Surface Space-Charge Dynamics and Surface Recombination on Silicon (111) Surfaces Measured with Combined Laser and Synchrotron Radiation

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The results of a new experiment, which records transient, pulsed-laser-induced surface photovoltages by following photoemission shifts measured with synchrotron radiation, are reported. Comparison of the surface photovoltage decays with numerical simulations reveals large surface-recombination rates for a variety of Si(111) surface preparations. The space-charge layer near the surface is found to govern the surface and bulk carrier concentrations to a remarkable extent, particularly when band bending is large.

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Electron-hole pairs introduced with a light pulse near the space-charge layer (SCL) at the surface of a semiconductor move to reduce the band bending, thereby producing a transient surface photovoltage (SPV). Since band bending represents a potential barrier to one sign of carrier and a potential well to the other, its instantaneous magnitude strongly influences the carrier densities near the surface. In spite of the importance of the surface carrier density to photochemical processes, such as etching, deposition, and desorption, there is little experimental knowledge of SPV transients and their role in controlling surface recombination and carrier density, particularly in larger excitation regimes. Here we report the first measurements and analyses of SPV on well characterized surfaces using a new photoemission technique which combines pulsed-laser excitation with synchrotron radiation and provides nanosecond resolution.[1] The method uses a pulsed copper-vapor laser to inject carriers within 1 μm of Si(111) surfaces, and the SPV is measured in real time via the shift of the Si $2p$ core-level photoemission spectrum.

The principal conclusions of the work thus far are as follows. To high accuracy, the core-level spectrum shifts rigidly with excitation up to carrier concentrations of 5×10^{18} cm^{-3} at the surface. A numerical transport model has been shown to simulate the SPV decay over a wide range of excitation levels, strongly suggesting that for this set of n- and p-type Si(111) samples with clean, hydrogenated, air-oxidized, or disordered surfaces, the primary determinant of the SPV decays on nanosecond and longer time scales is carrier transport within the SCL as opposed to dynamics of trapped surface charge. For all surfaces investigated, the recombination velocity at the surface, s_0, is large, of the order of 10^6 cm/s. In addition, we have discovered that, for large initial band bending, the SCL can play a dominant role in governing carrier diffusion into the bulk, because it acts as a reservoir for photoexcited carriers. Recombination is suppressed in the reservoir because electrons and holes are separated, and this can *enhance* carrier density long after the bulk recombination time. For low laser fluences, however, filling the reservoir *limits* the density of bulk carriers.

The experiments were performed on beam line X24C of the National Synchrotron Light Source.[2] Laser pulses (510 nm, 20 ns) triggered at 6 kHz were focused to a 5-mm spot concentric with the 1-mm synchrotron spot. The SPV was measured by recording, with a time-to-digital converter, the time-dependent change of count rate as the Si $2p$ core level shifted through the energy window of the cylindrical mirror electron analyzer. The changes in count rate were converted to SPV shifts by using the measured core line shape. The line shape was constant during the photovoltage shifts as verified by recording time-resolved spectra with the storage ring operating in single-bunch model. Samples were prepared from n-type (1.1×10^{16} P) and p-type (4.7×10^{16} B) Si(111) wafers chemically stripped of a 5000-Å oxide layer, and then subjected to the final step in the Shiraki cleaning method.[3] Resistive heating in UHV at 930 °C produced clean surfaces as verified with Auger-electron spectroscopy. The surface preparation is expected to produce the stable 7×7 surface.[4] Data were subsequently obtained after hydrogen dosing, Ar^+-ion sputtering, and sputtering and annealing.

The elements of the SPV are outlined in Fig. 1(a). For concreteness, we will limit the discussion to p-type samples unless otherwise stated. A SPV is created when photoexcited electrons and holes in the SCL separate to screen the surface charge responsible for the band bending, as shown in 1(b), thereby reducing the band bending Y_0 to a new value, Y, indicated by the dashed energy levels. The SPV is $\Delta V = Y_0 - Y$, which appears as a rigid shift of the photoemission spectrum.[5] An additional contribution to ΔV occurs if the surface charge density $e\Sigma_0$ assumes a new value, $e(\Sigma_0+\delta\Sigma)$, through surface-bulk carrier interchange or direct photoexcitation. The Dember voltage, a small correction, is included in the numerical simulations below.

