

Silicon Surface Passivation by Organic Monolayers: Minority Charge Carrier Lifetime Measurements and Kelvin Probe Investigations

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The silicon surface passivation of monolayers of organic compounds that are bound to Si surfaces by a covalent Si–C bond has been investigated. The effective lifetime τ_{eff} of minority charge carriers in the surface-modified semiconductor has been determined by modulated free carrier absorption (MFCA) measurements. The results show that on 1–2 $\Omega\cdot\text{cm}$ p-type Si(100) surfaces modified with a monolayer obtained from $\text{CH}_2=\text{CH}-(\text{CH}_2)_8-\text{C}(=\text{O})-\text{O}-\text{CH}_3$ maximum effective lifetimes $\tau_{\text{eff}} \geq 130 \mu\text{s}$ can be obtained. This value corresponds to a maximum surface recombination velocity S_{eff} of 120 cm/s, a value that is similar to those obtained using other passivation techniques, which demonstrates that these monolayers provide an interesting alternative for silicon surface passivation. During these MFCA measurements an unusual time dependence of the effective lifetime is observed: τ_{eff} rises continuously during illumination of the substrate. Kelvin probe measurements show that there is a slow shift of the Fermi level of the semiconductor under illumination, which seems to be the result of a slow, reversible filling of surface traps.

Introduction

During the past few decades extensive research has been performed to develop easy and cheap methods to reduce the surface recombination velocity of the charge carriers in silicon. The aim hereby is to determine the lifetime of the minority charge carriers in the bulk of the semiconductor, which is one of the important material properties. Two methods for surface passivation are now generally used: submerging of the silicon substrates in solutions of hydrofluoric acid (HF)^{1–3} or in a solution of I_2 in ethanol.^{3–5} Both methods give rise to excellent surface passivation. For a 150 $\Omega\cdot\text{cm}$ n-type float zone Si(111) substrate submerged in HF a surface recombination velocity of 0.25 cm/s has been reported,^{1,2} but in general much higher values (100–200 cm/s) are found for substrates with higher doping densities and for p-type Si wafers.³ For I_2 /ethanol surface recombination velocities <10 cm/s can be obtained,⁴ but this again depends on the resistivity of the Si substrate, and in general values ≤ 50 cm/s are measured.⁵

However, both methods have their drawbacks. Hydrofluoric acid is a dangerous, corrosive acid, which means that special safety precautions are required during the measurements, as the sample has to remain submerged in the HF solution. Alternatively, the H-passivated Si surface can also be removed from the HF solution and measured in air.^{3,6} Under these circumstances the Si surface is not stable, but is slowly oxidized, which

results in loss of the surface passivation and, thus, in an increase in the surface recombination velocity. Unfortunately, comparison of results is often difficult, as the rate of oxidation is strongly influenced by external factors, including the irradiation used in lifetime measurements.^{3,6} The formation of a monolayer of silicon oxide on crystalline, H-terminated Si surfaces has been reported to take anywhere from 1 h^{7–9} to a week^{10,11} and up to a month.¹² In these investigations it has been found that the silicon oxide growth rate depends on the type of surface (e.g., p-type or n-type surfaces, Si(100)- or Si(111)-oriented surfaces),^{8,9} on the environmental conditions (e.g., the humidity),⁹ and on the etching conditions.^{8,11} A second problem is that in lifetime measurements on hydrogen-passivated Si an immediate decrease of the surface passivation is seen due to oxidative processes; since only partial oxidation already yields a significant amount of traps, the decay of measured lifetimes τ is usually rapid, hampering the reproducibility of lifetime measurements. These two problems seriously limit the application of this method as a standard for Si surface passivation.

The other frequently used method for surface passivation involves submerging of a HF-etched wafer in I_2 /ethanol. This gives a more stable system; however, this surface also degrades after some time (~ 30 – 60 min).^{3,13} As with the measurements in the HF solutions, the wafer again has to be submerged during the whole measurement, which is inconvenient from a practical point of view.

