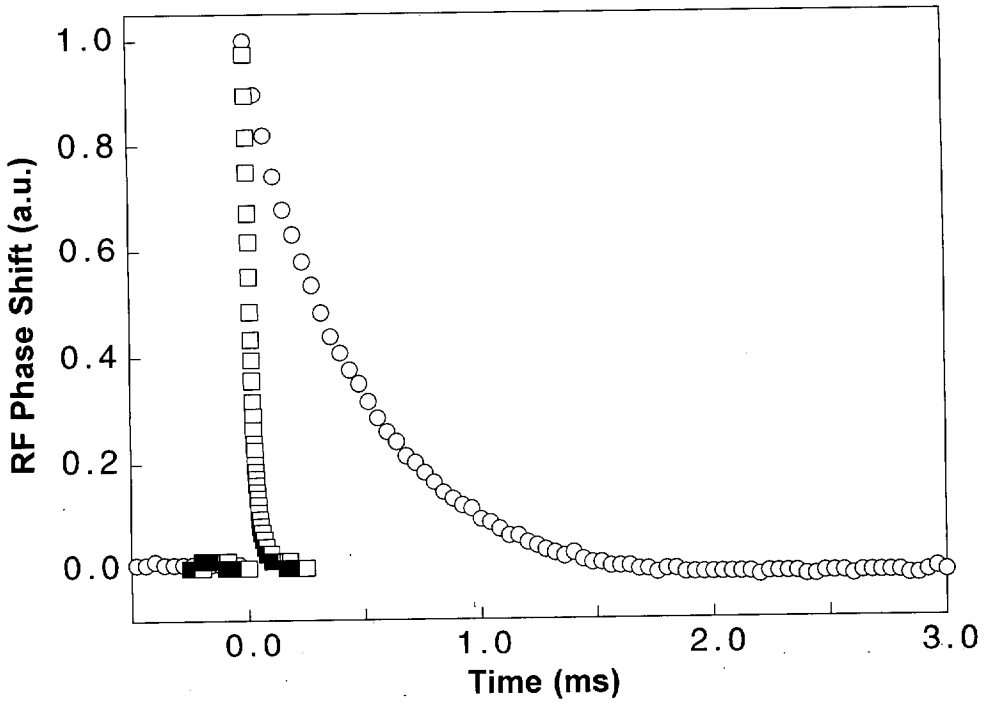

Figure S1. Time-resolved photoconductivity decay of hydrogen-terminated (111)-oriented n-type Si in contact with concentrated sulfuric acid (circles). Much more rapid conductivity decays were recorded after exposing this sample to air for 30 min (squares). A single-exponential fit to these decays (not shown) yielded a time constant of 458 μs for the $H_2SO_{4(aq)}$-immersed sample and 20 μs for the air-exposed sample. Measurements were made under low-level injection conditions (1.3×10^{-6} mJ cm^{-2} pulse^{-1}; 5.2×10^{11} injected charge carriers cm^{-3} pulse^{-1} in a 190 μm thick sample).

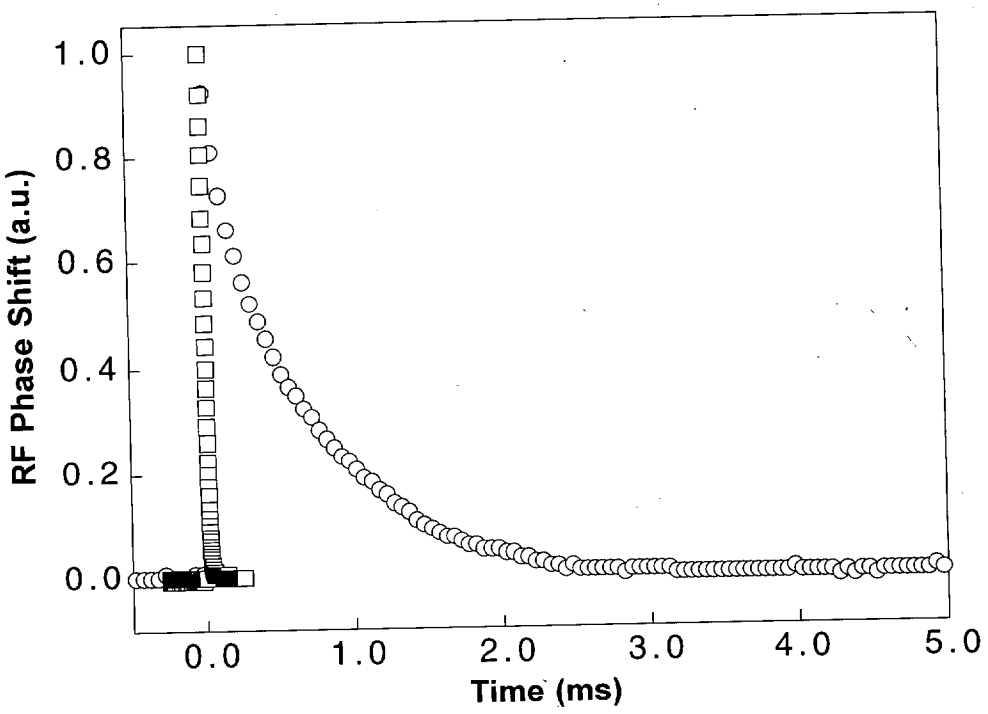

Figure S2. Time-resolved photoconductivity decay of $NH_4F_{(aq)}$-etched (111)-oriented n-type Si in contact with CH_3OH–0.05 M I_2 (circles) and in contact with $N_{2(g)}$ after immersion in CH_3OH–I_2 and a subsequent CH_3OH rinse (squares). A single-exponential fit to these decays (not shown) yielded a time constant of 657 μs and 11 μs for the CH_3OH–I_2-immersed and the $N_{2(g)}$-exposed samples, respectively. Measurements were made under high-level injection conditions (7.0×10^{-4} mJ cm^{-2} $pulse^{-1}$; 2.7×10^{14} injected charge carriers cm^{-3} $pulse^{-1}$ in a 195 μm thick sample).