If the quasi-Fermi levels for holes and electrons are

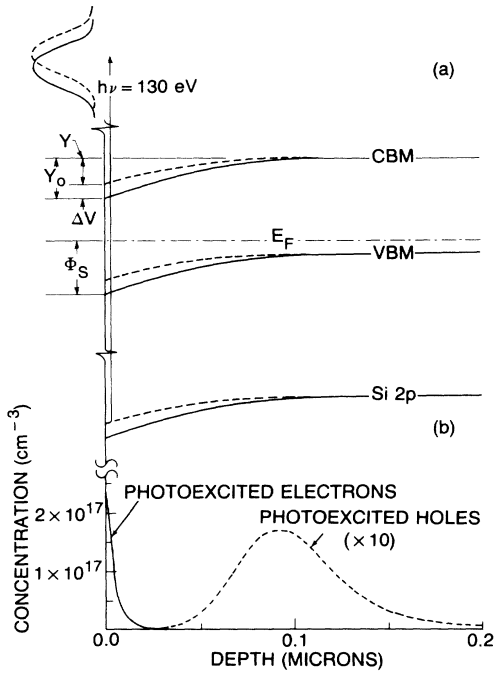

FIG. 1. (a) Band bending of the conduction-band minimum (CBM), valence-band maximum (VBM), and Si 2p core level for equilibrium (solid line) and photoexcited (dashed line) conditions. Note SPV shift of core-level spectrum. Fermi level, E_F, is undefined for excited conditions. (b) Nonequilibrium carrier densities 1 μs after the 100-μJ/cm^2 laser pulse.

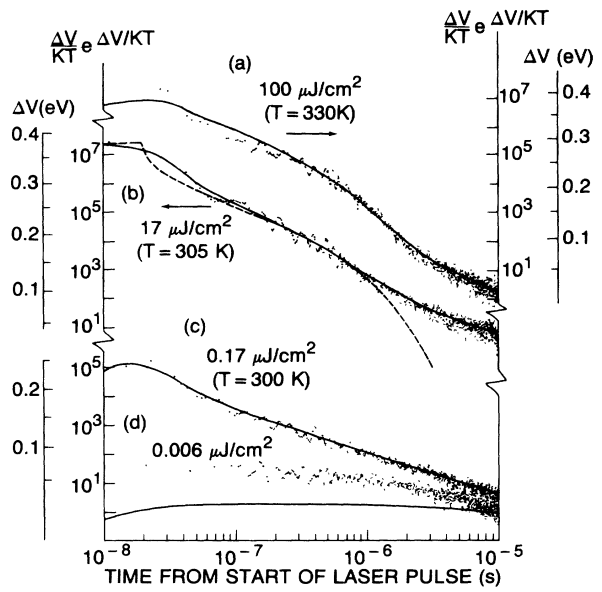

FIG. 2. Measured (dots), numerically (solid lines), and analytically (dashed lines) simulated SPV decays for the hydrogen-saturated, p-type, Si(111) surface.

flat throughout the SCL, if $Y_0 \gg kT$, and if $Y > kT$, then ΔV may be expressed as[6]

$$\frac{\Delta V}{kT} e^{\Delta V/kT} = \Delta_p e^{Y_0/kT} - \left(\frac{Y_0}{kT} - 1\right)\left[2\frac{\delta\Sigma}{\Sigma_0} + \left(\frac{\delta\Sigma}{\Sigma_0}\right)^2\right] e^{\Delta V/kT}, \quad (1)$$

where $\Delta_p \equiv \delta p(x_d)/p_0$, p_0 is the doping density, and $\delta p(x_d)$ is the excited carrier density just beyond the SCL, a distance x_d from the surface. For the data presented here, $x_d \sim 0.2$ μm. The first term on the right-hand side accounts for screening by carriers within the SCL; the second term accounts for changing surface charge. In general, $\delta\Sigma$ must be obtained from rate equations for carrier interchange between surface and bulk and among surface levels.[7] In the simulations of ΔV below, we find it unnecessary to incorporate $\delta\Sigma$, a point to which we return later.