Until the development of covalently attached monolayers on a Si surface,^{14–17} there were only several reports on the reduction of the surface recombination velocity of charge carriers. It has been shown that by evaporation of a thin film of a solid aromatic compound (tetracene) on top of a H-terminated Si surface the surface oxidation is inhibited,¹⁸ because the approach of oxygen and water to the Si surface is blocked by the organic layer. In

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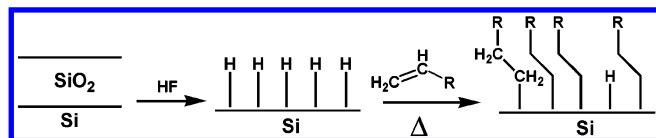


Figure 1. Schematic representation of the thermal reaction for the preparation of covalently attached organic monolayers on Si surfaces.

this modification the Si surface is, however, still passivated by hydrogen, not by the organic compound, as there are no covalent Si–C bonds formed between the organic compound and the Si surface. The reduction of the surface recombination velocity of charge carriers in Si wafers provided by covalently attached monolayers was first shown by us on p-type wafers, using monolayers derived from $\text{CH}_2=\text{CH}-\text{C}_8\text{H}_{16}-\text{C}(=\text{O})-\text{O}-\text{CH}_3$ (**I**).⁶ The preparation of covalently bound organic monolayers on Si surfaces, without an interfacial silicon oxide layer, has been a topic of intense research over the past decade.^{14–17} These monolayers are easily formed by the reaction depicted in Figure 1.^{19–22} The Si–H groups on the H-terminated Si surface react with 1-alkenes, which results in the formation of a densely packed monolayer. Because of the covalent Si–C bond that is formed between the Si surface and the organic compound,²³ the monolayers show a remarkable stability, both chemically^{14,19} and thermally.²⁰ It has also been shown that they completely inhibit the oxidation of the underlying silicon surface for at least several weeks.^{14,24,25} This means that these surfaces are much more stable over time than H-terminated Si surfaces and, thus, that the minority charge carrier lifetime measurements can be done on a system that shows no surface oxidation during the time required for the measurements.²⁶ More recently, the surface passivation of Cl-terminated Si surfaces that were modified with Grignard compounds was reported.²⁷ In this latter reaction a monolayer based on the formation of Si–C bonds is also obtained,²³ just as is the case in the reaction of 1-alkenes with H-terminated Si surfaces. Recombination velocities as low as 25 cm/s were reported for very high purity (3800 $\Omega\cdot\text{cm}$) n-type float zone Si(111) surfaces.²⁷

Of course other passivation techniques, such as the application of a layer of silicon oxide and silicon nitride, offer a similar advantage, but the monolayer preparation is done at lower temperatures and does not require special, expensive equipment. Therefore, these organic monolayers on H-terminated Si surfaces are an interesting candidate for solid-state silicon surface passivation.

In this paper the surface passivation of p-type Si(100) wafers (float zone (FZ) quality, 1–2 $\Omega\cdot\text{cm}$) by organic monolayers derived from 1-alkenes is further investigated. The Si surfaces are all modified with methyl 10-undecenoate, $\text{CH}_2=\text{CH}-(\text{CH}_2)_8-\text{C}(=\text{O})-\text{O}-\text{CH}_3$ (**I**), as the covalently attached monolayer derived from this 1-alkene showed good surface-passivating properties in our preliminary investigations.⁶ The lifetime of the minority charge carriers is determined by modulated free carrier absorption (MFCA) measurements.^{28,29} The substrates are also investigated by Kelvin probe measurements, as this technique can provide information about possible changes in the electronic properties of the semiconductor substrate—including band bending or changes in any surface dipole layer—upon modification with **I**.^{30–32} Both techniques are noncontact methods, which means that the surface of the modified substrate is not damaged during the measurements.

Experimental Section

General Procedures. **I** was prepared in batches on a 50 g scale as described (yields after distillation 84–89%).¹⁹ The

alkene was doubly distilled in vacuo (see the Results and Discussion), using a distillation setup that was cleaned with distilled methanol before use. The distillates were combined and stored in clean bottles. Used alkene could be recycled after one additional distillation step, without any consequence for the resulting surface passivation. The Si(100) wafers (1–2 $\Omega\cdot\text{cm}$, p-type, boron-doped, FZ quality, 375 \pm 15 μm thickness, singly polished) were obtained from Wacker Siltronic AG (Bayer Solar, Freiberg, Germany) and had a guaranteed bulk lifetime $\tau_b > 1000 \mu\text{s}$. In one experiment a shiny-etched wafer of 300 μm thickness with the same intrinsic properties was used. The wafers were cut into pieces of $\sim 2.5 \times 3 \text{ cm}^2$, which were stored separately in Teflon boxes. Solvents for substrate cleaning were distilled. Hydrofluoric acid was semiconductor grade.