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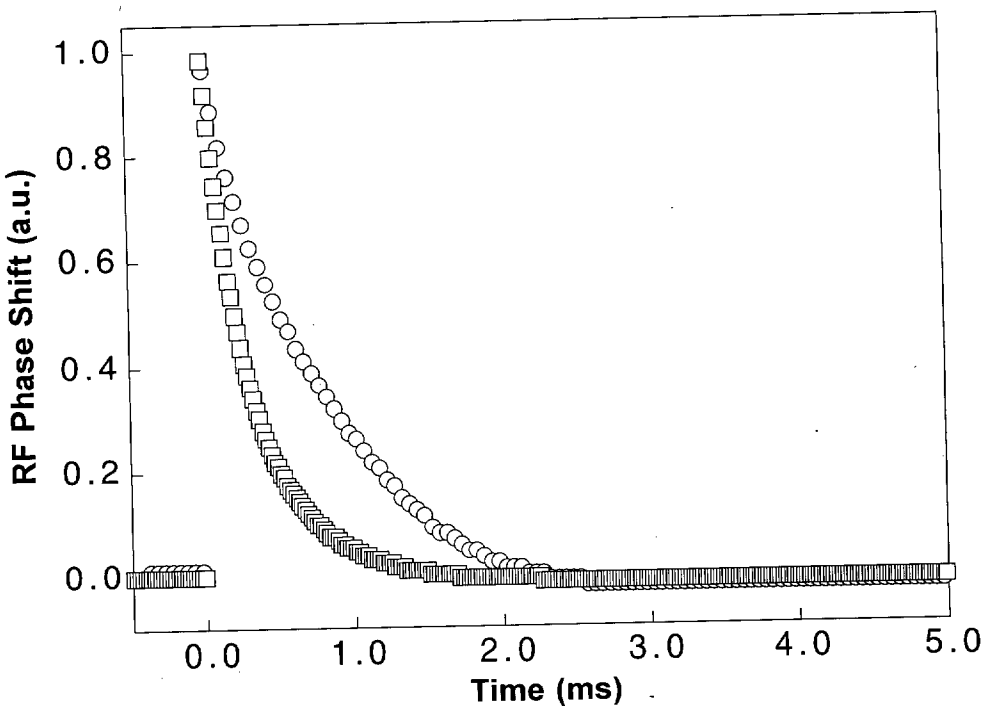

Figure S3. Time-resolved photoconductivity decay of $NH_4F_{(aq)}$-etched (111)-oriented n-type Si in contact with CH_3OH–0.05 M $Fc^{+/0}$ (circles) and in contact with $N_{2(g)}$ after immersion in CH_3OH–0.05 M $Fc^{+/0}$ and a subsequent CH_3OH rinse (squares). A single-exponential fit to these decays (not shown) yielded a time constant of 741 μs and 328 μs for the CH_3OH–0.05 M $Fc^{+/0}$-immersed and the $N_{2(g)}$-exposed samples, respectively. Measurements were made under high-level injection conditions (7.0×10^{-4} mJ cm^{-2} $pulse^{-1}$; 2.7×10^{14} injected charge carriers cm^{-3} $pulse^{-1}$ in a 197 μm thick sample).

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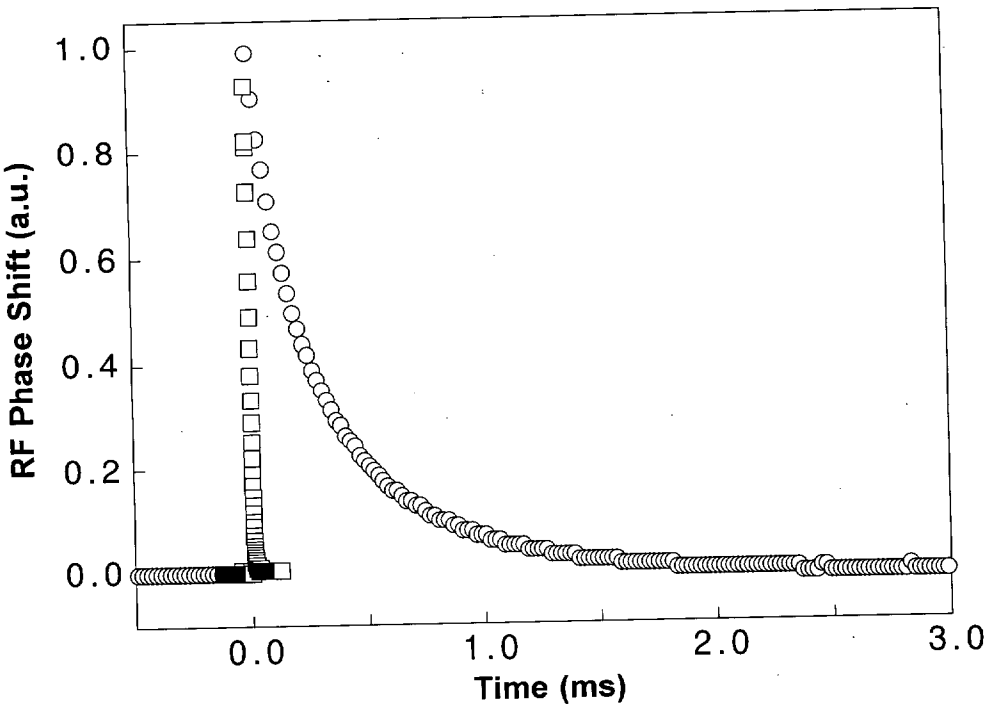

Figure S4. Time-resolved photoconductivity decay of $NH_4F_{(aq)}$-etched (111)-oriented n-type Si in contact with THF–0.05 M I_2 (circles) and in contact with $N_{2(g)}$ after immersion in THF–I_2 and a subsequent THF rinse (squares). A single-exponential fit to these decays (not shown) yielded a time constant of 341 μs and 3.8 μs for the THF–I_2-immersed and the $N_{2(g)}$-exposed samples, respectively. Measurements were made under high-level injection conditions (7.0×10^{-4} mJ cm^{-2} $pulse^{-1}$; 2.7×10^{14} injected charge carriers cm^{-3} $pulse^{-1}$ in a 195 μm thick sample).