We note in passing that the explicit temperature dependence of Eq. (1), which we have verified for 300 K $\leq T \leq$ 425 K, is entirely sufficient to account for the saturation by synchrotron radiation of the SPV observed in Si at cryogenic temperatures and attributed solely to a freezeout of surface recombination.[8]

Representative results are shown in Fig. 2 where, guided by Eq. (1), we plot $(\Delta V/kT)e^{\Delta V/kT}$ versus time. A hydrogen-saturated, p-type sample has been chosen for illustration because the large Y_0 provides a more telling example of the reservoirlike qualities of the SCL. Numerical simulations are shown in Fig. 2 as solid curves and are derived from PISCES,[9] a finite-difference code which simultaneously solves Poisson's and the continuity equations for electrons and for holes. Surface recombination is incorporated such that the electron and hole currents at the surface are equal at all times, i.e., $\delta\Sigma \equiv 0$. For the conditions of these experiments, the PISCES treatment reduces to a description of surface recombination through a recombination velocity, s_0, defined *at the surface*. The only free parameters are Y_0 and s_0, since the ambipolar diffusion[10] and optical-absorption[11] constants are known, the laser intensity was measured, and the bulk recombination time (0.4 μs for the p-type sample, and 14 μs for the n-type sample) was determined directly from separate band-gap luminescence measurements.

Within the accuracy of the measured input parameters, the PISCES simulations reproduce in detail a wide array of data surprisingly well, in both absolute magnitude and time dependence. For the decays of Fig. 2, we obtain $s_0 = (2 \pm 1) \times 10^6$ cm/s. The Fermi level at the surface is $\Phi_s = 0.64$ eV above the valence band (derived from Y_0). Y_0 and Φ_s depended on hydrogen dosing until saturation. From the core-level shift between the saturated and clean surfaces, we obtain $\Phi_s = 0.58$ eV for the clean surface, in agreement with published data.[8,12]

The PISCES solutions reveal that the quasi-Fermi levels are sufficiently flat through the SCL for Eq. (1) to be valid when $\Delta V > kT$. Thus, for $\delta\Sigma = 0$, Δ_p can be ob-

tained from the values of $(\Delta V/kT)e^{\Delta V/kT}$ via the proportionality factor $e^{Y_0/kT}$, equal to 2×10^7 for Fig. 2(a) and 2×10^8 for 2(b), 2(c), and 2(d). The difference is due to temperature and slightly different values used for Y_0. Furthermore, the electron and hole densities at the surface, which are relevant to surface photochemical processes, can be simply expressed as $n_s = p_0\Delta V/kT$ and $p_s = p_0\exp(\Delta V - Y_0/kT)$. Note that $n_s \sim 10^5 p_s$ for typical values of Y_0 (0.5 eV) and ΔV (0.25 eV). Also n_s decays rather slowly, as ΔV, which depends quasilogarithmically on Δ_p. The consequence of neglecting the SCL's influence on Δ_p is demonstrated by the dashed simulation of the 17-μJ/cm^2 curve, which is the prediction of Eq. (1) when $\Delta_p(t)$ is obtained from the analytical solution of the diffusion equation.[13] The simulation fails at late times, and will clearly fail for lower laser fluences since its shape is independent of fluence when plotted as in Fig. 2.

Since n_s/p_s is large, the surface-recombination carrier current density, J_{sr}, is limited by holes, the surface minority carrier. A simple kinetic model[14,15] then gives $s_0 = Pv/4$, where v is a thermal velocity and P is the effective probability that a hole striking the surface is captured by an occupied surface level. Using $v/4 = 4\times10^6$ cm/s, we find $0.1 \le P \le 1$ for all surfaces examined. Furthermore, for large n_s/p_s, it can be shown that the conventionally defined surface-recombination velocity, $s = J_{sr}/\delta p(x_d)$, is related to s_0 by $s = s_0/(\Delta V/kT)$.[16] We will not discuss the SPV decay for $\Delta V \le kT$, where s is limited by thermal emission from recombination levels, gradients in the quasi-Fermi levels, and the thermal velocity.