Sample Preparation.^{6,19} The Si substrates were modified in a specially designed vessel, which consists of three flattened tubes (inner dimensions of a tube $\sim 50 \times 30 \times 5 \text{ mm}$) to allow for the preparation of three samples within a single experiment. This is important for the reproducibility of the measurements, because the monolayer quality is influenced by the concentration of oxygen in the system.^{21,33} The vessel was filled with a sufficient amount of **I** to completely fill all three tubes, and dry nitrogen gas was bubbled through the solution for at least 1 h. During this time the tubes were partially submerged ($\sim 3 \text{ cm}$ deep) in an oil bath of 200 $^\circ\text{C}$ to preheat the alkene.³⁴ Subsequently, the Si substrates were etched in a 2.5% HF solution for 2 min, using a fresh solution for each sample. Each of the etched substrates was immediately transferred into the vessel, temporarily opening the large screw cap under vigorous nitrogen flow. If necessary, residual drops of the HF solution were blown off with N_2 . Each Si substrate was placed in a separate section of the vessel (i.e., in one of the flattened tubes), thus avoiding direct contact between the Si substrates. After all three substrates had been inserted the screw cap was closed, the vessel was lowered into the oil bath as deeply as possible, and the system was heated at 200 $^\circ\text{C}$ under a slow flow of N_2 for 2 h.

Subsequently, the vessel was removed from the oil bath. The major part of the alkene was poured off, and the samples were removed from the vessel using Teflon tweezers, again avoiding direct contact between the substrates. The modified substrates were thoroughly rinsed three times in petroleum ether (40–60 $^\circ\text{C}$), three times in methanol, and finally once in dichloromethane. For each rinsing step, as well as for each separate substrate, fresh solutions were used. All modified wafers were stored separately in the dark in Teflon boxes.

Measurement Procedure for MFCA Measurements. The MFCA technique was used to determine the lifetime of minority charge carriers, and the MFCA setup used has been described in detail previously.^{28,29} For clarity a short description of the technique is presented: charge carriers are generated in the Si substrate by excitation of electrons from the valence band to the conduction band, using 848 nm light from a laser diode. Mobile charge carriers are then detected using a 1550 nm laser. The power density (P) of the excitation light on the wafer surface can be varied using neutral density filters, thus allowing for measurements at both high-level and low-level injection conditions. To measure τ_{eff} , a small intensity modulation with a frequency ω is added to the bias-light power density. The generated excess charge carrier concentration in the sample will vary with this modulated light intensity, however, with a certain shifted phase angle ϕ , which is determined by the recombination properties of the charge carriers in the wafer. At a low modulation frequency the system (the moving and recombining

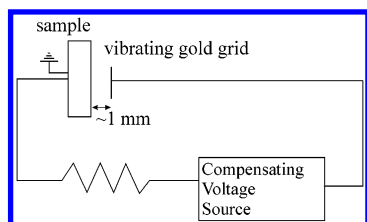


Figure 2. Schematic representation of the Kelvin setup.

charge carriers) can keep up with changes in the light intensity, which means that at a maximum (minimum) in the light intensity the number of charge carriers is also at a maximum (minimum). However, if the modulation frequency is increased, the system in the wafer starts to fall behind, because the recombination of the charge carriers is not fast enough. By measuring ω_{45} , the modulation frequency at which the phase shift between the two lasers is 45° , the effective minority charge carrier lifetime τ_{eff} can be determined according to $\tau_{\text{eff}} = 1/\omega_{45}$.^{28,29} This effective lifetime depends on the bulk lifetime τ_b of the Si substrate and on the recombination velocities S_1 and S_2 at the two interfaces of the wafer. Measurements on two sides of a wafer that had a monolayer on each side showed that the recombination velocities on both sides of the wafer were equal, i.e., $S_1 = S_2 = S_{\text{eff}}$. Consequently, τ_{eff} is in first approximation^{28,29}

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_b} + \frac{2S_{\text{eff}}}{W}$$

in which S_{eff} is the effective surface recombination velocity and W is the thickness of the wafer. [Additionally it was shown that polishing the surface or application of a shiny-etch procedure before monolayer formation had only a marginal effect (<5%) on the value of S .]

After the monolayer preparation all three samples were briefly scanned. Because of the observed time-dependent behavior of τ_{eff} (see the Results and Discussion), each sample was first illuminated for 10–15 min at a low power density ($P \approx 200$ mW/cm²) to get a quasi-stable system. Subsequently, τ_{eff} was rapidly determined at a few (usually four to six) different power densities. After all three samples were measured in this way, more prolonged, detailed studies were performed. To minimize the storage effects, the samples that were measured later (samples 2 and 3 from a set of three) were kept in the dark.