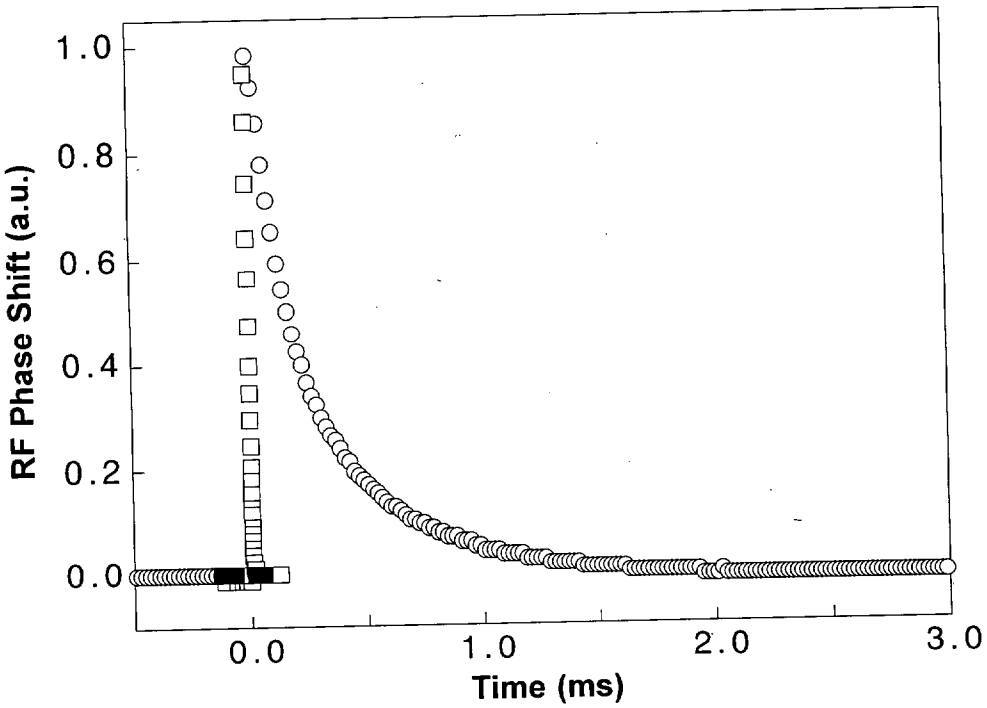

Figure S5. Time-resolved photoconductivity decay of $NH_4F_{(aq)}$-etched (111)-oriented n-type Si in contact with THF–0.05 M Fc–0.005 M Fc^+ (circles) and in contact with THF–0.05 M $Me_{10}Fc$–0.01M $Me_{10}Fc^+$ (squares). A single-exponential fit to these decays (not shown) yielded time constants of 291 μs and 3.2 μs for the THF–$Fc^{+/0}$-immersed and the THF–$Me_{10}Fc^{+/0}$-immersed samples, respectively. Measurements were made under high-level injection conditions (7.0×10^{-4} mJ cm^{-2} $pulse^{-1}$; 2.7×10^{14} injected charge carriers cm^{-3} $pulse^{-1}$ in a 195 μm thick sample).

