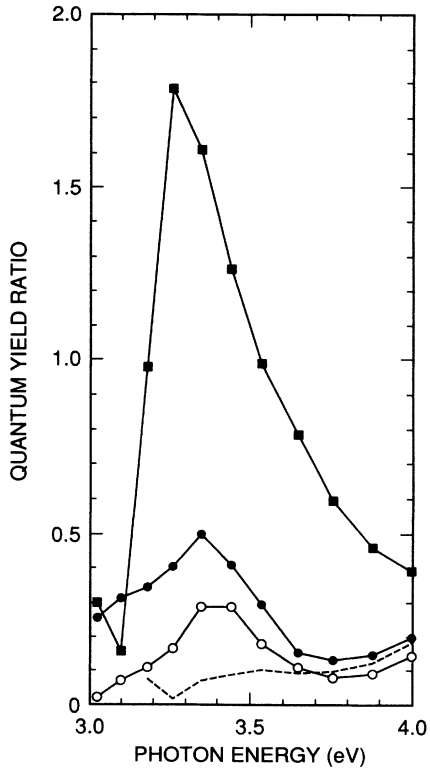

FIG. 2. The ratio of the quantum yield for the types of photodiodes shown in Fig. 1 to the upper limit for the quantum yield of field-free silicon. (The symbol key is given in the caption for Fig. 1.) Corrections for the difference between unity and the internal quantum efficiency of the oxide/p^+nn^+ photodiodes were applied in calculating these spectra. The spectra for the photodiodes with the surface fields are increased relative to that for the photodiode with the field-free (flatband) front region due to the field-assisted impact ionization of energetic photogenerated carriers. The spectrum for the depletion-layer photodiode is further increased due to the effect of band-gap narrowing in the depletion region.

If there is a local maximum in the quantum yield of field-free silicon near 3.5 eV, it is not resolved in the data of Fig. 2. On the other hand, the local maxima in the quantum yield spectra of the photodiodes having the strong surface fields are well resolved. The locations of the peaks in this figure have been shifted to lower photon energies from their locations in Fig. 1, and should be better estimates of the location of the Γ point in silicon in the presence of strong electric fields. Also, the local maximum in the quantum yield is much larger in the depleted silicon than in the inverted and accumulated silicon.

According to the theory of the quantum yield discussed earlier in this paper, there are two effects causing the local maximum in the quantum yield of the photodiodes with the strong surface fields. The first of these is the field itself, which will raise some of the energetic photogenerated carriers to even higher energy, greatly increasing the probability that they will impact ionize a valence-band electron before losing a significant amount of energy to photon emission. The strength of this effect depends directly upon the surface charge density at the oxide-silicon interface.

The discussion of the role of the surface field must remain qualitative because we do not know the interface-charge density for the photodiodes. A nominal interface-charge density of 2×10^{12} $|e|$ cm^{-2} creates a field that decreases from 300 to 200 kV/cm over about 1 nm, the exact distance depending upon whether the interface is accumulated, depleted, or inverted. The avalanche ionization coefficient for electrons is about 10^4 cm^{-1} for an electric field of 200 kV/cm.[2] This gives an avalanche multiplication factor in the range from 10^{-3} to 10^{-2} for band-edge electrons. This is too small to explain the size of the peaks in the quantum yield spectra for the accumulated and inverted silicon interfaces compared to the flatband spectra. However, this is not a problem. The electrons that are losing energy through impact ionization are not near the conduction-band edge, but are very high in the band due to photogeneration from the top of the valence band. Therefore a much greater avalanche multiplication factor can be imputed to them.

The second effect of a strong surface field that can contribute to an increase in the quantum yield is the band-gap narrowing associated with the charge imbalance in the silicon near the oxide-silicon interface. This effect must also be treated qualitatively. The calculations of Ref. 22 suggest that for inversion layers ΔE_i increases with increasing surface charge density, reaching a maximum value of about 25 meV at about 5×10^{11} $|e|$ cm^{-1}, and then decreases with increasing surface charge density. The reason for this is that the movement of the Fermi level into the conduction band fills the states near the band minimum in such a way that the energy E_i needed to create a new electron-hole pair by impact ionization across the indirect gap decreases very little even though E_g, the minimum energy difference between a valence-band hole and a conduction-band electron, decreases substantially starting at about 10^{11} $|e|$ cm^{-2} surface charge. Thus, even though there is substantial band-gap narrowing, its effect on the ionization energy E_i is compensated by the movement of the Fermi energy into the conduction band, and the net effect on the quantum yield is small.

Notice that the quantum yield for the experimental inversion-layer photodiodes is less than that for the UDT inversion-layer photodiodes, even though the experimental inversion-layer photodiodes have more positive charge trapped in their oxides, and therefore a larger surface field. This would suggest that the decrease ΔE_i in the impact-ionization band-gap energy E_i above a surface concentration of about 5×10^{11} $|e|$ cm^{-2} that is associated with the increased surface charge density in the experimental devices more than compensates for the increased surface field in its effect on the quantum yield. That this is plausible is shown by the very large quantum peak for the depletion-layer photodiode, which is discussed next.

Reference 4 reports that $\Delta E_i = 330$ meV in the depletion region of a p^+n^+ diode having a substrate doping concentration of 5×10^{18} cm^{-3}. This is the doping concentration at the oxide-silicon interface in the depletion-layer photodiode whose quantum efficiency is plotted in Fig. 1. However, Ref. 3 also points out that this result is very dependent upon the doping gradient as well as doping concentration, so this number is only illustrative.

Nevertheless, it is qualitatively true that a large amount of band-gap narrowing is expected in the silicon at the depleted interface compared to a small or negligible amount in the silicon at the inverted and accumulated interfaces. This difference in band-gap narrowing apparently increases the quantum yield for the depleted silicon well above that for the inverted silicon, while the field-assisted impact ionization increases the quantum yield for the latter well above that for the field-free silicon as shown in Fig. 2.

It would be quite difficult to replace the qualitative picture given above by a quantitative analysis. First, the competition with the indirect transition would have to be included. This would not be difficult. Second, the theories of field-assisted and photoexcited impact ionization would need to be combined. This is probably not too difficult, but obtaining experimental data for the multiplication factors might be. Third, the spatial dependence of the dopant profiles, and of the depletion- and inversion-charge densities, would have to be taken into account, as would the spatial dependence of the electric field, the band-gap narrowing, and the photon absorption density. Furthermore, the effect of the band-gap narrowing on the absorption coefficient could also be important. Handling all of these effects simultaneously would not be easy at the current state of the art. Finally, a much more accurate band structure than that used in Ref. 1 would be required before even considering the effects of the surface field and band-gap narrowing. We wonder whether the needed band-structure and band-gap narrowing calculations are within the current state of the theoretical and computational art. Finally, it is not clear that the surface charge densities in the heavily doped accumulation and depletion layers can be measured with existing techniques. Nevertheless, the qualitative discussion seems to have identified the major effects and their relative importance in the different surface-field effects.

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