For the excitation with 950 nm light, the 848 nm laser was replaced by a low-intensity light-emitting diode (LED), which was placed close to the substrate. For the experiment using 1025 nm light a 500 mW near-infrared laser was used.

Kelvin Probe Measurements. A Kelvin probe unit (Besocke Delta Phi type S) with a vibrating gold grid with a diameter of 2 mm, operating at a resonance frequency of ~ 170 Hz, was used (Figure 2). The distance between this grid and the Si substrate was ca. 1 mm. The ac current was monitored on an oscilloscope and was automatically set to zero. The compensating voltage required for this purpose was measured by a Keithley 2001 digital multimeter with intervals of 1 s. Measurements were carried out in ambient atmosphere. Since slow relaxation processes occur, stabilization of the dark signal could take up to 2 h, after which the fluctuations in V_{comp} were less than 10 mV. The work function of the gold grid was taken to be 5.0 ± 0.1 V.

Monochromatic irradiations with 848 nm light were done using a 250 W tungsten–halogen lamp (Oriel) in combination with a grating monochromator (ARC Spectrapro 275) and appropriate high-pass filters (Schott). The light was focused on

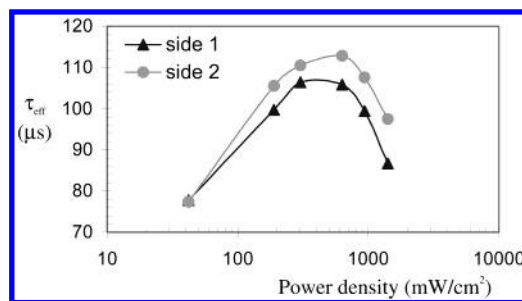


Figure 3. MFCA measurement (P – τ curve, power density P of the incident light vs the effective lifetime τ_{eff} of the minority charge carriers) of both sides of a shiny-etched, doubly polished p-type Si(100) wafer of 300 μm thickness passivated with **I**.

the gold grid with an intensity of approximately $100 \mu\text{W}/\text{cm}^2$. A 5 mW diode laser (Coherent) was used for irradiation with 670 nm light.

Results and Discussion

Lifetime Measurements. Silicon surface passivation is a process that is highly sensitive to contaminations in the reagents that are used.³⁵ A total of eight batches of three Si substrates each was modified with **I** for the lifetime measurements. The samples were indistinguishable according to the results of water contact angle measurements and IR spectroscopy. Nevertheless, small but significant sample-to-sample variations were found for the surface passivation characteristics, while different spots on the wafer and a different maximum power density P_{max} for the excitation light yield very similar results.

An illustration of the high sensitivity of these measurements to small amounts of impurities (defects in the monolayer) is provided by the significant improvement of the passivation by monolayers derived from doubly distilled rather than singly distilled alkenes. Although no effects on, e.g., IR spectra of the monolayer could be noticed, MFCA measurements showed an increase in τ_{eff} from ~ 50 to $\sim 130 \mu\text{s}$. Apparently, small amounts of impurities in the organic reagent can absorb onto the Si surface. As a result the overall still densely packed monolayer of **I** will have some defects, leading to defects at the Si surface that will act as sites for charge carrier recombination. Consequently, the maximum effective lifetime of the minority charge carriers will decrease.³⁵ Results from a typical substrate give $\tau_{\text{eff}} = 132 \mu\text{s}$. This value corresponds to a maximum surface recombination velocity S_{eff} of 125 cm/s. A comparable value, $S_{\text{eff}} = 120$ cm/s (derived from $\tau_{\text{eff}} = 110 \mu\text{s}$), was obtained on a Si wafer with a thickness of only 300 μm that had received a shiny etch (Figure 3).³⁶ The similarity in the curves obtained in subsequent runs, at either the same power density or different power densities, also shows that these modified substrates have a good stability, unlike for surfaces passivated by $\text{HF}^{3,6}$ or $\text{I}_2/\text{ethanol}$,^{3,13} as there is no degradation of the substrate during the time required for these two measurements.³⁷

It is difficult to compare the S_{eff} of 120 cm/s to literature values, as factors such as the doping density and the surface orientation all influence the recombination velocity.^{28,38,39} The value of S_{eff} is comparable to the value of S_{eff} of 130 cm/s that was measured on a HF -passivated $7 \Omega\cdot\text{cm}$ p-type Si(100) wafer,³ and approaches the S_{eff} of ~ 40 cm/s found for a $1.5 \Omega\cdot\text{cm}$ p-type Si(100) wafer passivated with $\text{I}_2/\text{ethanol}$.¹³ This result clearly demonstrates that these monolayers of 1-alkenes are highly suitable for Si surface passivation, specifically given their easy synthesis.²¹