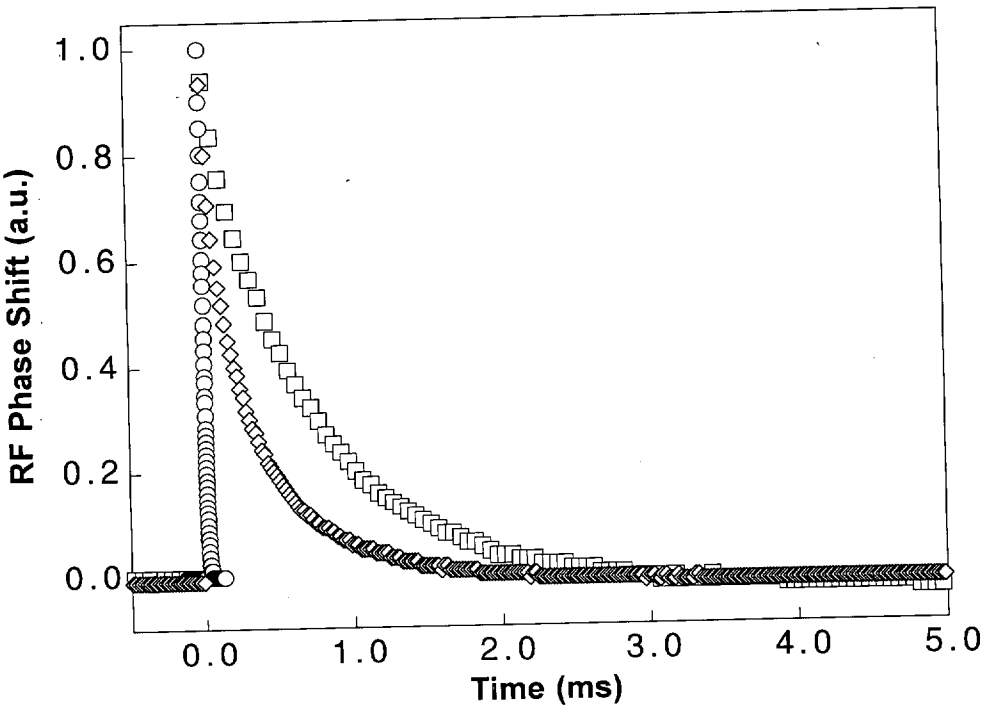

Figure S6. Time-resolved photoconductivity decay of $NH_4F_{(aq)}$-etched (111)-oriented n-type Si in contact with CH_3OH–0.01 M $CoCp_2^{+/0}$ (squares) and the subsequent exposure of the same sample to $N_{2(g)}$ (circles). A single-exponential fit to these decays (not shown) yielded time constants of 732 μs and 9 μs, respectively. Also shown is the photoconductivity decay for this sample in contact with CH_3CN-0.01 M $CoCp_2^{+/0}$ (diamonds). A single-exponential fit to this decay yielded a time constant of 348 μs. Measurements were made under high-level injection conditions (7.0×10^{-4} mJ cm^{-2} $pulse^{-1}$; 1.7×10^{14} injected charge carriers cm^{-3} $pulse^{-1}$ in a 306 μm thick sample).

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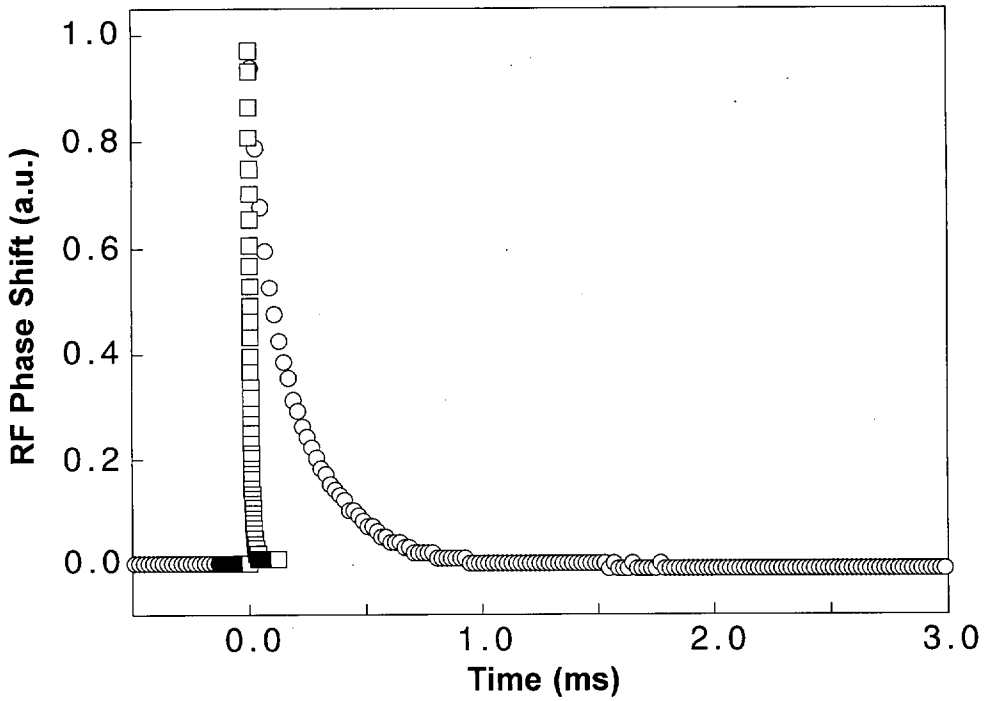

Figure S7. Time-resolved photoconductivity decay of air-oxidized (111)-oriented n-type Si in contact with CH_3OH–0.05 M $Fc^{+/0}$ (circles) and in contact with $N_{2(g)}$ (squares). A single-exponential fit to these decays (not shown) yielded a time constant of 193 μs and 6.7 μs for the CH_3OH–$Fc^{+/0}$-immersed and the $N_{2(g)}$-exposed samples, respectively. Measurements were made under high-level injection conditions (7.0×10^{-4} mJ cm^{-2} $pulse^{-1}$; 2.7×10^{14} injected charge carriers cm^{-3} $pulse^{-1}$ in a 195 μm thick sample).