An examination of the PISCES solutions, coupled with detailed calculations, leads to the following understanding of the SPV decays. As shown in Fig. 1(b), nonequilibrium electrons and holes are formed into separated populations by the SCL electric field, and thus cannot recombine efficiently. For the data in Fig. 2(a), the shoulder at ~1.7 μs [and the plunge in the analytical simulation of Fig. 2(b)] reflects the recombination in the bulk. The later tail is caused by the much longer lifetime of the separated space-charge populations. These serve as a reservoir, supplying carriers to the bulk at a rate sufficient to overcome the surface-recombination current after ~3 μs, so that the net carrier current at x_d *reverses* direction and begins flowing *into* the bulk, as shown by the falling PISCES-generated concentrations beyond 0.2 μm at 5.5 μs depicted in Fig. 3. Note that the tail at late time might be expected to introduce errors in photoconductive or luminescence measurements of surface and bulk recombination. At lower laser fluence, the peak SPV is smaller than expected if Δ_p is assumed proportional to fluence. As the pulse fluence is reduced, the SCL harbors a relatively greater fraction of the excited carriers, preventing their diffusion into the bulk and thereby reducing Δ_p more strongly than the fluence reduction. Consequently, both the measured ΔV and the simulation in Fig. 2(d) lie substantially lower than predicted from a linear dependence of Δ_p on fluence.

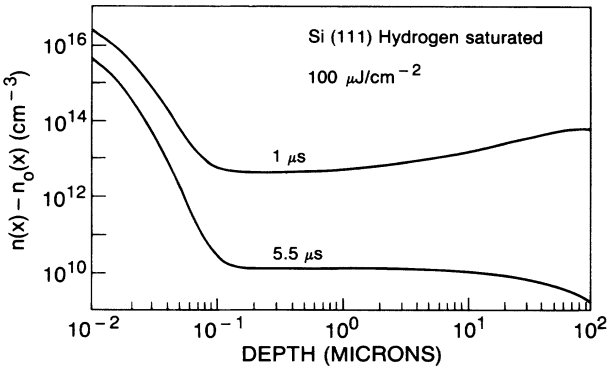

FIG. 3. PISCES-generated nonequilibrium electron density 1 and 5.5 μs after start of 20-ns laser pulse.

Surface recombination is generally assumed to occur through the intermediate capture of carriers by surface levels, which thus acquire a nonequilibrium occupation and hence, in general, a nonequilibrium charge, $\delta\Sigma$.[6] For example, large surface charging has been observed in the Π-Π^* surface states on cleaved Si 2×1 surfaces studied at subnanosecond time scales and mJ/cm^2 laser fluences.[7] For our much weaker fluences, the scale of $\delta\Sigma$ is much smaller. For the hydrogen-saturated surface of Fig. 2, the discrepancy between the simulation and the data in Fig. 2(d) may be evidence for a small transient change of surface change. If so, Eq. (1) gives a peak $\delta\Sigma$ of about $-0.05\Sigma_0$, corresponding to 2.5×10^{10} cm^{-2} additional electrons in the surface. The simulations at larger fluences in Fig. 2 are consistent with $|\delta\Sigma/\Sigma_0| < 0.1$. Although the value for Y_0 found from the simulations is consistent with the literature,[8,12] we note that a reduction in Y_0 of a few kT would lead to values for $-\delta\Sigma/\Sigma_0$ of several tenths and, from Eq. (1), surface charging would contribute significantly to ΔV. If this were the case, then for the simulations to reproduce correctly the time dependences of the SPV decays, which they do, it is sufficient that $\delta\Sigma$ be in quasiequilibrium with the surface majority carrier, and the SPV decays would still be governed by bulk transport.

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