In all measurements it was found that the τ_{eff} of the minority charge carriers depends on the power density P of the incident

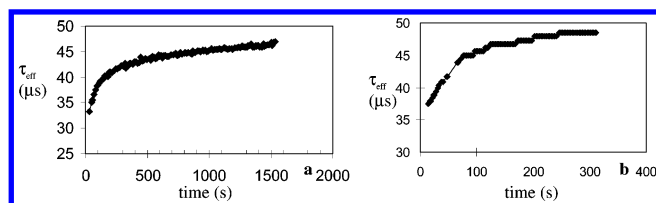


Figure 4. Time-dependent behavior of τ_{eff} as observed for (a) a wafer passivated with **I** and (b) a wafer passivated with 1-hexadecene. Panel b was reprinted with permission from ref 6. Copyright 1998 Joint Research Center of the European Commission.

light. An increase in P leads to an increase in τ_{eff} , up to a certain maximum value. A similar behavior is known for thermally oxidized^{40,41} and for silicon nitride-coated^{42,43} p-type Si wafers, where it has been attributed to an injection-level-dependent surface recombination velocity. Beyond the maximum value the effective lifetime decreases again, likely due to an increased bulk recombination. If the surfaces of the semiconductor are well passivated, Auger recombination in the crystalline bulk of the silicon becomes significant at high injection levels, and can even dominate the measured τ_{eff} .⁴⁴

Time-Dependent Behavior of τ_{eff} : MFCA Studies. During the lifetime measurements on these monolayer-passivated Si surfaces a remarkable phenomenon was observed: τ_{eff} increases continuously under illumination at a constant power density P of the excitation light. Such effects are known for SiO_2 -passivated silicon surfaces that are illuminated with very high intensity lasers,^{45,46} in which case multiphoton absorption takes place, but such processes can be excluded here. Two examples of this time-dependent behavior of τ_{eff} are shown in Figure 4. A rapid increase in τ_{eff} occurs in the beginning, after which τ_{eff} keeps increasing gradually, as was found for a sample that was illuminated constantly at a constant, low value of P for 3 days. The effective lifetime τ_{eff} had reached a value of 117 μs , from an initial value of $\tau_{\text{eff}} = 25 \mu\text{s}$.

This time-dependent behavior of τ_{eff} was found on all monolayer-modified samples, regardless of the power density of the excitation light or of the maximum effective lifetime of the sample. The initial part of the curves usually showed some variation; i.e., some samples showed a faster increase over time in the first few hundreds of seconds compared to other samples, but the slope of the subsequent continuous, approximately linear growth of τ_{eff} is always similar. The effect is observed both for monolayers of functionalized molecules, such as **I** (Figure 4a), and for monolayers of underivatized 1-alkenes, such as 1-hexadecene (Figure 4b). It is not observed for other surface passivation methods, such as silicon nitride passivation, which means that it must be a direct result of the surface modification with 1-alkenes.

The time dependence of τ_{eff} is reproducible in a series of measurements on a sample. After storage of the wafer in the dark for at least several hours (longer than the time it had been illuminated during a measurement), approximately the same curve for τ_{eff} is found in the second measurement if the same power density of the excitation light is used. This indicates that in the dark the wafer returns to what can be called its "original state", which suggests that under illumination neither the composition of the monolayer nor the structure of the Si surface is permanently changed. If such changes did occur, τ_{eff} would have been affected permanently, which would have become clear in subsequent second or third measurements. The reproducibility of the effect also shows that there is no observable degradation of the Si surface under illumination. This would result in a decrease of τ_{eff} , due to an increased number of Si surface defects, and consequently of the number of recombination sites.

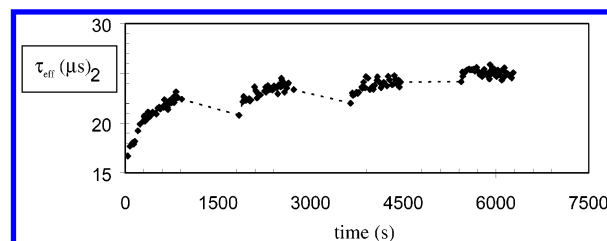


Figure 5. Behavior of τ_{eff} on a Si wafer modified with **I** if there are short intervals between the periods of illumination.