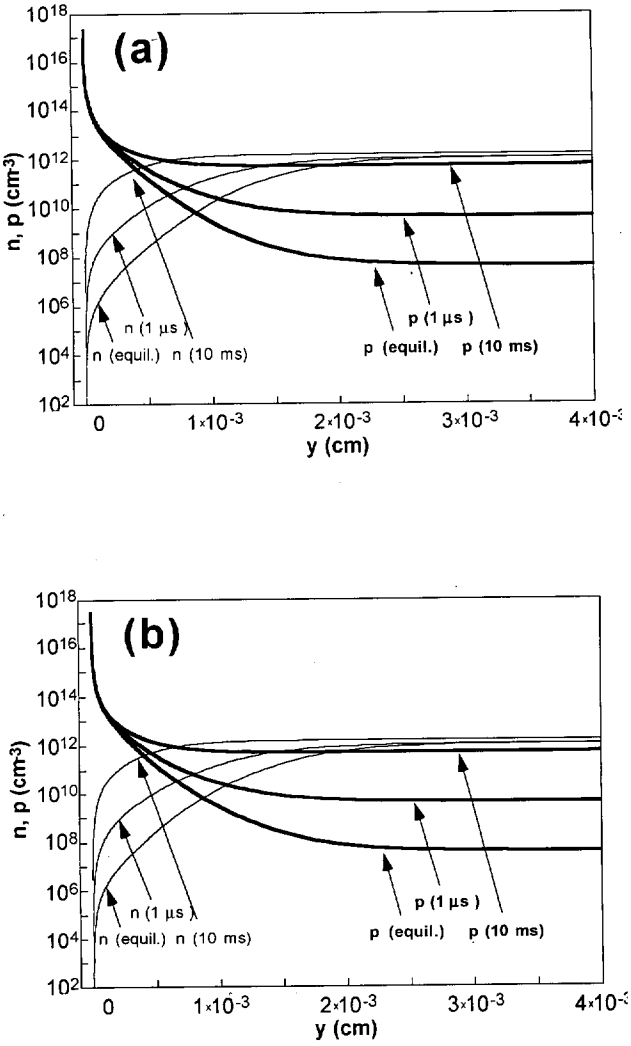

Figure S8. Charge carrier concentration profiles for Si/$Me_2Fc^{+/0}$ contacts (barrier height Φ_B = 1.03 V) under low-level injection conditions (3.3×10^{11} injected charge carriers cm^{-3} pulse^{-1}). Profiles are depicted at 1 µs and at 10 ms after optical light excitation and at equilibrium (equil.). For clarity, only the region adjacent to the semiconductor/liquid contact (y = 0 cm) is shown. (a) Simulation **XI**: surface trap density $N_{T,s} = 1\times10^7$ traps cm^{-2}. Lifetime of holes (p) in the bulk equals 2.1 ms (b) Simulation **XII**: surface trap density $N_{T,s} = 1\times10^{12}$ traps cm^{-2}. Lifetime of holes (p) in the bulk equals 2.1 ms.

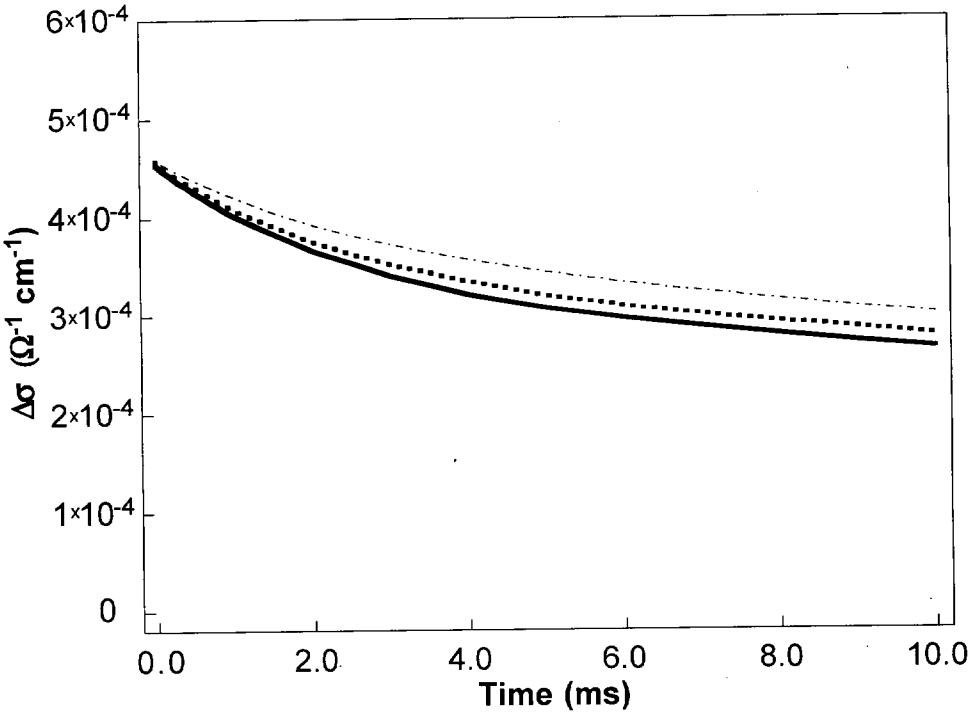

Figure S9. Plot of photoconductivity, $\Delta\sigma$, vs. time, t, for Si/$Me_2Fc^{+/0}$ contacts under low-level injection conditions (3.3×10^{11} injected charge carriers cm^{-3} $pulse^{-1}$). Photoconductivities were calculated using eq 2. Results are shown for: $N_{T,s} = 1\times10^{12}$ traps cm^{-2} (solid line, **XI**), $N_{T,s} = 1\times10^{7}$ traps cm^{-2} (dotted line, **XII**), and $N_{T,s} = 1\times10^{7}$ traps cm^{-2} and a surface acceptor concentration [A] = 3×10^{10} acceptor species cm^{-2} (dash-dot line, **XIIa**). The photoconductivity decay did not follow a single exponential. A decay time of 2 ms was dominant, but obtaining a good fit to the photoconductivity decay required the addition of a series of exponentials having slower decay times than 2 ms.