In experiments with only short intervals between the periods of illumination, i.e., with dark periods that are approximately equal to or even shorter than the period of illumination, the time- τ_{eff} curves are not identical. This means that, apparently, the sample does not instantaneously return to its original state when the excitation light is switched off. An example of such an experiment is shown in Figure 5, in which both the illumination period and the dark period are approximately 15 min. The τ_{eff} of each successive period of illumination starts at a higher value and also gives a higher end value for τ_{eff} , which clearly demonstrates that the substrate did not return to its original state. Moreover, the starting value of τ_{eff} in each successive illumination period is actually close to the last value of the previous illumination period. This indicates that the decay to the original state is a rather slow process.

Absorption of light by the monolayer may be responsible for the observed time-dependent behavior of τ_{eff} . The antisymmetric CH_2 stretching vibrations in the organic molecules show infrared absorptions at 2920–2925 cm^{-1} . These values correspond to wavelengths of ~ 3420 – 3425 nm , which means that the fourth harmonic of this vibration is around 855 nm, i.e., close to the excitation wavelength of 848 nm. Although the absorption of such overtones is low and will most likely be negligible in a monolayer of an organic compound, the continuous absorption of the 848 nm light by the organic molecules could in theory cause changes in the monolayer structure. The other wavelength used in the MFCA measurements, the detection wavelength of 1550 nm, is not absorbed by the monolayer.

To investigate the possible influence of the absorption of the excitation light by the monolayer, two control experiments were performed, in which different wavelengths (950 and 1025 nm) were used to generate the charge carriers in the semiconductor. Also with these two wavelengths the effective lifetime of the sample continuously increases during illumination with rates comparable to those obtained by irradiation with 848 nm light of the same intensity. Thus, the observed time dependence of τ_{eff} is not caused by absorption of the light by the monolayer.

Time-Dependent Behavior of τ_{eff} : Kelvin Probe Measurements. A possible explanation for the increase of τ_{eff} over time is a change in the properties of the silicon surface itself. A slow filling of surface traps under illumination will shift the positions of the bands of the semiconductor, and reduce the number of recombination centers at the surface. This results in a decrease of the recombination velocities, which means that τ_{eff} will increase over time. Such filling of traps is a reversible and slow process, two features that are observed in our experiments. Unfortunately, MFCA measurements cannot provide information about this process, since they only show the net result of these changes on τ_{eff} . Also, MFCA measurements cannot be used to investigate processes that occur in the dark, which are important because of the reproducibility of the observed effect and the rather slow decay process that occurs.

This possible trapping and detrapping of electrons was therefore investigated by Kelvin probe measurements. In the

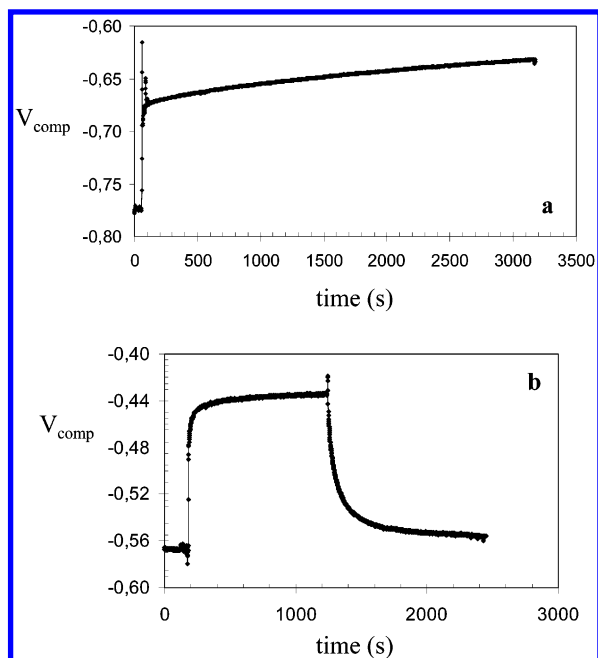


Figure 6. Surface photovoltage measurements on Si wafers passivated with I: (a) with light of 848 nm, (b) with light of 670 nm.

case of semiconductors the position of the Fermi level of the semiconductor relative to that of a reference electrode is determined. Trapping of charges at the illuminated semiconductor surface will shift the Fermi level of the semiconductor. As discussed above, in the case of the monolayer-modified Si substrates such charging of the semiconductor surface can cause the observed time-dependent behavior of τ_{eff} . With the Kelvin probe this surface charging can be measured by continuously monitoring the position of the Fermi level of the illuminated semiconductor. Also, the Kelvin probe can measure in the dark, which means that these measurements can provide information about the subsequent decay process that occurs. Therefore, it is interesting to investigate the modified Si substrates with this technique.

Figure 6 shows the results of two measurements on monolayer-modified Si substrates. In Figure 6a the sample was irradiated with low-intensity 848 nm light, in Figure 6b with high-intensity 670 nm light. A fast jump of V_{comp} of +0.10 V is observed when the light is switched on, followed by a slow, continuous increase. The fast jump is due to the light-induced flattening of the bands of the semiconductor. The subsequent slow increase is due to slow additional charging of the surface. It is interesting to note that there are no differences between the two samples, which suggests that there is not much effect of either the intensity or the wavelength of the applied irradiation on the rate of the slowly growing surface photovoltage signal. This was also found for the time-dependent behavior of τ_{eff} in the MFCA measurements. Figure 6b shows that, when the light is turned off (here at $t = 1275$ s), the reverse process occurs: the signal first decreases rapidly due to reoccurrence of the band bending, and then continues to relax slowly toward its initial value.

Figure 7 shows the result of a measurement on a hydrogen-terminated Si substrate, which was performed as a control experiment. This surface shows a stable contact potential difference versus gold both in the dark and under illumination. The jumps in V_{comp} as a result of switching the light on or off are again rapid (within 10 s), as already observed for the monolayer-modified Si substrates. This confirms that the lifting of the band bending upon irradiation is a fast process.

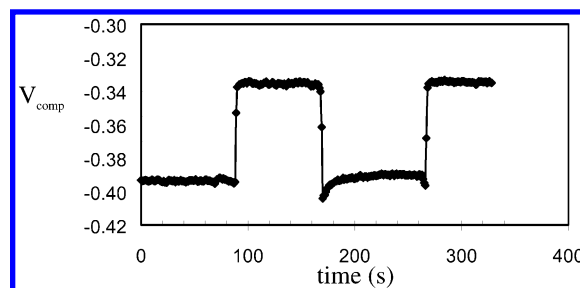


Figure 7. Surface photovoltage measurement on a H-passivated p-type Si wafer. At $t = 90$ s the light is turned on, and at $t = 160$ s the light is turned off. At $t = 270$ s the second cycle was started (not fully shown) to test for the stability of the substrate.

The observed jump in V_{comp} upon illumination of the passivated Si substrates is indicative of the band bending for these surfaces. For the monolayer-covered sample this is calculated as 0.09 ± 0.02 eV, and for the H-terminated Si surface this value is 0.06 ± 0.02 eV, both upon irradiation with 848 nm light. Since band bending is caused by charges—both mobile and immobile—at the surface that are located at surface defects, these small values show that on these monolayer-covered Si surfaces the number of electronic defects is negligible. This can explicitly be derived from eq 1, which yields the surface charge per surface side.

$$Q_{\text{sc}} = (2\epsilon\epsilon_0 e N_a)^{1/2} (\varphi_{\text{scd}} - kT/e)^{1/2} \quad (1)$$

Using 11.9 for the dielectric constant of Si, $kT/e = 0.025$ V at room temperature, and 10^{16} cm^{-3} for the acceptor density N_a yields $Q_{\text{sc}} = 3 \times 10^{12}$ elementary charges per cubic centimeter. The number of surface atoms is roughly 10^{15} cm^{-2} , from which it follows that there is only one elementary charge available per 330 surface atoms. This explains the excellent passivating properties of the organic monolayers.

The observed slow, continuous increase of V_{comp} and τ_{eff} during illumination is the likely result of changes in the properties of the modified semiconductor substrate. Since under illumination the bands are flattened, this response of V_{comp} cannot be related to a change in the band bending, which means that it must be due to a change in the position of the bands at the surface. Such shifts of the band edges can be caused by (additional) polarization of the surface dipole layer. The sign of the slow increase of the signal indicates that a negative charge is formed at the monolayer side of the Si–monolayer interface, and that positive charges are present on the Si surface itself. This means that electrons are trapped on the organic molecules or on adsorbed molecules on the outside of the monolayer.