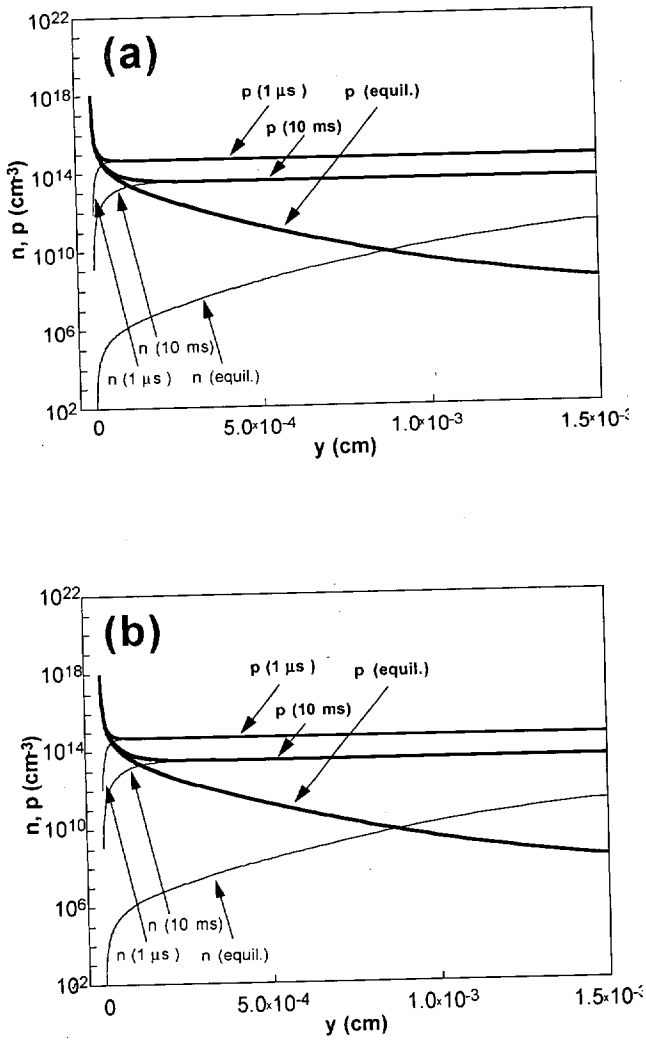

Figure S10. Charge carrier concentration profiles for $Si/Me_2Fc^{+/0}$ contacts (barrier height Φ_B = 1.03 V) under high-level injection conditions (2.3×10^{14} injected charge carriers cm^{-3} $pulse^{-1}$). Profiles are depicted at 1 µs and at 10 ms after optical light excitation and at equilibrium (equil.). For clarity, only the region adjacent to the semiconductor/liquid contact (y = 0 cm) is shown. (a) Simulation **XIII**: surface trap density $N_{T,s} = 1\times10^7$ traps cm^{-2}. Lifetime of holes (p) in the bulk equals 3.7 ms (b) Simulation **XIV**: surface trap density $N_{T,s} = 1\times10^{12}$ traps cm^{-2}. Lifetime of holes (p) in the bulk equals 3.5 ms.

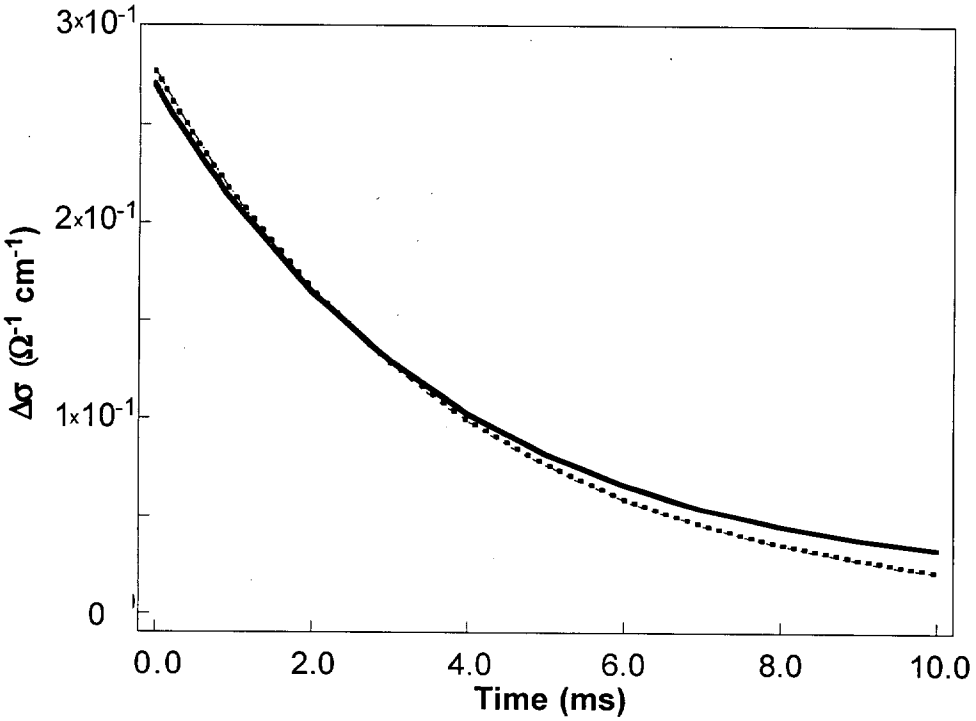

Figure S11. Plot of photoconductivity, $\Delta\sigma$, vs. time, t, for Si/$Me_2Fc^{+/0}$ contacts under high-level injection conditions (2.3×10^{14} injected charge carriers cm^{-3} $pulse^{-1}$). Photoconductivities were calculated using eq 2. Results are shown for: $N_{T,s} = 1\times10^{7}$ traps cm^{-2} (dotted line, **XIII**), $N_{T,s} = 1\times10^{12}$ traps cm^{-2} (solid line, **XIV**), and $N_{T,s} = 1\times10^{7}$ traps cm^{-2} and a surface acceptor concentration [A] = 3×10^{10} acceptor species cm^{-2} (dash-dot line, **XIIIa**). Photoconductivity decays are single exponentials and have decay times of 3.9 ms (**XIII**), 3.7 ms (**XIV**), and 3.9 ms (**XIIIa**), respectively.