Once the light is switched off the band flattening will disappear; i.e., the band bending will reoccur. In this situation the monolayer and the Si surface can no longer be permanently charged, and some process starts to reach a thermodynamically stable state again. In general, electron-trapping processes are reversible, unless a chemical reaction or degradation occurs. The observed complete reversibility for these monolayer-modified Si substrates, in both the Kelvin probe and the MFCA measurements, thus suggests that chemical and/or degradation reactions can be ruled out. The detrapping of the electrons, like the trapping itself, will be a slow process, because the electrons have to cross the barrier of the organic material again. Therefore, it will take place on a similar time scale as the trapping process, which is confirmed by the result shown in Figure 7b. The observed time-dependent behavior of V_{comp} and of τ_{eff} is thus explained by trapping of electrons at the surface of the monolayer.

A simple calculation can give an estimate of the degree of trapping of electrons, if it is assumed that the electrons are trapped on the organic molecules in the monolayer and that the trapping rate is constant in time. This will give an indication about the number of electrons that are trapped per second and can also indicate how long this process can go on. This is relevant, as it was already mentioned above that τ_{eff} was still not stable after 3 days of continuous illumination. The contact potential difference grows with a rate of ~ 0.01 mV/s, which means that the current that flows in the process is $dQ/dt = C(dV/dt) \approx 27$ pA cm $^{-2}$, using an effective dielectric constant of 3 and a distance of 1 nm between the Si surface and the outside of the monolayer. This corresponds to $\sim 1.7 \times 10^8$ (electrons/cm 2)/s. Since the monolayer contains one molecule per 24 Å,^{2,14,19} it would at this rate take approximately 2.5×10^6 s, or 29 days, to store one electron on all organic molecules in the monolayer. Of course the process will eventually slow upon additional charging, so the above calculation gives a clear demonstration that it will at least take many days before a stable situation is reached.

Conclusions

The possibility to use covalently attached monolayers of 1-alkenes on H-terminated Si surfaces for silicon surface passivation was investigated. MFCA measurements show that maximum effective lifetimes τ_{eff} of the minority charge carriers of 130 μ s can be obtained on 1–2 Ω ·cm p-type Si(100) surfaces modified with a monolayer derived from compound **I**. This lifetime corresponds to an effective surface recombination velocity S_{eff} of 125 cm/s. The whole surface of the semiconductor is equally well passivated, and the values for τ_{eff} and S_{eff} are well reproducible. These values are of the same order of magnitude as those obtained using other passivation techniques, such as HF and I $_2$ /ethanol passivation, and clearly demonstrate that monolayers derived from 1-alkenes such as **I** can be used for silicon surface passivation.

During the MFCA measurements an unusual time-dependent behavior of the effective lifetime is observed: τ_{eff} rises continuously during illumination of the substrate. The effect is not dependent on the precise nature of the monolayer (ester functionality either present or absent) or on the power densities of the bias light. Kelvin probe measurements showed that this behavior of τ_{eff} is the result of a slow, reversible filling of surface traps. This leads to charging of the Si surface, which shifts the bands of the semiconductor. The filling of surface traps reduces the number of recombination sites at the surface, thus leading to a decrease of the surface recombination velocity, which is observed as an increase in τ_{eff} in the MFCA measurements.

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Note Added in Proof. During the proof correction stage of this paper a highly relevant and detailed paper by Webb and Lewis⁴⁷ has appeared that reports the recombination velocities S of a variety of covalent monolayers on Si(111) surfaces. These authors show that even subtle changes in the preparation and condition of these monolayers can influence the electrical passivation of the resulting Si surfaces significantly.

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- (26) Care should be taken that the inhibition of the Si surface oxidation is not interpreted as an absolute stability of the modified Si surface. First, the amount of silicon oxide that is formed after a certain period of time can be below the detection limits in the XPS measurements. Second, at defect sites in the monolayer oxidation of the Si surface can certainly occur, although this reaction will probably be on a much slower time scale compared to the oxidation of the H-terminated surfaces. Water is required for the oxidation (see ref 9), and the (hydrophobic parts of the) organic layer will make it difficult for the water molecules to reach the Si surface. Another point that has to be taken into account is that the oxidation of the H-terminated Si surface takes much longer than the observed decay of the charge carrier lifetimes, as was already discussed in the Introduction. The monolayers used here inhibit the oxidation of the Si surface for a long time, but—as observed for the H-terminated surfaces—this does not imply that the decay of the charge carrier lifetimes is similarly decelerated.
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(37) The measurement of the curve as shown in Figure 2 can easily take up to 1 h, depending on the number of power densities that are used. As the wafer has to be stored in the dark for at least the same time as has been used for this measurement before the second measurement can be performed (see the sections on the time-dependent behavior of τ_{eff}), it is clear from the observed reproducibility of τ_{eff} that the samples are stable for at least several hours.

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