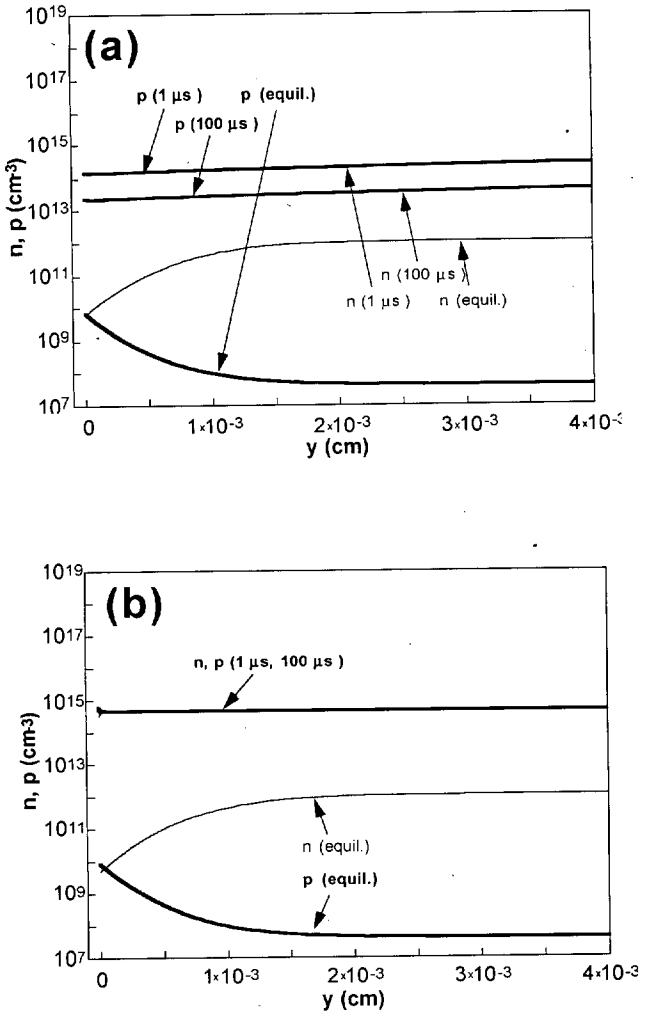

Figure S12. Charge carrier concentration profiles for Si/$Me_{10}Fc^{+/0}$ contacts (barrier height Φ_B = 0.56 V) under high-level injection conditions (2.3×10^{14} injected charge carriers cm^{-3} $pulse^{-1}$). Profiles are depicted at 1 µs and at 100 µs after optical light excitation and at equilibrium (equil.). For clarity, only the region adjacent to the semiconductor/liquid contact (y = 0 cm) is shown. (a) Simulation **XV**: surface trap density $N_{T,s} = 1\times10^{12}$ traps cm^{-2}. Decay of holes did not follow a single exponential. (b) Simulation **XVI**: surface trap density $N_{T,s} = 1\times10^{7}$ traps cm^{-2}. Lifetime of holes (p) in the bulk equals 3.7 ms.

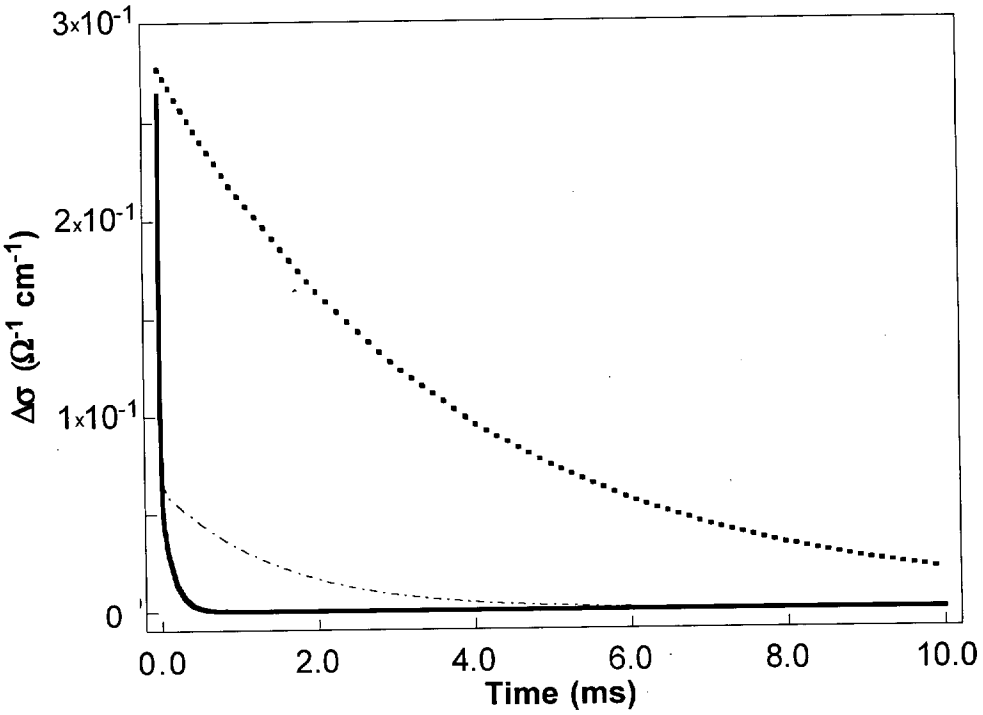

Figure S13. Plot of photoconductivity, $\Delta\sigma$, vs. time, t, for Si/$Me_{10}Fc^{+/0}$ contacts under high-level injection conditions (2.3×10^{14} injected charge carriers cm^{-3} $pulse^{-1}$). Photoconductivities were calculated using eq 2. Results are shown for: $N_{T,s} = 1\times10^{12}$ traps cm^{-2} (solid line, **XV**), $N_{T,s} = 1\times10^{7}$ traps cm^{-2} (dotted line, **XVI**), and $N_{T,s} = 1\times10^{7}$ traps cm^{-2} and a surface acceptor concentration [A] = 3×10^{10} acceptor species cm^{-2} (dash-dot line, **XVIa**). Photoconductivity decay **XVI** is a single exponential with a decay time of 3.8 ms. Photoconductivity decays **XVIa** and **XV** did not follow a single exponential. The dominating decay times for **XVIa** and **XV** are on the order of μs.

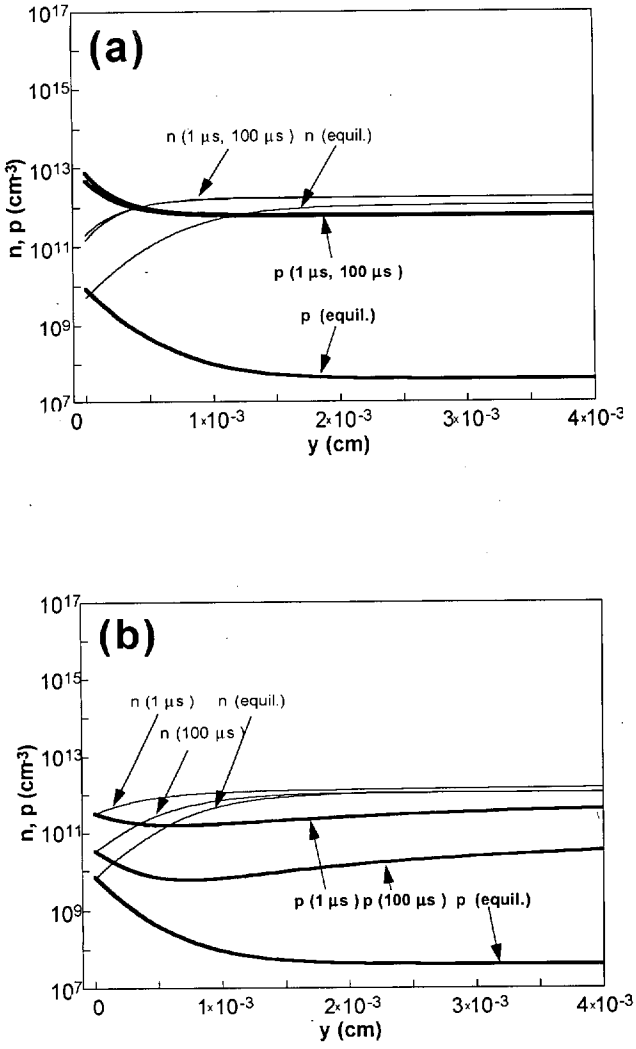

Figure S14. Charge carrier concentration profiles for Si/$Me_{10}Fc^{+/0}$ contacts (barrier height Φ_B = 0.56 V) under low-level injection conditions (3.3×10^{11} injected charge carriers cm^{-3} $pulse^{-1}$). Profiles are depicted at 1 µs and at 100 µs after optical light excitation and at equilibrium (equil.). For clarity, only the region adjacent to the semiconductor/liquid contact (y = 0 cm) is shown. (a) Simulation **XVII**: surface trap density $N_{T,s} = 1\times10^{7}$ traps cm^{-2}. Lifetime of holes (p) at y = 9.5×10^{-3} cm (not shown) equals 2.6 ms. (b) Simulation **XVIII**: surface trap density $N_{T,s} = 1\times10^{12}$ traps cm^{-2}. The decay of holes did not follow a single exponential. The dominating decay times are on the order of µs.

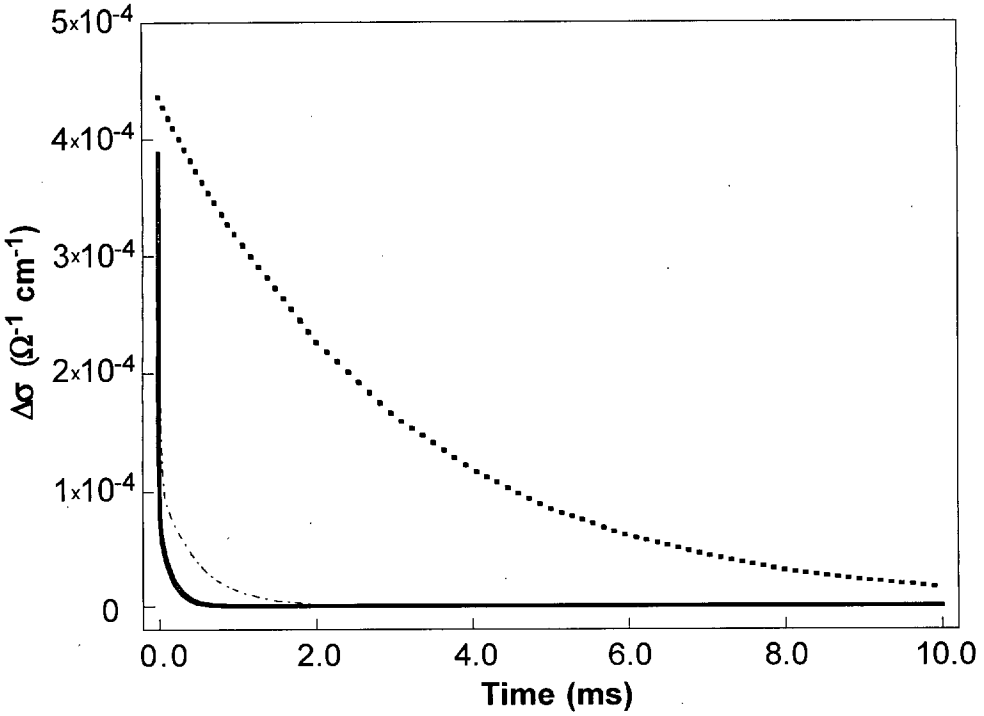

Figure S15. Plot of photoconductivity, $\Delta\sigma$, vs. time, t, for Si/$Me_{10}Fc^{+/0}$ contacts under low-level injection conditions (2.3×10^{11} injected charge carriers cm^{-3} $pulse^{-1}$). Photoconductivities were calculated using eq 2. Results are shown for: $N_{T,s} = 1\times10^{7}$ traps cm^{-2} (dotted line, **XVII**), $N_{T,s} = 1\times10^{12}$ traps cm^{-2} (solid line, **XVIII**), and $N_{T,s} = 1\times10^{7}$ traps cm^{-2} and a surface acceptor concentration [A] = 3×10^{10} acceptor species cm^{-2} (dash-dot line, **XVIIa**). Photoconductivity decay **XVII** is a single exponential with a decay time of 3.1 ms. Photoconductivity decays **XVIIa** and **XVIII** could not be fitted by a single exponential decay. The dominating decay times are on the order of μs.